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Environmental Protection Technology Series

INDUSTRIAL PROCESS PROFILES FOR ENVIRONMENTAL USE: Chapter 6. The Industrial Organic Chemicals Industry



Industrial Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268

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INDUSTRIAL PROCESS PROFILES

FOR ENVIRONMENTAL USE

CHAPTER 6

THE INDUSTRIAL ORGANIC CHEMICALS INDUSTRY

by

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INDUSTRY DESCRIPTION

INDUSTRIAL ORGANIC CHEMICALS INDUSTRY

INDUSTRY DESCRIPTION

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A precise definition of the Industrial Organic Chemicals Industry is difficult to formulate because of the close interrelationship between it and other elements of the petrochemical industry in general. For the purpose of this study, industrial organic chemicals are defined as solvents or chemical intermediates prepared from products of the Basic Petrochemicals Industry (Chapter 5). Industrial organic chemicals are the product of at least one chemical reaction in this industry and will undergo at least one additional treatment step in a downstream processing industry. Thus, these compounds are intermediate materials in the manufacture of such products as plastics, synthetic fibers, pharmaceuticals, and surfactants from basic petrochemicals such as olefins, aromatics and paraffins.

The Industrial Organic Chemicals Industry does not lend itself to separation into various segments, but the chemical trees, flow sheets and process descriptions are grouped according to feedstock. This arrangement according to feedstock results in ten groups of processes or sections: benzene, butylene, cresol, ethylene, methane, naphthalene, paraffin, propylene, toluene and xylene. Each section is preceded by a chemical tree and flow sheets illustrating products and processing steps described. The chapter includes 364 processes describing the production of 442 industrial organic chemicals.

The principal feedstocks to the industry are the hydrocarbon products (olefins, paraffins, and aromatics) from the Basic Petrochemicals Industry

described in Chapter 5. Many of these feedstocks come to the industry as mixtures of olefins, paraffins and/or aromatics and must go through a separation process such as distillation, extraction, absorption or crystallization to separate the components. The flow sheets and process descriptions for this industry include separation processes as well as the conversion processes used in manufacturing the organic chemicals.

There are limited data available describing precisely the particular group of companies defined in this chapter as producers of industrial organic chemicals. In a separate study performed under EPA Contract No. 68-02-1319, Task 51, an intensive effort was made to characterize the industry defined herein. The 1976 Directory of Chemical Producers and additional sources of information were used to compile data concerning production facilities for some 358 industrial organic chemicals. The product slate described in that study differs only slightly from the one defined in this chapter. The study identified 260 companies with 544 plant sites for the manufacture of 442 industrial organic chemicals. The product slate is given in Appendix D and the list of producers in Appendix E.

Because of the close functional and even physical relationships between manufacturing establishments in the Basic Petrochemicals, industrial organic chemicals and numerous downstream processing industries, classification of industrial organic chemical manufacturers according to a single SIC code is impossible. The Index to Industrial Organic Chemicals (pages iv through xix) and the Industrial Chemicals and Solvents Glossary (Appendix A) indicate that manufacturing establishments are classified in SIC codes 2865 and 2869. However, tenancy in these classifications is shared with establishments

engaged primarily in manufacturing dyes and organic pigments (Chapter 7), basic petrochemicals (Chapter 5), plasticizers (Chapter 13), and pesticides (Chapter 8). The only available data on employment statistics and energy and raw materials consumption are compiled for the groups of companies classified in these SIC codes.

Data published in the 1972 Census of Manufacturers indicate there were 173 establishments classified in SIC code 2865 (Cyclic Crudes and Intermediates, Dyes and Organic Pigments). Of these, 49 were classified under product code 28651 (Cyclic Intermediates) which is within the scope of the chapter. The 1972 Census of Manufacturers also indicates there were 514 establishments classified in SIC code 2869 (Industrial Organic Chemicals, not elsewhere classified). Some 331 of these appear to produce chemicals defined as products of this industry: 42 were producers of miscellaneous cyclic chemicals, except urea (product code 28692); 69 produced synthetic organic chemicals, not elsewhere classified, not bulk (product code 28693); and 52 were producers of ethyl alcohol and other industrial chemicals not elsewhere classified (product code 28695).

Figures given for establishments classified in SIC codes 2865 and 2869 include establishments producing materials outside the scope of this study. Some establishments may appear in any or all of the several industry and product codes cited above. For these reasons, no precise accounting of total industrial populations may be derived from SIC category data, either by summation or by elimination.

Information relating to the physical size of industrial organic chemical manufacturing facilities is not available, because these operations are generally completely integrated with facilities classified in other industries.

Employment statistics for manufacturing establishments classified in SIC codes 2865 and 2869 are presented in Tables 1 and 2. The caveat imposed above applies also to data contained in these tables. Employment statistics for selected product classification codes are presented in Table 1. Statistics describing employment size of establishments specific for selected product codes are not available, but composite statistics for SIC code 2865 and 2869 are contained in Table 2.

Production data for materials classified under product codes 2865 and 2869 are presented in Table 3. This table includes data reported not only by establishments classified in SIC codes 2865 and 2869 but also by establishments classified in other industries and shipping these products as "secondary" products. Certain of the data relating to products outside the scope of this chapter are included in order to demonstrate the interrelationship and convolutions of processes and products within the petrochemical industry in general and the Industrial Organic Chemicals Industry in particular. Data for 1967 as well as 1972 production are presented and indicate an almost universal pattern of growth.

A tabulation of materials consumed in 1972 by establishments in SIC codes 2865 and 2869 is presented in Table 4. This tabulation includes the consumption of not only process chemicals and raw materials, but also other materials, supplies and machinery necessary to the presentation of a product ready for shipment.

TABLE 1. GENERAL STATISTIC FOR ESTABLISHMENTS, BY

INDUSTRY SPECIALIZATION AND PRIMARY PRODUCT CLASS SPECIALIZATION: 1972

This table presents selected statistics for establishments according to their degree of specialization in products primary to their industry. The measures of plant specialization shown are (1) industry specialization-the ratio of primary product shipments to total product shipments, primary plus secondary, for the establishments, and (2) product class specialization-the ratio of the largest primary product class shipments to total product shipments, primary plus secondary, for the establishment. See the source for method of computing these ratios. Statistics for establishments with specialization ratios of less than 75 percent are included in total lines but are not shown as a separate class. In addition, data may not be shown, for some industries, product classes or specialization ratios for various reasons; e.g., to avoid disclosure of individual company data.

		Establish-	All em	ployees	Pro	duction worke	rs	Value	Cost of	Value of	Capital
Industry or product class	Industry or product class by percent of specialization	ments	Number	Payrol1	Number	Man-hours	Wages	added by manufac- ture	materials	shipments	expendi- tures, new
code		(number)	(1,000)	(million dollars)	(1,000)	(millions)	(million dollars)	(million dollars)	(million dollars)	(million dollars)	(million dollars)
2865	Cyclic crudes and intermediates										
	Entire industry Establishments with 75% or more	173	28.2	317.6	18.7	38.4	190.9	925.2	1 109.7	2 044.5	158.7
	specialization	141	16.8	181.1	11.1	22.7	108.6	512.6	622.7	1 141.3	80.4
28651	Cyclic intermediates (Primary product class of establishment)	49	11.3	139.1	7.4	15.6	81.5	504.4	659.3	1 176.4	116.1
	Establishments with 75% or more										
	specialization	26	3.6	43.0	2.2	4.8	24.3	195.7	253.1	463.3	45.5
2869	Industrial organic chemicals, nec										
	Entire industry	514	101.7	1 240.2	64.1	129.1	707.6	4 965.1	4 209.5	9 179.1	645.4
	Establishments with 75% or more specialization	407	42.3	503.9	27.6	56.1	299.7	2 299.5	2 059.3	4 371.2	224.3
28691	Miscellaneous cyclic chemical products										
	(Primary product class of establishment)	42	5.7	61.1	3.7	7.5	35.9	190.4	187.8	378.4	26.2
	Establishments with 75% or more specialization	21	1.8	19.8	1.0	2.1	9.7	46.2	52.9	101.0	8.3
28692	Miscellaneous acyclic chems., exc. urea										
	(Primary product class of establishments)	168	78.6	981.3	50.2	101.6	570.6	4 080.7	3 298.7	7 399.4	508.1
	Establishments with 75% or more specialization	93	17.1	215.5	11.4	23.0	129.2	1 048.0	1 020.7	2 071.2	120.7
28693	Synthetic organic chems., nec, not bulk										
	(Primary product class of establishment)	60	9.7	112.6	5.6	11.4	59.2	288.6	431.3	713.9	46.3
	Establishments with 75% or more specialization	39	2.0	21.6	1.1	2.3	10.8	83.2	117.1	201.0	15.2
29 69 5	Ethyl alcohol, other indust. organic chems., nec										
	(Primary product class of establishments)	52	3.1	30.5	1.7	3.3	13.7	66.9	85.8	152.3	5.7
	Establishments with 75% or more specialization	33	2.0	18.1	1.1	2.1	8.7	45.2	49.5	93.9	5.0

Source: U.S. Department of Commerce, Social and Economic Statistics Administration, Bureau of the Census, "1972 Census of Manufacturers", Industrial Organic Chemicals, Sic Industry Group 286.

	Establish-	A11 em	ployees	Prod	uction work	ers	Value added by	Cost of	Value of shipments	Capital	End-of- year	
Item	ments	Number Payroll		Number	Man-hours	Wages	manufac- ture	materials	Bripmenco	expendi~ tures, new	inven- tories	
	(number)	(1,000)	(million dollars)		(millions)		(million dollars)	(million dollars)	(million dollars)	(million dollars)	(million dollars)	
65Cyclic crudes and intermediates								,				
Establishments, total	173	28.2	317.6	.18.7	38.4	190.9	925.2	1 109.7	2 044.5	158.7	355.6	
Establishments with an average of -												
1 to 4 employeesE7	23	(Z)	. 4	(Z)	.1	.3	1.2	1.5	2.7	.3	• !	
5 to 9 employeesE4	16	.1	1.1	.1	. 2	.7	3.2	4.4	7.6	.6	1.	
10 to 19 employees	17	.2	2.4		.3		11.1	18.6	29.4	1.1	4.	
20 to 49 employees	27	.9	8.8		1.2		29.3	47.2	75.8	3.9	12.	
50 to 99 employees	29	1.9	20.3		2.8		60.6	104.1	165.7	5.3	25.	
100 to 249 employees	29	5.0	53.7	3.0	6.4		213.1	253.2	474.4	53.7	72.	
250 to 499 employees	17	6.1	64.5		8.5		239.4	291.2	529,5	53.4	78.	
500 to 999 employees	9	5.9	72.0		7.8		169.5	204.0	375.3	21.1	81.	
1,000 to 2,499 employees	6	7.9	94.3	5.6	11.1	61. l	198.0	185.4	384.1	19.3	78.	
Estabs. covered by admin. record ¹ .	26	.1	1.1	.1	. 2	.6	3.1	3.5	6.7	.9	1.	
869Industrial organic chemicals, nec												
Establishments, total	514	101.7	1 240.2	64.1	129.1	707.6	4 965.1	4 209.5	9 179.1	645.4	1 075.	
Establishments with an average of -												
1 to 4 employeesE7	119	. 2	2.5		.3		7.9	5.9	13.7	31.7	2.	
5 to 9 employeesE2	50	.3	3.6		.4		11.4	17.8	28.9	(D)	4.	
10 to 19 employeesEl	50	.7	7.2		.9		22.7	31.2	54.6	3.7	5.	
20 to 49 employees	82	2.7	28.6		3.3		125.9	125.3	246.3	23.0	29.	
50 to 99 employees	56	4.0	45.3		4.9		195.5	260.0	457.7	12.9	49.	
100 to 249 employees	77	12.0	135.7	7.4	15.5		703.9	744.3	1 429.4	64.9	176.	
250 to 499 employees	31	11.1	127.8	7.2	15.3		550.0	586.4	1 139.7	64.9	120.	
500 to 999 employees	24	16.6	204.5		22.0		869.1	672.4	1 542.5	104.7	162	
1,000 to 2,499 employees	19	30.4	383.5		37.7		1 515.3	1 054.4	2 580.3	195.0	277	
2,500 employees or more	6	23.5	301.6	14.5	28.6	164.6	963.4	711.8	1 686.1	144.7	248	
Estabs. covered by record ¹ .	99	.3	2.7	.2	.3	1.5	9.2	8.0	17.1	1.6	2	

TABLE 2. GENERAL STATISTICS, BY EMPLOYMENT SIZE OF ESTABLISHMENTS: 1972

(D) Withheld to avoid disclosing figures for individual companies. Data for this item are included in the underscored figures above. (Z) Less than half of the unit of measurement shown.

¹ Report forms were not mailed to companies that operated only one establishment--generally single-unit companies with less than 10 employees. Payroll and sales for 1972 were obtained from administrative records supplied to other agencies of the Federal Government. These payroll and sales data were then used in conjunction with industry averages to estimate the balances of the items shown in the table. Data are also included in the respective size classes shown for this industry.

Source: U.S. Department of Commerce, Social and Economic Statistics Administration, Bureau of the Census, "1972 Census of Manufactures", Industrial Organic Chemicals, SIC Industry Group 286. See source for explanation of terms. (Includes quantity and value of the products reported not only by establishments classified in this industry, but also by establishments classified in other industries, and shipping these products as "secondary" products. See source for explanation of term.

	_		1972			1967	
1972 product code	Product	Total product shipments including interplant transfers	Commercial shipments only	Interplant transfers only	Total product shipments including interplant transfers	Commercial shipments only	Interplant transfers only
		(million dollars)	(million dollars)	(million dollars)	(million dollars)	(million dollars)(million dollars)
2865	CYCLIC CRUDES AND INTERMEDIATES, TOTAL ¹	2,332.4	(X)	(X)	1,654.2	(X)	(X)
28651 11 28650 00	Cyclic (coal tar) intermedistes ¹ Cyclic crudes and intermediates, n.s.k., for companies with 10	1,538.0	1,151.7	386.3	1,066.1	795.6	270.5
28650 02	employees or more. (See note). Cyclic crudes and intermediates n.s.k., for companies with less than 10 employees.	8.5	(X)	(X)	11.9	(X) (X)	(X) (X)
	(See note)	6.7	(X)	(X)	.8	(X)	(A)
2869	INDUSTRIAL ORGANIC CHEMICALS, N.E.C., TOTAL ²	7,465.7	(X)	(X)	5,539.4	(X)	(X)
28691 11	Miscellaneous cyclic (coal tar) chemical products ¹	465.0	417.0	48.0	315.1	271.0	44.1
28692 13	Miscellaneous acyclic chemicals and chemical products, ex- cluding urea ^{1 2}	5,435.2	4,107.4	1,327.8	4,052.2	3,164.7	887.5
28693	Synthetic organic chemicals, N.E.C., except bulk surface	700.0	(1)		585.6	(X)	(X)
28693 11	active agents Flavor and perfume	723.0	(X)	(X)			(N) (D)
	materials ¹	123.4 228.2	116.3 190.8	7.1 37.4	119.0 152.3	(D) 137.1	
28693 31 28693 51 28693 00	Rubber-processing chemicals ¹ Plasticizers ¹ Synthetic organic chemicals,	362.6	306.5	56.1	309.2	283.1	
	n.e.c., n.s.k Pesticides and other synthetic organic agricultural chemicals,	8.8	(X)	(X)	5.1	(X)	(X)
	except preparations ¹	489.3	434.1	55.2	308.2	282.7	25.5
28695	Ethyl alcohol and other in- dustrial organic chemicals, n.e.c	·-					
	Ethyl alcohol ³	280.3	(X)	(X)	239.4	(X)	
28695 11 28695 21	Pure (natural) Denatured (special or com- plete), including natural and synthetic for uses	35.0	(D)	(D)	33.6	(D)	
	other than rubbing	42.6	(D)	(D)	44.2	(D)	• •
28695 31 28695 37	Flavor oil mixtures and blends Reagent and high purity grades of organic chemicals refined from purchased technical	34.7	34.7		27.9	27.9	
28695 51	grades Natural organic chemicals,	23.0	22.0	1.0	19.3	7 1 9 .	7 -
	n.e.c	60.4	(D)	(D)	44.(0 (1)) (D)
	chemicals	78.8	(D)	(D)	67.1	8 64.	4 3.4
28695 00	Other industrial organic chemicals, n.s.k	5.6	(X)	(X)	2.3	2 ()	(X) (X)
28690 00	Industrial organic chemicals, n.e.c., u.s.k., for companies with 10 employees or more. (See note)	58.2	(X)	(X)	33.5	5 ()	() (V)
28690 02	Industrial organic chemicals, u.e.c., n.s.k., for companies with less than 10 employers.	50.2			33.	. (2	(X) (X)
	(See note)	14.7	(X)	(X)	5.3	2 ()	(X) (X

Note: In the 1972 Census of Manufactures, shipments data for establishments of small companies, typically those with fewer than 10 employees, were estimated from administrative record data rather than collected from respondents. These shipments figures (which are further discussed in the text) are included in the code ending with "002." In both the 1972 and 1967 censuses of manufactures, products which were not completely identified on the standard forms were coded to the appropriate product-class code (5 digits) followed by "00," or in some cases to the appropriate product-group code (4 digits) followed by "000."

Represents zero. (X) Not applicable. (D) Withheld to avoid disclosing figures for individual companies. (S) Withheld because the estimate did not meet publication standards either on the basis of the associated standard error of estimate or on the basis of a consistency review. (X) Less than half of the unit of measurement shown (less than 0.1 when rounded).

¹ Data for quantities produced and values shipped for many of the synthetic organic chemicals included in this grouping are shown in the U.S. Tariff Commission's Annual Report, "Synthetic Organic Chemicals, United States Production and Sales."

² 1967 and 1972 figures are not comparable. The 1967 totals for code 28692 13 include the values for ureas. Due to revisions in the Standard Industrial Classification product classes, urea became code 28732 15 in 1972.

³ For quantity information, refer to the U.S. Treasury Department, Internal Revenue Service publication: Alcohol and Tobacco-1972. Excludes shipments reported as rubbing alcohol (primary to industry 2834, Pharmaceutical Preparations), and as antifreeze (primary to industry 2899, Chemical Preparations, N.E.C.).

Source: U.S. Department of Commerce, Social and Economic Statistics Administration, Burea of the Census, "1972 Census of Manufactures", Industrial Organic Chemicals, SIC Industry Group 286.

TABLE 4. MATERIALS CONSUMED, BY KIND: 1972

		INDUSTRY 2865CYCLIC CRUDES AND INTERMEDIATES							INDUSTRY 2869INDUSTRIAL ORGANIC CHEMICALS, N.E.C.							
		Basis	Unit of weasure	Total consumption of materials	received	n of materials from other Lshments	Materials made and consumed in	Basis	Unit of measure	Total consumption of materials	received	on of materials I from other ishments	Materials made and consumed in			
1972 code	Material			(quantity)	Quantity	Delivered cost	same plant (quantity)		-	(quantity)	Quantity	Delivered cost	same plant (quantity)			
						(million dollars)						(million dollars)				
	Materials, containers, and supplies,															
	total Inorganic chemicals:			(X)	(X)	945.8	(x)			(X)	(X)	3,436.5	(X)			
281944	Acids, except spent acids. Hydrochloric acid	100% HC1	1,000 s.	50.8	43.5	2.0	7.3	100% HC1.	1,000 s.	1,324.5	396.1	14.8	928.4			
281946	Hydrofluoric acid	•••••	tons.	(X)	(X)	(X)	(X)	100% HF	tons	144.6	(D)	(D)	(D)			
287311	Nitric acid	100% HNO3	do	589.5	101.4	7.2	488.1	100% HNO3	do	982.4	221.2	15.9	761.2			
287410	Phosphoric acid		do	(X)	(X)	(X)	(X)	100% P205	do	44.2	(D)	(D)	(D)			
281931	Sulfuric acid	100%H2SO.	do	800.7	331.0	9.3	469.7	100%H2SO4	do	1,363.6	1,202.1	25.3	161.5			
287312	Ammonia, synthetic, anhydrous	100% NH3	do	191.9	191.9	7.4	-	100% NH3.	do	1,503.8	640.0	25.4	863.8			
281211	Chloride	100% C1	do	(D)	331.8	16.4	(D)	100% Cl	do	6,903.6	1,789.3	76.4	5,114.3			
281996	Phosphorus, elemental		do	(X)	(X)	(X)	(X)	Technical	do	59.8	(D)	(D)	(D) (D)			
281228 281238	Sodium carbonate (soda ash) Sodium hydroxide (caustic soda)	58% NazO 100% NaOH	do do	42.0 474.3	42.0 474.3	2.2 20.7	-	58% Na20. 100% NaOH	do do	56.7 1,742.9	(D) 793.6	(D) 38.3	949.3			
286952 286920	Organic chemicals: Alcohol, ethyl (pure and denatured) Other alcohols, including amyl, butyl,			(X)	(X)	1.0	(X)			(X)	(X)	39.8	(X)			
200720	methyl, and propyl		Mil. gal.	53.7	53.7	9.3	-		Mil. gal	1,135.4	917.5	122.4	217.9			
286511	Aniline	100%	М11. 1ь	(NA)	79.7	12.0	(NA)	100%	Mil. 1b	(NA)	122.6	15.9	(NA)			
286552	Benzol (benzene)	100% C ₅ H ₅	do	(D)	1,100.3	35.2	(D)	100% C ₆ H ₆	••••do•••••	3,168.6	2,793.0	80.0	375.6			
286923	Formaldehyde Liquefied petroleum and refinery gases	37% HCHO.	do	77.1	77.1	2.2	-	37% НСНО.	do	2,416.3	233.7	5.2	2,182.6			
	for chemical feedstocks:							}								
291165	Ethylene	••••	do	(D) (X)	(D) (X)	(D) (X)	(D) (X)		do do	11,275.9 (NA)	4,788.9 7,791.6	154.9	6,487.0			
291164	Propane		do	(D)	(A) (D)	(D)	(A) (D)		do	3,843.5	2,043.4	98.2 54.6	(NA) 1,800.1			
291166 291169	Propylene		do	(NA)	(D)	(D)	(NA)		do	(NA)	1,462.4	173.3	(NA)			
286555	Naobthanlene		do	213.5	(D)	(D)	(D)		do	612.8	612.8	27.8	_			
286512	Nitrobenzene	100%	do	438.9	12.0	.3	426.9		do	(X)	(X)	(X)	(X)			
286513	Pheno1	100%	do	61.9	46.4	3.4	15.5	100%	do	464.2	(D)	(D)	(D)			
286514	Phthalic anhydride	100%	do	19.2	19.2	1.8 38.1	(NA)	100%	do	443.7	151.9	11.2	291.8			
286533	Tar, crude	·····	1,000 s. tons	(NA)	1,299.5	36.1	(NA)	••••••	do	(X)	(x)	(X)	(X)			
147701	Crude materials: Sulfur	••••	1,000 long tons	(X)	163.5	4.4	(X)		1,000 long tons	(x)	462.7	13.1	(11)			
333348	Zinc and zinc-base alloy refinery shapes		1,000 в.	(X)	.7	.3	(X)			(X)	(X)	(X)	(X) (X)			
131152	Used as raw materials: Natural gas		tons. Mil.cu.ft.	(X)	6,491.0	3.0	(X)		Mil.cu.ft	(X)	241,928.0	64.8	(X)			
355911	Parts and attachments for chemical indus- tries, machinery, and equipment			(X)	(X)	29.4	(X)			(X)	(X)	114.0				
970099	All other materials and components,									,		114.0	(X)			
5/0077	parts, containers, and supplies	<i>.</i>		(X)	(X)	630.9	(X)			(X)	(X)	2,096,9	(X)			
976000	Materials, containers, and supplies, n.s.k, ¹			(X)	(X)	41.0	(X)			(17)	(X)	104.9	(X) (X)			

- Represents zero. (X) Not applicable. (NA) Not available. (D) Withheld to avoid disclosing figures for individual companies. (S) Withheld because the estimate did not meet publication standards, either on the basis of the associated standard error or on the basis of a consistency review. (Z) Less

than half of the unit of measurement shown. (n.e.c.) Not elsewhere classified.

² This item represents the total cost of materials for establishments that did not report detailed materials data. It also includes estimates for companies that were not mailed report forms.

Source: U.S. Department of Commerce, Social and Economic Statistics Administration, Bureau of the Census, "1972 Census of Manufacturers", Industrial Organic Chemicals, SIC Industry Group 286.

Although producing plants for industrial organic chemicals are scattered throughout several states, many are located near refineries which are located near domestic sources of oil or points of entry for imported oil. Some of the petrochemical plants border refineries, thus permitting an easy exchange of products. This results in a heavy concentration of chemical production along the Gulf coast and the east coast particularly in the area of New York, New Jersey and Pennsylvania. Additional concentrations occur along natural gas pipeline routes and water transportation arteries throughout the central United States and in the oil and gas fields of California. Significant organic chemical production occurs in some 30 states.

Table 5 presents general statistical data by geographical area for establishments classified in SIC codes 2865 and 2869. The tabulated entries reflect data for certain facilities and products which are outside the scope of this study, so the absolute value stated for any particular parameter must be considered high. Nevertheless, proportional relationships among the parameters and relative geographic/economic influence may be considered typical of the Industrial Organic Chemical Industry.

The industry has experienced a high growth rate almost since its beginning. U.S. production of industrial organic chemicals has increased over the years from an average of 16 Tg (35.3 billion pounds) during 1957 through 1959) to 25.7 Tg (60.0 billion pounds) in 1964, 47.3 Tg (104.3 billion pounds) in 1969 and 62.9 Tg (138.7 billion pounds) in 1974. However, the recent energy crisis has doubly affected the industry. Refined petroleum products and natural gas, traditional feedstocks for the production of the basic petrochemicals necessary to the industrial organic chemicals industry, are also

	[286	5 CYCLIC C	RUDES AND INTE	RMEDIATES					28	9 INDUSTRI	AL ORGANIC C	IEMICALS, NEC		
	Establi	shments	All emp	loyees	Value added by	Cost of materials	Value of shipments	Capital expendi-	Establi	shpents	All empl	oyees	Value added by	Cost of materials	Value of shipments	Capital expendi-
Geographic Area	Total	With 20 employees or more	Number ¹	Payroll	manufac- ture			tures, nev	Total	With 20 employees or more	Number ¹	Payroll	manufac- ture		(million	tures, new (million
	(number)	(number)	(1,000)	(million dollars)	(million dollars)	(million dollars)	(million dollars)	(million dollars)	(number)	(number)	(1,000)	(million dollars)	(million dollars)	(million dollars)	(million dollars)	dollars)
UNITED STATES	173	117	28.2	317.6	925.2	1 109.7	2 044.5	158.7	514	295	101.7	1 240.2	4 965.1	4 209.5	9 179.1	645.4
NORTHEAST REGION,	77	54	13.9	152.7	363.1	394.0	759.1	(D)	174	98	27.1	316.5	.725.4	938.4	1 670.0	(D)
NEW ENGLAND DIVISION MAINE NEW HAMPSHIRE MASSACHUSETTS RHODE ISLAND	11 (NA) (NA) 7 3 1	7 (NA) (NA) 4 2 1	1.2 (NA) (NA) BB CC AA	10.8 (NA) (NA) (D) (D) (D)	29.7 (NA) (NA) (D) (D) (D)	28.4 (NA) (NA) (D) (D) (D)	60.5 (NA) (NA) (D) (D) (D)	(D) (NA) (NA) (D) (D) (D)	33 1 10 4 17	15 1 2 2 9	5-8 AA AA AA CC FF	61.4 (D) (D) (D) (D) (D)	83.3 (D) (D) (D) (D) (D)	120.3 (D) (D) (D) (D) (D) (D)	212.3 (D) (D) (D) (D) (D) (D)	(D) (D) (D) (D) (D)
MIDDLE ATLANTIC DIVISION NEW YORK NEW JERSEY PENNSYLVANIA	66 12 39 15	47 6 31 10	12.7 2.6 8.3 1.8	141.9 29.4 94.6 17.9	333.4 48 1 234.0 50.3	365.6 54.5 248.8 62.3	698.6 101.0 485.1 112.4	(D) (D) (D) (D)	141 38 76 27	83 21 49 13	21.4 6.1 13.1 2.2	255.0 64.1 169.6 21.3	642.1 158.6 446.9 36.7	818.1 165.6 570.8 81.7	1 457.7 320.7 1 015.6 121.4	(D) (D) (D) (D)
NORTH CENTRAL REGION	33	22	5.7	65.4	166.1	223.8	390.9	(D)	103	51	15.1	182.3	569.5	443.6	1 016.2	(D)
EAST NORTH CENTRAL DIVISION. OHIO	29 14 (NA) 10 3 (NA)	21 10 (NA) 7 3 (NA)	FF EE (NA) 2.6 CC (NA)	(D) (D) (NA) 35.4 (D) (NA)	(D) (D) (NA) 78.5 (D) (NA)	(D) (D) (NA) 104.7 (D) (NA)	(D) (D) (NA) 187.6 (D) (NA)	(D) (D) (NA) (D) (D) (NA)	82 31 5 20 17 9	45 19 5 6 9	FF 3.1 EE CC FF BB	(D) 35.6 (D) (D) (D) (D) (D)	(D) 99.6 (D) (D) (D) (D)	(D) 113.9 (D) (D) (D) (D)	(D) 215.0 (D) (D) (D) (D)	(D) 7.6 (D) (D) (D) (D)
WEST NORTH CENTRAL DIVISION. IOWA MISSOURI	4 (NA) (NA)	1 (NA) (NA)	AA (NA) (NA)	(D) (NA) (NA)	(D) (NA) (NA)	(D) (NA) (NA)	(D) (NA) (NA)	(D) (NA) (NA)	21 3 10	6 1 3	EE AA EE	(D) (D) (D)	(D) (D) (D)	(D) (D) (D)	(D) (D) (D)	(D) (D) (D)
SOUTH REGION	52	38	8.4	97.1	390.0	481.7	878.4	107.5	186	124	56.6	707.7	3 526.4	2 702.0	6 224.8	474.7
SOUTH ATLANTIC DIVISION DELAWARE. MARYLAND. VIRGINIA. WEST VIRGINIA. NORTH CAROLINA. SOUTH CAROLINA. GEORGIA. FLORIDA.	24 2 (NA) 5 5 5 (NA) (NA)	18 2 3 (NA) 4 4 3 (NA) (NA)	4.8 CC (NA) EE BB CC (NA) (NA)	53.1 (D) (NA) (D) (D) (D) (NA) (NA)	169.9 (D) (NA) (D) (D) (D) (D) (NA) (NA)	188.4 (D) (D) (NA) (D) (D) (D) (NA) (NA)	368.5 (D) (NA) (D) (D) (D) (NA) (NA)	74.3 (D) (D) (NA) (D) (D) (D) (NA) (NA)	69 (NA) 6 14 14 11 7 6	41 (NA) (NA) 3 12 7 7 4 4	13.7 (NA) (NA) EE 9.4 CC .6 AA CC	149.4 (NA) (D) 106.3 (D) 6.2 (D) (D)	720.8 (NA) (D) 549.6 (D) 26.8 (D) (D)	443.9 (NA) (D) 268.9 (D) 30.7 (D) (D)	1 164.8 (NA) (D) 822.7 (D) 57.3 (D) (D)	44.4 (NA) (D) 30.2 (D) 2.5 (D) (D)
EAST SOUTH CENTRAL DIVISION. KENTUCKY	10 (NA) 4 5	7 (NA) 1 5	1.4 (NA) CC CC	15.1 (NA) (D) (D)	94.9 (NA) (D) (D)	88.8 (NA) (D) (D)	185.6 (NA) (D) (D)	7.3 (NA) (D) (D)	30 8 12 5	18 7 8 3	8.2 EE FF .4	94.8 (D) (D) 4.9	311.4 (D) (D) 29.3	358.4 (D) (D) 30.8	666.5 (D) (D) 57.9	33.4 (D) (D) .8
WEST SOUTH CENTRAL DIVISION. LOUISIANA	18 2 16	13 2 11	2.2 AA EE	29.0 (D) (D)	125.2 (D) (D)	204.6 (D) (D)	324.4 (D) (D)	25.9 (D) (D)	87 26 57	65 24 39	34.7 FF 23.9	463.5 (D) 318.3	2 494.2 (D) 1 843.4	1 899.6 (D) 1 320.7	4 393.6 (D) 3 161.4	396.9 (D) 251.9
WEST REGION	11	3	.2	2.4	6.1	10.2	16.1	.9	51	22	2.9	33.8	143.7	125.5	268.1	19.8
MOUNTAIN DIVISION	(NA) (NA)	(NA) (NA)	(NA) (NA)	(NA) (NA)	(NA) (NA)	(NA) (NA)	(NA) (NA)	(NA) (NA)	54	3 2	BB AA FF	(D) (D) (D)	(D) (D) (D)	(D) (D) (D)	(D) (D) (D)	(D) (D) (D)
PACIFIC DIVISION	9 7	32	AA AA	(D) (D)	(D) (D)	(D) (D)	(D) (D)	(D) (D)	46 38	19 16	EE	(D) (D)	(D) (D)	(D) (D)	(D) (D)	(D) (D)

TABLE 5. INDUSTRIAL ORGANIC CHEMICALS: GENERAL STATISTICS BY GEOGRAPHICAL AREA

Note: The payroll and sales data for small establishments (generally single-unit companies with less than 10 employees) were obtained from administrative records of other government agencies instead of from a Census report form. These data were then used in conjunction with industry averages to estimate the balance of the items shown in the table for these small establishments. This technique was also used for a small number of other establishments whose reports were not received at the time the data were tabulated. The following symbols are shown for those States where administrative records data were used and account for 10 percent or more of the figures shown:

E110 to 19 percent	E330 to 39 percent	E550 to 59 percent	E770 to 79 percent	E990 to 99 percent
E220 to 29 percent	E440 to 49 percent	E660 to 69 percent	E880 to 89 percent	EO100 percent

(NA) Not available. (D) Withheld to avoid disclosing figures for individual companies.

'General statistics for some producing areas are withheld to avoid disclosing figures for individual companies. However, for such areas with 150 employees or more, the number of establishments is shown and the employment size range is indicated by one of the following symbols:

AA--150 to 249 employees BB--250 to 499 employees CC--500 to 999 employees EE--1,000 to 2,499 employees FF--2,500 employees and over

Source: U.S. Department of Commerce, Social and Economic Statistics Administration, Bureau of the Census, "1972 Census of Manufacturers", Industrial Organic Chemicals, SIC Industry Group 286. the prime sources for the energy required by an industrialized nation as well as by chemical production facilities. With the demand placed on refinery products and natural gas for use as fuels, there is little economic incentive to increase production of refinery products and natural gas liquids to be used as petrochemical feedstocks. Thus, the industry has been affected not only by increased costs but also by feedstock shortages.

For this reason growth over the next several years is anticipated to be at a continuing slow rate and will probably be governed by improved production technology and energy conservation techniques. The continuity of feedstock supply is almost more important than feedstock price. As a result the industry has been under considerable pressure to acquire its own sources of raw material. The need for such backward integration could lead not only to the acquisition of basic petrochemical production facilities but even to the acquisition of sources of raw materials for these and finally to control of the well or mine.

Table 6 presents data for fuels and electrical energy consumed by establishments classified in SIC codes 2865 and 2869 during 1971. Specific data relating to only those companies producing industrial organic chemicals as defined herein were not found in the sources consulted for this study. The tabulation indicates that some on-site generation of electrical energy occurred at facilities classified under these codes, but quantitative data were not available.

Raw Materials

The raw materials for the industry consist primarily of the products of the Basic Petrochemicals Industry. Thus, any adverse environmental impact

Table 6. FUELS AND ELECTRIC ENERGY CONSUMED IN 1971 BY COMPANIES IN SIC CODES 2865 AND 2869

	SIC 2865	SIC 2869
Coal	(497,000 s tons) 450.8 Gg	(5,036,600 s tons) 4,569 Tg
Distillate and Residual Fuel Oil	(4,748,100 bbl) 754.3 dam ³	(4,358,000 bbl) 692.4 dam ³
Natural Gas	$(69.4 \times 10^9 \text{ ft}^3) 1.97 \text{ km}^3$	$(586.1 \times 10^9 \text{ ft}^3) 16.59 \text{ km}^3$
Purchase Electric Energy	3.324 TWh	19.7 TWh
Total Energy Used for Heat and Power	40.3 TWh equiv.	286.0 TWh equiv.

Source: U.S. Department of Commerce, Social and Economic Statistics Administration, Bureau of Census, "1972 Census of Manufactures", <u>Industrial Organic Chemicals</u>, SIC Industry Group 286. associated with the production of raw materials for this industry is that associated with production, transfer, and interim storage of olefins, aromatics, and paraffins. Hydrocarbon emissions during raw material production are estimated to range from 0.1 to 0.6 percent of plant throughput. Nonhydrocarbon pollutants include water treatment wastes, products from sulfur and nitrogen removal processes, combustion and incineration products, catalyst cleaning waste, spent catalysts and solid absorbents. For a more complete examination of pollutant and potential pollutant generation from raw materials production, the reader is referred to Chapter 5.

As noted above, the primary raw materials for this industry are olefins, aromatics and paraffins. Olefins are characterized by a highly reactive double bond which renders them extremely useful in a variety of syntheses. Ethylene surpasses all other hydrocarbons both in production volume and in diversity of commercial use. Ethylene production has grown from 136 Cg (300 million pounds) in 1940 to 2.27 Tg (5 billion pounds) in 1960 and to over 8.16 Tg (18 billion pounds) in 1970. Propylene, though not produced in as great a quantity as ethylene, is also an important raw material for this industry. In 1969, about 3.87 Tg (8.5 billion pounds) of propylene was consumed to make chemicals.

Benzene is the most important aromatic, second only to ethylene as a building block for synthetic organic chemicals. Figures for total consumption of benzene by the industry are not available. Data published in the 1972 Census of Manufacturers for those establishments classified in SIC code 2869 indicate a benzene consumption of 1.44 Tg (3.17 billion pounds). Toluenes and mixed xylenes are likewise important feedstock materials, though not on

a level with benzene. Napthalene and cresols comprise the balance of the significant aromatic feedstocks to this industry.

The paraffins, or alkanes, are saturated hydrocarbons. Methane, CH₄, is the simplest member of this class, with subsequent members differing by multiples of one carbon and two hydrogen atoms. Paraffins containing one to four carbons are gases at standard temperature and pressure, while those containing five or more carbons are liquids or solids. Paraffins are the least reactive of the hydrocarbons and all of the common processing methods require elevated temperature and pressures. Paraffins with four or more carbons can exist in branched-chain forms, the number of possible isomers increasing with the number of carbon atoms. The principal paraffin feedstocks used by the industry are one- to five-carbon molecules.

Toxicity ratings for selected hydrocarbons used as industry feedstocks are shown in Table 7. A complete list of raw materials used in the production of the chemicals treated in this chapter is contained in Appendix B. Chemicals which are listed as raw materials but which are also themselves products of the industry and for which process descriptions are included in this chapter are identified with an asterisk. Materials which function as catalysts are listed in Appendix C.

Products

Process descriptions for some 442 industrial organic chemicals are included in this study. These chemicals are used as solvents or chemical intermediates by downstream industries to produce organic chemical products estimated by one source to number from 8,000 to 10,000. During 1974 nearly 64 Tg (139 billion pounds) of cyclic and acyclic chemicals and chemical intermediates

Table 7. TOXICITY OF SELECTED FEEDSTOCKS FOR THE INDUSTRIAL

ORGANIC CHEMICALS INDUSTRY

ethylene	Low toxicity.		
propylene	Low toxicity.		
butylene	Butene-1, <u>cis</u> -butene-2, and <u>trans</u> -butene-2 isomers are asphyxiant gases; isobutene isomer is non-toxic.		
benzene	Highly toxic by ingestion, inhalation and skin absorption; tolerance 25 ppm in air.		
toluene	Moderately toxic by ingestion, inhalation and skin absorption; tolerance 200 ppm in air.		
xylene	Moderately toxic by ingestion or inhalation; tolerance 100 ppm in air.		
napthalene	Moderately toxic; tolerance 10 ppm in air.		
cresols	Moderate to highly toxic irritant; corrosive to skin and mucous membranes; absorbed through skin; tolerance 5 ppm in air; 22 mg/m ³ in air; low toxicity.		
ethane	Not available.		
propane	Non-toxic.		
butane	Asphyxiant gas.		
n-pentane	Tolerance 500 ppm in air.		
isopentane	Low toxicity.		

Source: Hawley, Gessner, G. Condensed Chemical Dictionary. 8th Ed. N.Y., Van Nostrand-Reinhold, 1971. with a value of approximately 7 billion dollars were produced in the United States. In general, the products of the Industrial Organic Chemical Industry are used as feedstock to such downstream industries as adhesives; agricultural chemicals; automotive chemicals; dyes; elastomers; explosives; paints and protective coatings; refrigerants and propellant gases; petroleum production and processing; pharmaceuticals, plastics, resins and synthetic fibers; solvents; surfactants; and others, including the chemical manufacturing industry itself. Because of the number of processing steps from feedstock to end-product, intra-industry sales reach significant levels.

Table 8 lists the 25 organic chemicals with the highest production volume in 1973. The chemicals listed accounted for 62.6 percent of the total production of this industry for 1973. Eighteen of the 25 chemicals listed find direct application in the plastics, plasticizers and fibers industries. Nine of the chemicals are used directly in the preparation of solvents and as intermediates in the production of other organic chemicals. Eight of the chemicals find direct application in manufacturing of agricultural chemicals, seven each in the preparation of dyes, pharmaceuticals, and paints or other protective coatings. Twelve of the chemicals listed are used as primary or alternate feedstocks for the production of other members of the list.

A list of the 25 organic chemicals with the highest market value is presented in Table 9. Tetraalkyl lead compounds exclusive of tetraethyl lead, for which no sales data were available, accounted for over 7.2 percent of the total chemical sales in 1973 as reported to the U.S. International Trade Commission. During 1974 domestic consumption of these compounds dropped by 12.4 percent. The relative economic importance of tetraalkyl lead compounds can be expected to diminish still further, as automotive gasoline

BY PRODUCTION VOLUME IN 1973

Chemical	Production Gg	Sales Volume Gg	Market Value \$1000	
Ethylene dichloride	4215	613.0	40,489	
Urea	3214	3065	228,103	
Methanol	3204	1743	64,306	
Formaldehyde (37% by weight)	2914	1257	51,578	
Styrene	2710	1288	199,141	
Ethylbenzene	2580	188.3	20,873	
Vinyl chloride	2427	1612	147,518	
Ethylene oxide	1890	231.4	34,913	
Ethylene glycol	1487	1283	193,317	
Cumene	1209	635.4	52,510	
Dimethyl terephthalate	1163	594.9	165,875	
Acetic acid	1102	276.1	32,069	
p-Xylene	1055	711.8	100,635	
Phenol	1032	595.2	100,508	
Cyclohexane	962.8	900.2	89,860	
Acetone	902.4	702.0	67,928	
Ethyl alcohol	889.9	689.6	84,015	
Isopropyl alcohol	832.3	408.1	52,533	
Propylene oxide	795.2	NA	NA	
Acetic anhydride	757.5	NA	NA	
Adipic acid	710.8	69.28	24,757	
Vinyl acetate	681.6	436.7	67,095	
Acrylonitrile	614.2	218.0	50,878	
o-Xylene	484.4	351.5	37,998	
Carbon tetrachloride	475.1	448.8	59,531	

NA - Indicates data not available.

Source: U.S. International Trade Commission. Synthetic Organic Chemicals, United States Production and Sales, 1973. ITC Publication 728. Washington, GPO, 1975.

Chemical	Production Gg	Sales Volume Gg	Market Value \$1000
Tetraalkyl lead compounds*	346.3	435.0	518,667
Urea	3214	3065	228,103
Styrene	2710	1288	199,141
Ethylene glycol	1487	1283	193,317
Dimethyl terephthalate	1163	594.9	165,875
Vinyl chloride	2427	1612	147,518
Foluene-2,4- and 2,6-diisocyanate (80/20 mix)	229.5	198.8	126,261
Dichlorodifluoromethane	221.7	210.4	110,812
p-Xylene	1055	711.8	110,635
Phenol	1032	595.2	100,508
Cyclohexane	962.8	900.2	89,680
Ethyl alcohol	889.9	689.6	84,015
Acetone	902.4	702.0	67,928
Vinyl acetate	681.6	436.7	67,095
Methanol	3204	1743	64,306
Frichlorofluoromethane	151.4	149.2	61,352
Phthalic anhydride	463.8	290.8	61,326
Polymethylene polyphenylisocyanate	128.0	101.4	59,536
Carbon tetrachloride	475.1	448.8	59,531
Caprolactam	297.7	133.3	57,944
Ispropyl alcohol	832.3	408.1	52,533
Cumene	1209	635.4	52,510
Formaldehyde (37% by weight)	2194	1257	51,578
Acrylonitrile	614.2	218.0	50,878
,1,1-Trichloroethane	248.7	256.8	49,534

Table 9. THE MOST SIGNIFICANT SYNTHETIC ORGANIC CHEMICALS

BY MARKET VALUE IN 1973

*Exclusive of tetraethyl lead

Source: U.S. International Trade Commission. Synthetic Organic Chemicals, United States Production and Sales, 1973. ITC Publication 728. Washington, GPO, 1975.

*

producers shift to a higher percentage output of unleaded products in order to service the increasing population of vehicles requiring such fuel.

Dichlorodifluoromethane, trichlorofluoromethane, and 1,1,1-trichloroethane accounted for over 3 percent of total reported chemical sales in 1973. Production and sales volume of these halocarbons can be expected to diminish somewhat as a result of concern over the theoretically adverse effect of halocarbons on atmospheric ozone.

Four of the listed chemicals, toluene-2,4- and 2,6-diisocyanante, phthalic anhydride, polymethylene polyphenylisocyanate and caprolactam, are used primarily in the production of plastics and synthetic fibers and collectively accounted for 4.25 percent of total chemical sales during 1973. Seventeen of the chemicals listed in Table 9 appear also in Table 8. The chemicals listed in Table 9, in aggregate, accounted for 39.4 percent of the total market value of industrial organic chemical sales in 1973. Appendix D lists 358 organic chemicals considered significant to the industry by reason of production volume, economic impact, environmental impact or toxicity factors.

Companies

The bulk of the output of industrial organic chemicals is contributed by large multi-line chemical companies and by chemical divisions or subsidaries of the major oil companies. Many of these are multi-national organizations, some being headquartered outside the United States. A list of the leading chemical companies operating in the United States during 1973 is presented in Table 10. The companies listed are all producers of industrial organic chemicals. However, the tabulated sales figures also include sales of basic petrochemicals as well as downstream industrial products including plastics

TABLE 10. LEADING CHEMICAL COMPANIES IN THE U.S. DURING 1973

	CHEMICAL SALES \$ MILLIONS		1			
	1973	1972	1971	1973	1972	1971
Du Pont	\$4250	\$3550	\$2950	\$ 5,276	s 4.366	\$ 3,848
Union Carbide	2400	1960	1884	3,939	3.261	3,038
lonsanto	2355	1924	1776	2,648	2,225	2,087
Dow Chemical	2250	1800	1550	3,068	2,404	2,053
Exxon	1563	1258	1077	25,724	20,310	18,701
Celanese	1508	1279	1131	1,609	1,385	1,236
I. R. Grace ^a	1317	1088	974	2,808	2,315	2,049
Allied Chemical	1114	1001	892	1,665	1,501	1,326
Occidental Petroleum	1080	831	705	3,456	2,721	2,635
ercules	1000	795	678	1,155	932	812
astman Kodak	792	694	612	4,036	3,478	2,976
ohm and Haas	750	588	482	789	619	507
hell 011	748	645	556	4,884	4,076	3,892
MC	745	657	646	1,719	1,498	1,354
merican Cyanamid	708	644	600	1,472	1,359	1,283
hillips Petroleum	697	490	408	2,990	2,513	2,363
Borden	690	515	450	2,554	2,193	2,070
itauffer Chemical	621	543	493	621	543	493
lobil 011	570	470	493	11,390	9,166	8,243
tandard Oil(Ind.)					•	
thyl Corp. ^a	510	410	341	5,416	4,503	4,054 577
kzona	499	458	416	699 704	632 572	506
	485	391	351		572	
exaco ulf Oil	480	400	350	11,407	8,693	7,529
	455	363	300	8,417	6,243	5,940
iamond Shamrock	454	404	368	651	617	573
• F. Goodrich ^a	452	363	286	1,661	1,507	1,237
PG Industries	440	405	359	1,513	1,396	1,238
shland Oil ^a	427	352	327	2,053	1,780	1,635
tandard Oil of California (Includes Chevron Chemical Company) .S. Steel	422 394	30 4 310	277 298	7,762 6,952	5,829	5,143
ir Products ^{a, b}					5,429	4,963
	388	342	297	399	351	308
iba-Geigy	380	350	380	550	500	550
lin	370	329	281	1,239	1,098	1,145
ities Service	367	424	391	2,035	1,862	1,810
ASF Wyandotte	356	299	254	378	316	254
obay (Formerly Baychem)	333	263	209	333	263	209
oodyear Tire	325	250	236	4,675	4,072	3,602
illiam Cos.	312	205	50	744	578	412
l Paso Natural Gas	301	254	271	983	1,097	1,037
enneco	299	277	254	3,910	3,275	2,841
ichnold Chemicals	294	217	194	294	217	194
erck	280	235	210	1,115	958	829
fizer ^a	279	222	204	1,284	1,093	952
ubrizol	274	217	198	274	217	198
org-Warner ^a	264	201	165	1,547	1,283	1,148
b Lrco	262	240	192	584	492	441
merican Hoechst	260	220	200	339	260	235
hemetron	249	224	224	353	314	276
ennwalt	246	199	183	504	441	406

(a)Significant nonchemical sales (welding and cryogenic equipment, fabricated plastics products, coatings, metals, textiles, and the like) included with the chanical sales. (b)For fiscal year ended Sept. 30. (na = not available).

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Source: Chemical and Engineering News, June 3, 1974.

and resins, dyes, plasticizers and agricultural chemicals. In addition, as noted in the table, the sales figures may include significant nonchemical sales. Nevertheless, the relationship between tabulated data for chemical sales and total sales during 1971 through 1973 is indicative of the degree of specialization as chemical producers.

In addition to the companies listed, there are hundreds of smaller companies specializing in a limited line of intermediate or end-product chemicals. In general, sales and profits are commensurate with the limited product line.

A number of factors account for the dominance of this industry by large multi-line and multi-national companies. Among these are:

- Substantial costs for product and process research and development,
- 2) High plant investment in order to affect reduced product prices through large scale production techniques.
- 3) Competition for world supplies of raw materials,
- 4) Necessity of an extensive product line (horizontal integration) in order to provide a broad economic base for the company,
- 5) Economic advantages realized by integration of basic operations common to the production of a number of different end products, and
- 6) Ability to compete in the world market and to take advantage of world wide supply and demand fluctuation.

Traditionally, the industrial organic chemicals industry has relied heavily upon horizontal integration to assure some level of economic stability. In recent years, however, the main influence has been the need for vertical integration. Firms that until recently were secure in the production of intermediates or of end-products have been under pressure either to integrate backward, by acquiring their own sources of raw materials, or to integrate forward by gaining control of client industries.

Thus, it may be expected that the more highly capitalized chemical companies are better equipped for such vertical integration and can be expected to maintain their present dominance of the industry. Most have already enlarged the scope of their activites, both by diverse acquisition and by internal expansion, and have advanced their position in the market at the expense of companies which have maintained an original structure.

A list of 260 companies involved in the production of industrial organic chemicals at 544 sites is presented in Appendix E.

Environmental Impacts

Hydrocarbons are major constituents of the gaseous emissions from industrial organic chemical plants. Hydrocarbons may be emitted to the atmosphere in a number of ways. Vent gases from various process operations may contain hydrocarbons, and large quantities of hydrocarbon carrying gases may sometimes be vented as a result of upset conditions in a plant or by the passage of gases through safety valves or relief vents. Leaks in vessels, pump seals, and pipe walls are also a source of fugitive hydrocarbom emissions. Reaction or process air required for a number of organic chemical manufacturing processes can be a source of significant hydrocarbon emissions. Some examples of air requirements for processes are: (1) for synthesis gas, every ton of product requires 4 tons of the air; (2) the production of hydrogen cyanide requires 10 tons of air per ton of product; and (3) acetic anhydride requires 5 tons of air per ton of product. Feedstock shortages stemming from the

current energy crisis have caused the industry to expand efforts in developing technology for increased product recovery. This, combined with more effective recovery and recycling of reagent materials, should lead to a significant decrease in atmospheric emissions from the chemical industry.

While air pollution constitues a problem for manufacturers of organic chemicals, its magnitude does not compare with that posed by industrial water pollution. The sources of liquid waste streams can be divided into five general categories: (1) waste containing a principal raw material or product resulting from the stripping of the product from solution; (2) by-products produced during reactions; (3) spills, slab wash-downs, vessel cleanouts, sample overfiows, etc; (4) cooling tower and boiler blowdown, steam condensate, water treatment waste, and general wash water; and (5) storm waters, for which the degree of contamination depends on the nature of the drainage area. The principal contaminants in the wastewaters include organics from residual products and by-products, oils from the bottom of distillation and stripping columns, suspended solids, and catalysts. Many of the compounds present in the effluents from typical processes are indicated in Table 11.

Numerous solvent processes are utilized in the purification of chemical feedstocks, intermediates, and products used and manufactured by the organic chemicals industry. Since the solvents used are expensive, recovery and recycle operations are usually employed. Therefore, it is doubtful that large quantities will be found in waste streams. Nevertheless, even low concentrations of many of the solvents used by the industry have possible carcinogenic or other biological effects.

Process	Source	Pollutants
Alkylation: Ethylbenzene		Tar, hydrochloric acid, caustic soda, fuel oil
Cyanide production	Water slops	Hydrogen cyanide, unreacted soluble hydrocarbons
Dehydrogenation: Butadiene product from n-Butane and Butylene	Quench waters	Residue gas, tars, oils, soluble hydrocarbons
Ketone production	Distillation slops	Hydrocarbon polymers, chlorinated hydrocarbons, glycerol, sodium chloride
Styrene from	Catalyst	Spent catlayst (Fe, Mg, K, Cu, Cr, Zn)
ethylbenzene	Condensates from spray tower	Aromatic hydrocarbons, including styrene, ethyl benzene, and toluene, tars
Extraction and purification:		
Isobutylene	Acid and caustic wastes	Sulfuric acid, C4 hydrocarbon, caustic soda
Butylene	Solvent and caustic wash	Acetone, oils, C. hydrocarbon, caustic soda, sulfuric acid
Styrene	Still bottoms	Heavy tars
Butadiene	Solvent	Cuprous ammonium acetate, C, hydrocarbons, oils
Extractive distillation	Solvent	Furfural, C ₄ hydrocarbons
Halogenation (principally chlorination)		
Addition to olefins	Separator	Spent caustic

Table 11. INDUSTRIAL ORGANIC CHEMICAL PROCESSES AS WASTE SOURCES

Process	Source	Pollutants
Halogenation: (continued)		
Substitution	HCl absorber, scrubber	Chlorine, hydrogen chloride, spent caustic, hydrocarbon isomers and chlorinated products, oils
	Dehydrohalogenation	Dilute salt solution
Hypochlorination	Hydrolysis	Calcium chloride, soluble organics, tars
Hydrochlorination	Surge tank	Tars, spent catalyst, alkyl halides
Hydrocarboxylation (OXO Process)	Still slops	Soluble hydrocarbons, aldehydes
Hydrocyanation (for acrylonitrile, adipic acid, etc.)	Process effluents	Cyanides, organic and inorganic
Isomerization in general	Process wastes	Hydrocarbons; aliphatic, aromatic, and derivative tars
Nitration Paraffins		Byproduct aldehydes, ketones, acids, alcohols olefins, carbon dioxide
Aromatics		Sulfuric acid, nitric acid, aromatics
Oxidation Ethylene oxide and glycol mfg	Process slops	Calcium chloride, spent lime, hydrocarbon polymers, ethylene oxide, glycols, dichloride
Aldehydes, alcohols, and acids from hydrocarbons	Process slops	Acetone, formaldehyde, acetaldehyde, methanol, higher alcohols, organic acids

Table 11. INDUSTRIAL ORGANIC CHEMICAL PROCESSES AS WASTE SOURCES

Process	Source	Pollutants
Oxidation (Cont.)	********	
Acids, anhydrides	Condensates	Anhydrides, aromatics, acids
from aromatic oxidation	Still slops	Pitch
Phenol, acetone from aromatic oxidation	Decanter	Formic acid, hydrocarbons
Sulfation of olefins		Alcohols, polymerized hydrocarbons, sodium sulfate, ethers
Sulfonation of aromatics	Caustic wash	Spent caustic
Utilities	Boiler blow-down	Phosphates, lignins, heat, total dissolved solids, tannins
	Cooling system blow- down	Chromates, phosphates, algicides, heat
	Water treatment	Calcium and magnesium chlorides, sulfates, carbonates

Table 11. INDUSTRIAL ORGANIC CHEMICAL PROCESSES AS WASTE SOURCES

Caustic washes utilizing aqueous sodium hydroxide solutions are frequently used. Sodium hydroxide solutions are used to extract from process streams various acidic contaminants such as hydrogen sulfide, mercaptans, phenols, biphenyls, and organic acids. Most spent caustic streams can therefore be expected to contain some or all of these compounds in the form of sodium salts as well as some unreacted sodium hydroxide, small quantities of the process product, and feed chemicals. Caustic washes are also used to recover unreacted acidic chemicals in such processes as chlorination, sulfation, sulfonation, polymerization, or oxidation.

Organic chemical processing also involves the use of various acid washes to remove basic materials from product streams. Acidic washes are often used also in removing contaminants from various phenolic product streams. Acid process effluents also are present in some operations, notably alkylation processes.

Caustic or acid washing is often followed by a clear water rinse to remove traces of the washing compounds. Off-gases from various units also are scrubbed with water to remove contaminants. Effluent waters usually will contain pollutants similar in nature to those found in the preceding spent caustic or acid washes, but at significantly lower concentration levels.

Other possible processing operations which may contribute pollutants include spillage of organic chemicals during transport or storage operations and run-off from processing areas. Spent catalyst material may be a component of aqueous waste streams and often can be a serious pollutant in terms of biological toxicity, even though it may be present only in small quantities.

The major solid waste from organic chemical processing is usually associated with bottoms from process tanks, from distillation and stripping columns, and in wastes from the cleaning of storage tanks. This material is usually in the form of a sludge which contains unreacted raw chemicals or products and spent catalysts. These sludges are usually disposed of either by incineration or by landfill.

Specific information relating to pollutants and abatement procedures, when available, is included in the process descriptions.

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INDUSTRY ANALYSIS

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INDUSTRY ANALYSIS

The Industrial Organic Chemicals Industry is discussed in terms of ten feedstock groups: benzene, butylenes, sources of cresylic acids, ethylene, methane, naphthalene, paraffins, propylene, toluene and xylenes. In an effort to complete this study within the imposed time limitations process descriptions vary from very detailed to somewhat general. This is an extremely complex industry and the prescribed brevity of process descriptions has, no doubt, led to process oversimplifications in many cases.

Each feedstock group is discussed in terms of a chemical tree--giving an overview of the products and processing steps described; a process flow sheet--giving a synopsis of the reaction steps involved in the generation of a product and the more important input and output materials for each reaction step; and a concise process description. Examination of the various feedstock chemical trees and process flow sheets will reveal that many products could have come from more than one feedstock group and that many more products could not have been generated without the use of products of the other feedstock groups.

Data are given in metric units according to the System Internationale described in the ASTM Metric Practice Guide.

For each process description an attempt was made to present data first from a recognized authoritative source [e.g., Kirk-Othmer, "Encyclopedia of Chemical Technology"; Lowenheim and Moran, "Industrial Chemicals," 4th Ed. (1975)] and, if not available there then from various specialized publications. The recognized deficiencies in the data prepared for this chapter exist in the general lack of information on waste streams and to a somewhat lesser extent on utilities. For those processes for which no waste

stream information could be found in the literature best professional judgement was used to indicate possible pollutants. Another general characteristic of the Industrial Organic Chemicals Industry is that there appears to be a continuing change in processes for many of the products generated. Thus, this should be at least one of the industrial segments that should require a periodic update. SECTION I BENZENE BENZENE

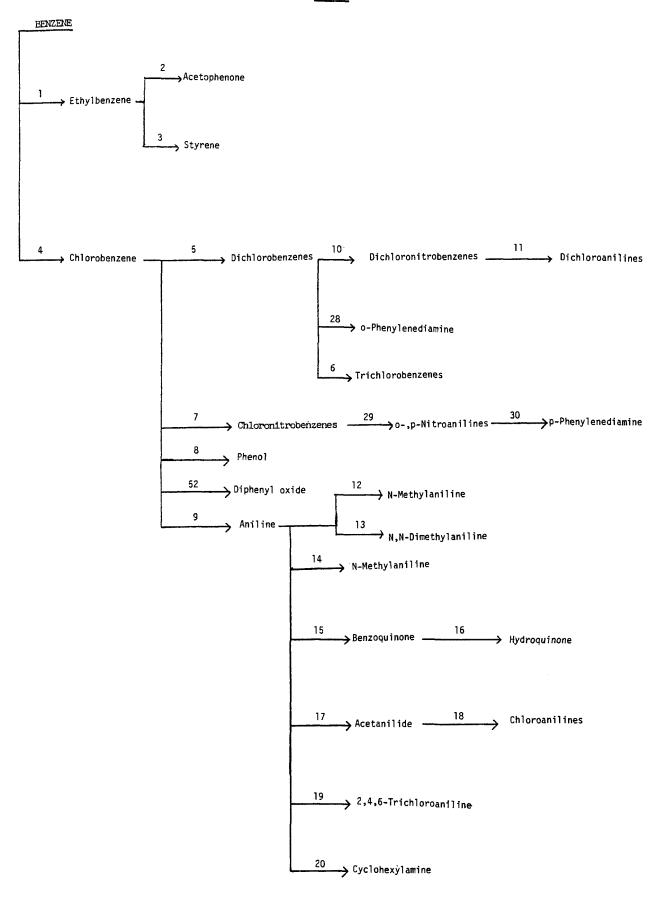


Figure 1. Benzene Section Chemical Tree 6-36

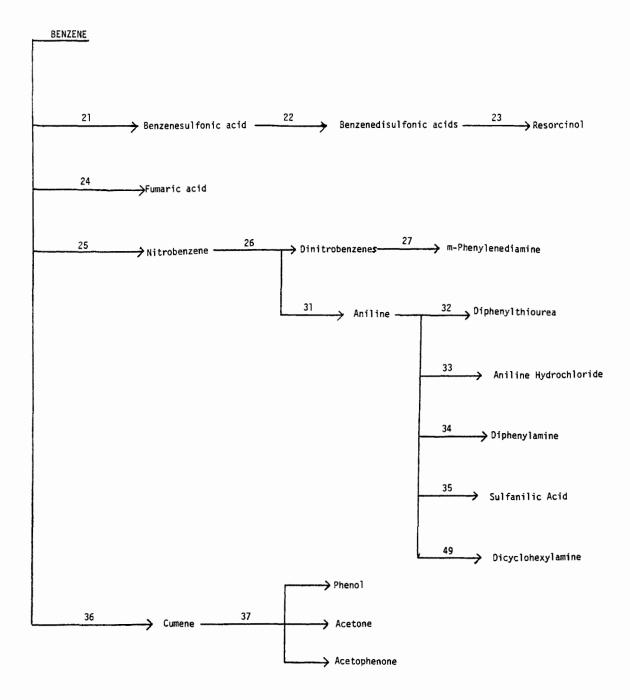


Figure 1. Benzene Section Chemical Tree (Cont.)

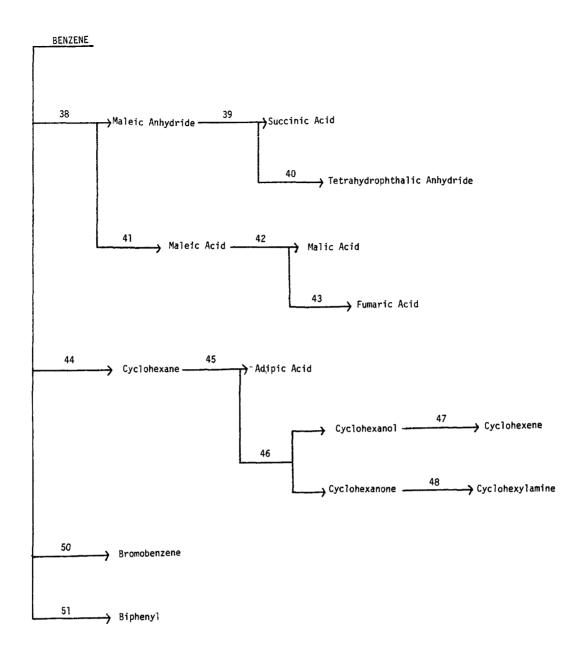


Figure 1. Benzene Section Chemical Tree (Cont.)

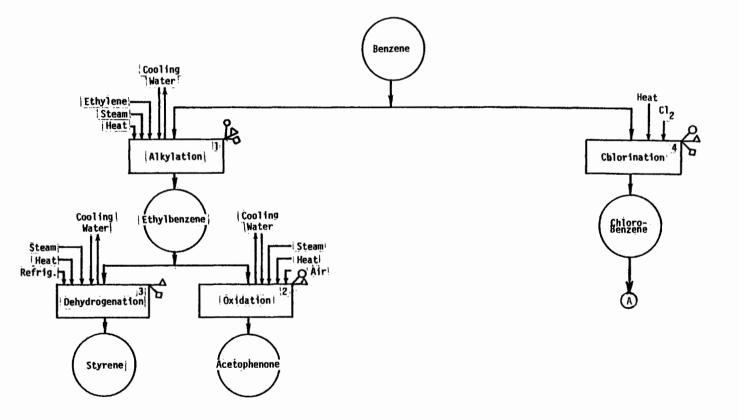


Figure 2. Benzene Section Process Flow Sheet

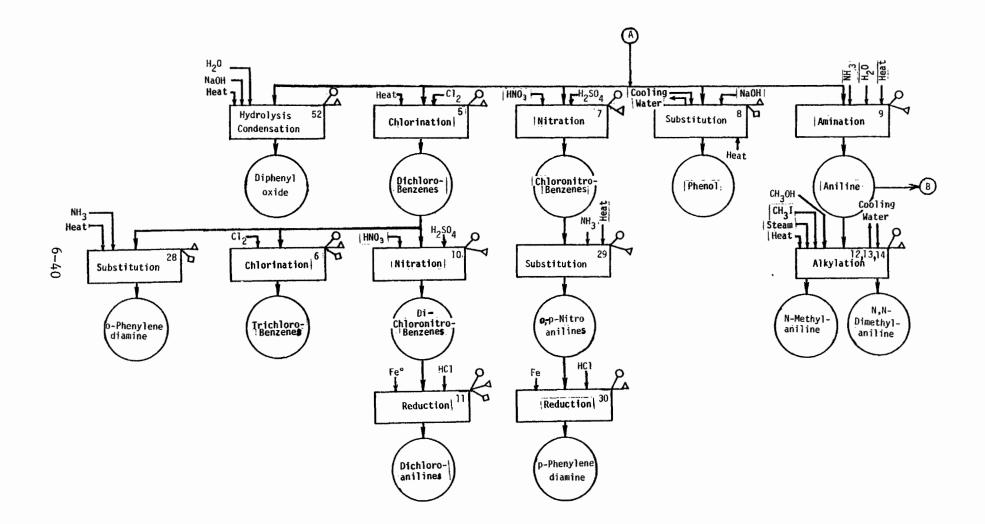


Figure 2. Benzene Section Process Flow Sheet (Cont.)

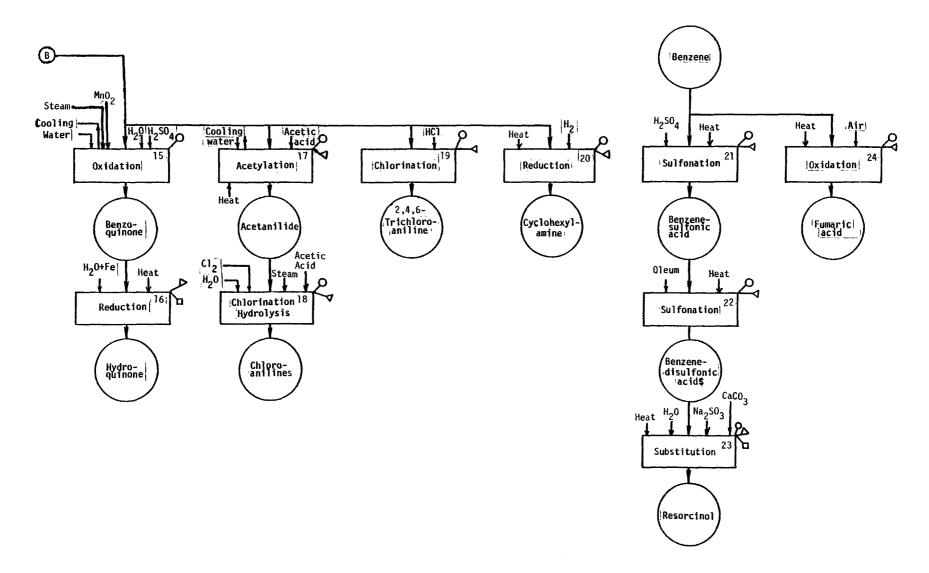


Figure 2. Benzene Section Process Flow Sheet (Cont.)

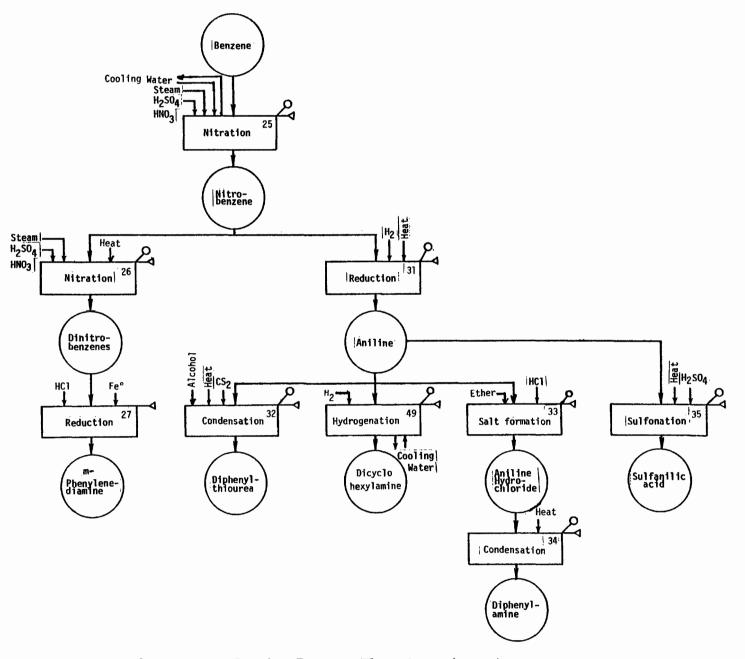


Figure 2. Benzene Section Process Flow Sheet (Cont.)

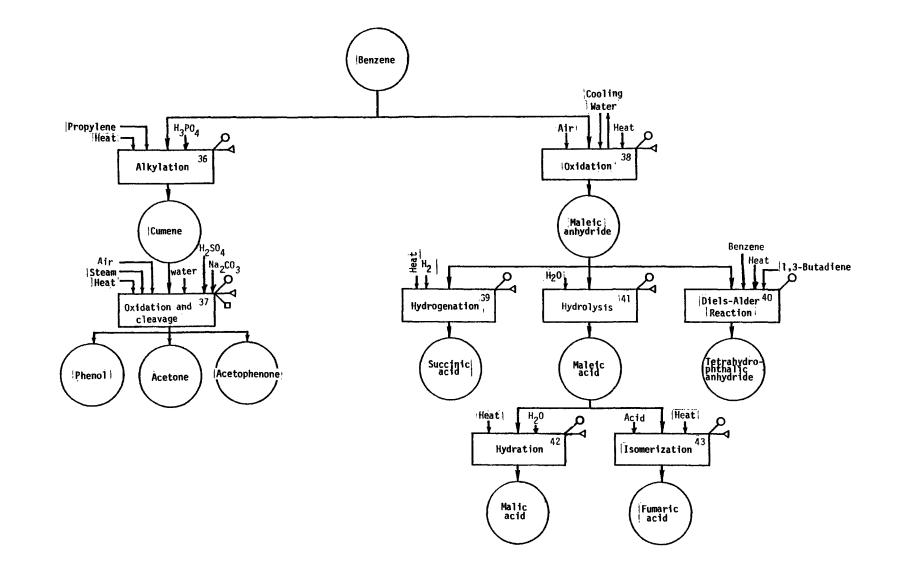


Figure 2. Benzene Section Process Flow Sheet (Cont.)

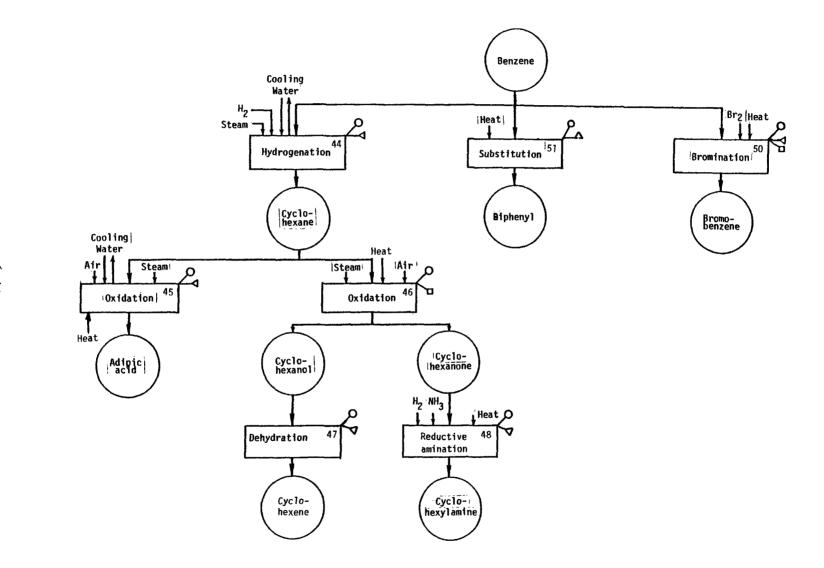


Figure 2. Benzene Section Process Flow Sheet (Cont.)

Ethylbenzene (from benzene and ethylene)



1. Function - Over 90% of ethylbenzene is produced synthetically and 10% is recovered by careful fractionation of selected gasoline fractions, or of the C_8 cut of aromatic naphtha.

Two synthetic processes are used, one of which involves a lowpressure liquid-phase reaction using aluminum chloride catalyst while the other operates in the vapor phase at high pressure with various solid catalysts.

The liquid-phase process is carried out in a brick-lined steel tower or a glass-lined reactor operating at the boiling point of the reaction mixture (80-100°C) at atmospheric pressure. The benzene used is known as "Styrene grade," which defines a benzene with a boiling range of 1°C and a minimum freezing point of 4.85°C (this ordinarily corresponds to a purity slightly above 99%). In general, ethylene at least 90% pure is used. Aluminum chloride is added to a reactor feed stream as a solid and forms the complex in the reactor. Benzene, both feed and recycle, enters the process through a benzene drying column. Hydrogen chloride in the form of HCl or ethyl chloride is also added to the reactor.

The liquid products from the alkylator are cooled and pass through a settler where the complex is removed and returned to the alkylator. The alkylate is then washed with water (which breaks any residual complex)

and scrubbed with 20% caustic soda for netralization, after which it is separated into components in a series of distillation columns.

A prime example of a vapor-phase reaction is the Alkar process which offers the advantage of less corrosion than the aluminum chloride process and which can operate on refinery gas streams containing 8-10% ethylene. The temperature and pressure in this process are typically 290-310°C and 6.3 MPa, respectively. Fresh benzene is mixed with recycle benzene and ethylene and, after heating, is introduced into the fixedbed alkylator. The high-pressure effluent is then flashed and fed into the benzene recycle column where the benzene is recovered as overhead product. The bottoms become the feed to the following column where the product ethylbenzene is separated from the (polyalkyl) benzenes. Most of the (polyalkyl) benzenes are recycled to a separate deaklylator along with the necessary benzene for conversion back to ethylbenzene. The dealkylator effluent is then combined with the alkylator effluent for flashing. The improved catalyst for the alkylation is apparently a boron trifluoride-modified anhydrous γ -alumina, BF₃ being added also in the alkylator feed. The dealkylator presumably uses the identical catalyst and operates under less severe conditions (202°C and 3.45 MPa).

2. Input Materials

Benzene - 775 kg/Mg (1b/1000 1b) product Ethylene - 270 kg/Mg 1b/1000 1b) product

3. Operating Parameters

Temperature: 80-100°C (176-212°F) (liquid phase) 290-310°C (554-590°F) (vapor-phase alkylator) 202°C (396°F) (vapor-phase dealkylator) Pressure: atmospheric (liquid-phase) 6.3 MPa (62.2 atm) (vapor-phase alkylator) 3.55 MPa (35.0 atm) (vapor-phase dealkylator) Catalysts: Aluminum chloride - HC1 complex (liquid-phase) BF₂ on modified γ -alumina support (vapor-phase) 4. Utilities Steam - 37.5 kg/Mg (1b/1000 1b) product Cooling water - 300 kg/Mg (1b/1000 1b) product Electricity - 76 MJ/Mg (9.6 kWh/1000 1b) product Fuel - 5.0 GH/Mg (2.160 MM Btu/1000 1b) product 5. Waste Streams Liquid-phase process: Scrubber effluent (water) - benzene: 11 kg/Mg (1b/1000 1b) Hydrogen chloride: 3.9 kg/Mg (1b/1000 1b) Separator effluent (water) - aluminum salts: trace tarry material: 26.6 kg/Mg (1b/1000 1b) Vapor process: The major waste streams of this process are the spent caustic and washing streams from the crude alkylate washing step. These streams will contain significant amounts of tars, benzene. ethylbenzene, and other polymers. The heavy aromatics fractions from the separation column are usually disposed of by incineration.

Flow - $3.15 \times 10^{-4} \text{ m}^3/\text{kg} (37.7 \text{ gal}/10^3 \text{ lbs})$ COD - 5,980 mg/l 1.88 g/kgBOD₅ - 433 mg/l 0.136 g/kgTOC - 2,091 mg/l0.66 g/kg

6. EPA Source Classification Code - None

7. References

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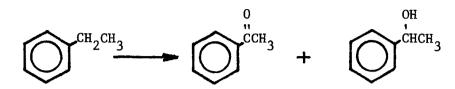
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"1975 Petrochemical Handbook," Hydrocarbon Processing," November, 1975, p. 129-140.

Acetophenone (from ethylbenzene)



1. <u>Function</u> - Acetophenone is produced by the oxidation of ethylbenzene. The reaction is carried out in two acid proof, brick-lined reactors in series. Ethylbenzene and manganese acetate catalyst (15% aqueous solution) are fed into the top of the first reactor and air is dispersed into the liquid at the bottom. Liquid from the bottom of the first reactor is pumped to the top of the second reactor and more air is added at the bottom. The temperature is maintained at 126°C and the pressure at 308 kPa in both reactors. Total contact time between the air and ethylbenzene is 1.5 hours.

About 16% of the ethylbenzene is oxidized in the first reactor and an additional 10% in the second. Eighty-eight percent of the ethylbenzene that reacts forms acetophenone (2 parts) and α -phenylethyl alcohol (1 part).

The remainder is oxidized to acids (including benzoic acid) and residue. The product is treated with 10% aqueous sodium hydroxide to extract acids and precipitate the manganese catalyst. Distillation of the organic layer yields ethylbenzene, which is recycled, and a mixture of acetophenone (68%) and α -phenylethyl alcohol (32%). α -Phenylethyl alcohol is dehydrogenated at 200°C in the presence of a catalyst with a stream of nitrogen flowing through the reactor to remove hydrogen. A mixture containing 80% acetophenone, 6% α -phenylethyl alcohol, and

14% ethylbenzene is produced. Purified acetophenone is obtained by distillation. Purity control is achieved by controlling the freezing point of the distillate which is bulked to give a product with a minimum freezing point of 18.3°C.

2. Input Materials

Ethylbenzene - 1.176 Mg/Mg (1,176.5 1b/1000 1b) product Air - 455 kg/Mg (1b/1000 1b) product Nitrogen - Not given Sodium hydroxide - Not given Manganese acetate catalyst (15% aqueous solution) - Not given

3. Operating Parameters

Oxidation temperature - 126°C (259°F) Oxidation pressure - 308 kPa (3.04 atm) Dehydrogenation temperature - 200°C (392°F) Product freezing point - 18.3°C (64.9°F) (minimum) Catalyst - Manganese acetate (15% aqueous solution) Contact time - 1.5 hrs.

4. <u>Utilities</u> - Basis - 0.454 kg (1 lb) of product Electricity - 144 kJ (0.04 kWh) Fuel gas - 9.06 dm³ (0.32 cubic feet) Cooling water - 102 dm³ (27 gallons) Steam - 3.2 kg (7.0 lb) Compressed air - 404 dm³ (14.3 cubic feet)

5. Waste Streams

<u>Air</u>: Excess air from the oxidation reactors and nitrogen from the dehydrogenator may be vented to the atmosphere and would contain ethylbenzene, acetophenone, and α -phenylethyl alcohol in unknown quantities. Emission from distillation should be minimal. <u>Water</u>: Still bottom residues, excess and sodium salts of by-product acids would be the major wastewater pollutants with possibly small quantities of ethylbenzene, acetophenone and α -phenylethyl alcohol included.

6. EPA Source Classification Code - None

7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 168. "Synthetic Organic Chemicals," U. S. Tariff Commission, TC Publication 681, 1972. Styrene (dehydrogenation of ethylbenzene)



1. <u>Function</u> - The present commercial process for styrene production involves the catalytic dehydrogenation of ethylbenzene. Dehydrogenation of ethylbenzene is effected at 600-700°C and atmospheric pressure in the presence of catalysts, e.g., Si0₂-A1₂0₃, solid phosphoric acid, zinc oxide promoted with alumina and chromates, and cobalt oxides. Yields of 90% are commonly attained, with conversions of 30-40% per pass.

The styrene recovery section consists of three columns. The small amount of benzene and toluene produced by cracking is removed in the first column and returned to the ethylbenzene system. Ethylbenzene for recycle is separated from styrene in the second column, and polymerization inhibitors such as sulfur, para-tertiary butylcatechol or 2-nitro-4,6-dichlorophenol are added. In the third column, styrene monomer is separated from small amounts of tar and polymer formed during the operation.

- 2. Input Materials Ethylbenzene 1.12 kg/kg styrene
- 3. Operating Parameters

4. Utilities - Basis: 2.87 kg/sec (6.3 1b/sec) capacity

	Dehydro- genation	Separ- ation	<u>Total</u>
<u>Steam</u> kg/sec (1b/sec)	27.2 (60)	13.1 (28.9)	40.3 (88.9)
Cooling Water m ³ /sec (gals/sec)	0.94 (248)	0.64 (169)	1.58 (417)
Refrigeration Mg (tons)	27.2 (30)	90.7 (100)	117.9 (130)
Natural Gas sm ³ /sec (scf/sec)	0.17 (6)		0.17 (6)
Electric Power (kW capacity) Process Utilities	108 466	160 270	268 736

5. Waste Streams - Separator (water)

Heavy ends and tarry matter * - 0.393 kg/Mg (1b/1000 1b) styrene Super heater (water) tarry matter * and heavy ends - 5.9 kg/Mg (1b/1000 1b) styrene

Still bottom (solids) tarry matter * and heavy ends - 7.05 kg/Mg (1b/1000 1b) styrene

	<u>Plant 1</u>	Plant 2
Flow	0.0235 m ³ /kg (2,810 gal/ 10 ³ 1bs)	0.00548 m ³ /kg (657 gal/ 10 ³ 1bs)
COD	219 mg/1 5.13 g/kg	426 mg/1 2.34 g/kg
BOD ₅	69 mg/1 1.62 g/kg	70 mg/1 0.381 g/kg
TOC	22 mg/1 0.53 g/kg	22 mg/1 0.12 g/kg

^{*} Contains sytreme trimer, stilbene, biphenylnaphthalene, phenathreme, ethylphenanthreme, and other unidentifiable products.

- 6. EPA Source Classification Code None
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 8," "Chemical Engineering," July 22, 1974, p. 113,114.

"1973 Petrochemical Handbook," "Hydrocarbon Processing," November, 1973, p. 179,180.

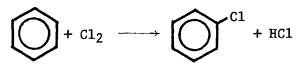
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Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corp., Park Ridge, N.J., 1974, p. 191-195.

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 779-782.

"1975 Petrochemical Handbook," "Hydrocarbon Processing," November, 1975, p. 204,205.

Chlorobenzene



- 1. Function Chlorobenzene is manufactured by passing dry chlorine into benzene in the presence of a catalyst. The catalysts which may be used are molybdenum chloride, FeCl₃, AlCl₃, Fuller's earth, or simply iron turnings. The reaction takes place in a boiling mixture of chlorobenzene and benzene at 101 kilopascals (1 atmosphere) pressure and 80-100°C (175-212°F). HCl released by the reaction is scrubbed with recycled benzene to remove hydrocarbons and then absorbed with water to form 20°Be hydrochloric acid. The bottoms are washed with sodium hydroxide to remove remaining HCl and dichlorobenzenes. The sodium hydroxide solution is decanted and the product fed to a stripping column where benzene is stripped off overhead and recycled to the HCl scrubber. The bottoms are fed to a fractionating column where the pure monochlorobenzene is taken off overhead.
- 2. <u>Input Materials</u> Basis 1 metric ton chlorobenzene Chlorine - 875 kg (1929 lbs) Benzene - 950 kg (2094 lbs) Sodium hydroxide Catalyst (Fe turnings) - small
- 3. Operating Parameters

Temperature - 80-100°C (175-212°F) Pressure - 101 kPa (1 atm) Catalyst - molybdenum chloride FeC1₃, AlC1₃, fuller's earth, iron turnings

4. Utilities

Electric power - Not given Water - Not given

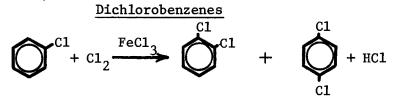
- 5. <u>Waste Streams</u> Main pollutant by-products are: HC1, dichlorobenzene, heavies and spent caustic sludge. The HC1 and dichlorobenzenes are absorbed. Benzene is also a major air pollutant. Two sources are the vent on the HC1 absorber and on the stripper.
- 6. EPA Source Classification Code None
- 7. References

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corp., Park Ridge, N.J., 1974, p. 103-104.

Austin, G. T., "The Industrially Significant Organic Chemicals - Part 2," "Chemical Engineering," February 18, 1974, p. 128.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 373.

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 258-260.



- 1. <u>Function</u> Dichlorobenzenes can be produced by chlorinating chlorobenzene in the presence of ferric chloride at 150-190°C. This reaction produces basically a mixture of o- and p-dichlorobenzenes with the latter predominating. The ortho isomer can be removed from the crystalline para isomer by washing the crystals of the para isomer with methanol. The p-dichlorobenzene is finally freed from alcohol by heating at 100°C under vacuum. The meta isomer of ditchlorobenzene does not occur in high enough quantities in the above reaction process to make it a practicable source of that isomer. Usually, m-dichlorobenzene is obtained from the ortho and para isomer by subjecting these to an isomerizing process. This isomerizing process is to heat the mixture to 120°C under approximately 4.5 x 10³ kilopascals in the presence of aluminum chloride and hydrogen chloride; aluminum chloride in a small amount of water; or aluminum chloride alone at higher temperature.
- 2. Input Materials

Chlorobenzene

Ferric chloride

Chlorine

3. Operating Parameters

Temperature: 150-190°C (302-374°F)

Pressure: not given

4. Utilities

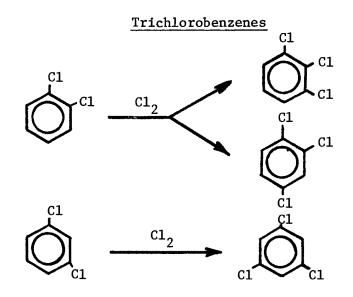
Not given

- 5. <u>Waste Streams</u> No specific information was available, but one would expect some hydrogen chloride to be given off and possibly some benzene, trichlorobenzene, and ionic salts.
- 6. EPA Source Classification Code None

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 259-260.

<u>Chemical Technology</u>, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 213.



- <u>Function</u> The 1,2,3- and 1,2,4-isomers of trichlorobenzene can be obtained by chlorinating o-dichlorobenzene at 25-30°C, in the presence of ferric chloride, to a density of 1.4 (at 15°C), neutralizing the acid present, and fractionally distilling. Similarly, by chlorinating m-dichlorobenzene, 1,3,5 trichlorobenzene can be obtained.
- 2. Input Materials

Dichlorobenzenes

Ferric chloride

Chlorine gas

3. Operating Parameters

Temperature - 25-30°C (77-86°F) Pressure - not given

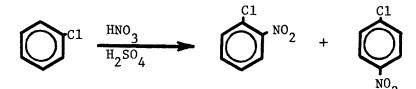
Catalyst - ferric chloride

4. Utilities - Not given

- 5. <u>Waste Streams</u> Waste water from distillation bottoms may contain traces of dichlorobenzenes and trichlorobenzenes, as well as polychlorinated benzenes.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964) p. 260-262.

Chloronitrobenzenes (from chlorobenzene)



- 1. <u>Function</u>- Chloronitrobenzenes can be manufactured by the nitration of chlorobenzene using a mixed acid of nitric acid and sulfuric acid. Since the chlorine is ortho-para directing the substitution into the ring with the nitric group is on the ortho (34%) and para (65%) positions. Thus the product from this reaction is a mixture of ortho and para chloronitrobenzenes. The para isomer is separated by recrystal-lization. The o-chloronitrobenzene is purified by rectification.
- 2. Input Materials

Chlorobenzene - 4536 kg (10,000 lbs) Nitric acid (30-35%) Sulfuric acid (52-55%)

3. Operating Parameters

Temperature - 40-70°C (104-158°F)

Pressure - not given

Reaction time - 12 hrs.

- 4. Utilities Not given
- <u>Waste Streams</u> Possible aromatic emissions from the distillation process;
 possible NO_v emissions during nitration process and acid wastes.
- 6. EPA Source Classification Code None

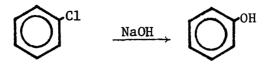
7. References

Hedley, W. H., et al., <u>Potential Pollutants From Petrochemical Processes</u>, Technomic Publishing Co., Westport, Conn., 1975.

Austin, G. T., "The Industrially Significant Organic Chemicals - Part 3," "Chemical Engineering," March 18, 1974, p. 90.

<u>Chemical Technology</u>, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 552.

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corp., Park Ridge, N.J., 1974, p. 172,173. Phenol (from chlorobenzene)



1. Function - Phenol is formed from chlorobenzene by reacting the chlorobenzene with sodium hydroxide at elevated temperature and pressure. In this process, chlorobenzene and a 10 - 15% aqueous sodium hydroxide solution are introduced into a high pressure pump with approximately 10% by weight of diphenyl oxide. Small quantities of anti-corrosion agents, emulsifiers, and a catalyst may also be added to the reactants. This process stream is fed to a continuousflow tubular reactor system in which the stream temperature is raised to 400°C (752°F) approximately 27.6 x 10^3 - 34.5 x 10^3 kilopascals (4000 - 5000 psi) and maintained at this temperature and pressure for 10 - 30 minutes. The heat exchanger in which this reaction is carried out is a steel pipe, nickel-lined exchanger using flue gas, and organic heat transfer agent, direct flame, or electrical heating coils as a heat transfer medium. After leaving the exchanger the product stream is cooled. The reaction products, consisting of sodium phenate, sodium chloride, water, and unchanged reactants, produce a two phase system. The first phase is an aqueous phase containing sodium phenate, and the second phase is an oil phase consisting principally of diphenyl oxidate and unreacted monochlorobenzene. The oil phase is distilled to produce diphenyl oxide or is recycled to the reactor. The aqueous phase is treated with hydrochloric acid to convert sodium phenate to phenol which is decanted and distilled under vacuum. The sodium

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chloride that is formed is electrolized to form sodium hydroxide and chlorine which is recycled.

2. Input Materials

Chlorobenzene - 1.27 kg (1b)/kg (1b) phenol produced Aqueous sodium hydroxide - 0.12 kg/Mg (0.24 1b/ton) phenol produced Diphenoloxide - 0.13 kg (1b)/kg (1b) phenol produced

3. Operating Parameters

Temperature: 400°C (752°F) Pressure: 27.6 x 10^3 - 34.5 x 10^3 kilopascals (4000 - 5000 psi) Catalyst: not given

4. <u>Utilities</u>

Electric power - not given

Cooling water - 3.85 kg (1b)/kg (1b) phenol produced

5. Waste Streams

Acid stream dichlorobenzene column (water):

Chlorobenzene

Dichlorobenzene

Other chlorinated compounds (assumed to be mainly chlorotoluene) -

4.0 kg/Mg (7.9 1b/ton) pheno1

Ortho-dichlorobenzene column waste (solid):

Ortho-dichlorobenzene - 0.6 kg/Mg (1.2 lb/ton) phenol

Other chlorinated compounds (chlorotoluene) - 1.2 kg/Mg (2.4 lb/ton) phenol

Extractor brine (water):

Pheno1 - 0.75 kg/Mg (1.5 1b/ton) pheno1

Sodium chloride - 1.559 kg/Mg (3,118 1b/ton) phenol

Benzene - 12.2 kg/Mg (24.4 lb/ton) phenol

Diphenyl ether column wastes (solid): Diphenyl ether - 0.665 kg/Mg (1.33 lb/ton) phenol Phenyl diphenyl ether - 19.4 kg/Mg (38.7 lb/ton) phenol

- 6. <u>EPA Source Classification Code</u> None
- 7. References

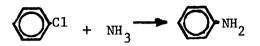
Yen, Y. C., "Phenol," Report No. 22, Stanford Research Institute, Menlo Park, California, 1967.

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corporation, Park Ridge, N.J., 1974, p. 181.

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 8," "Chemical Engineering," July 22, 1974, p. 107, 108.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 15 (1968), p. 153-155.

Aniline



- <u>Function</u> Aniline is produced by combining chlorobenzene, and liquid ammonia at high temperatures and high pressures in the presence of a catalyst. The catalyst used is the cuprous chloride made from the reaction of the cuprous oxide and ammonium chloride. The reaction takes place at 200°C and 6.2 megapascals (900 psi).
- 2. <u>Input Materials</u> Basis 1 metric ton aniline Chlorobenzene - 1250 kg (2,756 lbs) Cuprous oxide - 175 kg (386 lbs) Liquid ammonia - (28% solution) 3725 kg (8,212 lbs) NH₃: C₆H₅Cl ratio should be at least 5:1
- 3. Operating Parameters

Temperature: 180-220°C (356-428°F)

Pressure - 6.2 MPa (61.2 atm)

4. Utilities

Electric power - not given Water - not given

5. Waste Streams

Ammonia

Benzene

Pheno1

- 6. EPA Source Classification Code None
- 7. <u>References</u>

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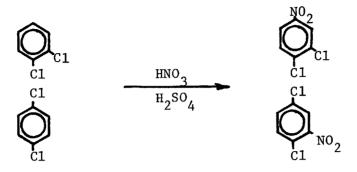
Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 419.

Austin, G. T., "The Industrially Significant Organic Chemicals - Part 1", "Chemical Engineering," January 21, 1974, p. 132.

Astle, M. J., <u>Industrial Organic Nitrogen Compounds</u>, Reinhold Publishing Corp., New York, N.Y., 1961, p. 87.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition John Wiley and Sons, New York, N.Y., 1975, p. 111,112.

Dichloronitrobenzenes (from dichlorobenzenes)



- 1. <u>Function</u> The dichloronitrobenzenes (3,4-dichloro- and 2,5-dichlorol-nitrobenzenes) are prepared commercially by nitrating their corressponding dichlorobenzenes. In many cases two immiscible layers are present in the nitrator. For safety reasons and ease of operation, atmospheric pressures and temperatures from 0-120°C are used. At the higher temperatures, competing oxidation reactions becomes important.
- 2. Input Materials

Dichlorobenzenes

Nitric acid

Sulfuric acid

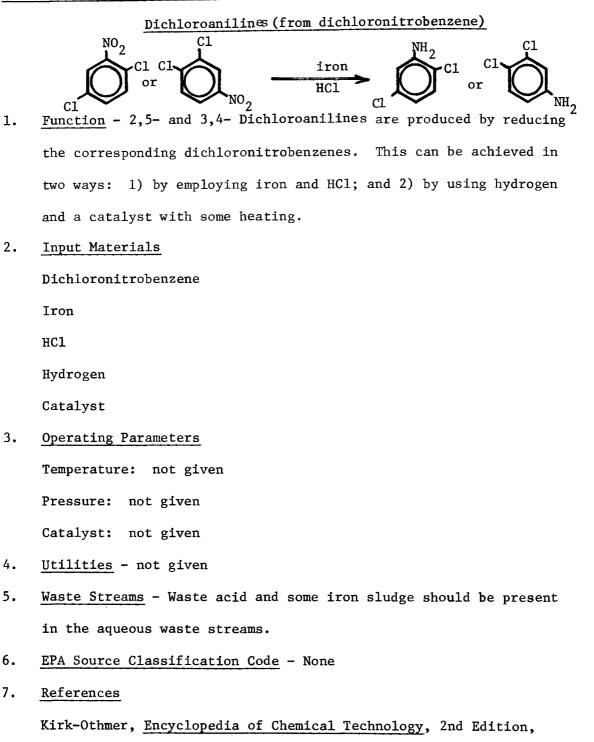
- 3. <u>Operating Parameters</u> Temperature - 0-120°C (32-248°F) Pressure - 101 kPa (1 atm) Residence Time - 1-60 minutes
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Some chlorinated benzenes, chloronitro-phenols, nitric, and sulfuric acid may be present in the waste streams.

6. EPA Source Classification Code - None

7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 13 (1967), p. 785-790, 244.

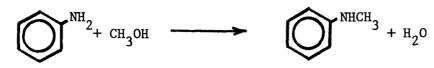
INDUSTRIAL ORGANIC CHEMICALS



Interscience Publishers, New York, N.Y., Vol. 2(1963) p. 424.

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N-Methyl Aniline (from aniline and methanol)



 <u>Function</u> - N-Methyl aniline is most economically produced by the vapor - phase reaction of aniline and methanol at 285-325°C over a catalyst containing 86% alumina, 9% calcium oxide (or ZnO, CrO, MgO, FeO, MnO), and 5% (2-20%) copper.

Tertiary amine formation is suppressed by the use of hydrogen at 207 - 414 kPa (2.04 - 4.09 atm). Yields of 96-98% are obtained.

2. Input Materials - Basis: 1 kg N-Methyl aniline

Aniline 0.90 kg

Methanol 0.46 kg

Hydrogen 4.8 g

3. Operating Parameters

Temperature: 285-325°C (545-617°F)

Pressure: 101 kPa (1 atm)

Catalyst: 86% alumina, 9% CaO, 5% copper

- 4. Utilities not given
- 5. <u>Waste Streams</u> Off-gases from the separator may contain methanol, aniline, methyl aniline, and by-products such as N,N-dimethyl aniline.
- 6. EPA Source Classification Code 3-01-034-01
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963) p. 368,420.

U.S. Patent No. 2,580,284 (Dec. 25, 1951)

N, N-Dimethylaniline (from aniline and methanol)

 $C_6H_5NH_2 + 2 CH_3OH \xrightarrow{H_2SO_4} C_6H_5N(CH_3)_2 + 2 H_2O$

- 1. <u>Function</u> Dimethylaniline is produced by heating aniline and methanol under pressure in an autoclave with an acid catalyst, commonly hydrochloric or sulfuric acid. Sulfuric acid is used commercially since it is less corrosive than hydrochloric acid. The aniline, methanol, and sulfuric acid are mixed together, stirred (to suspend the aniline sulfate which precipitates out), and pumped into an unlined steel autoclave. The autoclave is heated (93.3-121.1°C superheat given to steam at 689.5 kPa) during the course of two hours to around 200°C and kept there for five or six hours, during which time the internal pressure may rise to 3,620-3,792 kPa. The autoclave may be allowed to cool or the hot mixture may be discharged through a cooling condenser into a vessel where the acid is neutralized with caustic soda. Vacuum distillation allows the recovery of excess methanol and purification of the dimethylaniline produced.
- 2. Input Materials Basis 1 metric ton product

Aniline, kg		1052.6
Methanol, kg		1158.1
Sulfuric acid (66° Be)	kg	105.5

3. Operating Parameters

Temperature, °C	200	(392°F)
Pressure, kPa	3,620-3,792	(35.7-37.4 atm)
Reaction time, hrs	5-6	
Reaction Vessel: unlined s	teel autoclave	

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4. Utilities

Not given

- 5. <u>Waste Streams</u> Specific information was not available, but some aniline, monomethylaniline, and sulfate salts may be in the waste water.
- 6. EPA Source Classification Code None
- 7. References

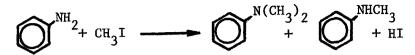
Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 420.

Groggins, P. H., <u>Unit Processes in Organic Synthesis</u>, 5th Ed., McGraw-Hill Book Co., New York, N.Y., 1958, p. 850, 851.

Shreve, R.N., <u>Chemical Process Industries</u>, 3rd Ed., McGraw-Hill Book Co., New York, N.Y., 1967, p. 821, 822.

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 275.

N-Methyl Aniline (from aniline and methyl iodide)



- Function An alternate route to N-methyl aniline involves the reaction of aniline and methyl iodide at elevated temperatures. This results in a mixture of N-methyl aniline and N,N-dimethyl aniline, which may be separated by a series of distillations.
- 2. Input Materials

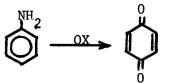
Aniline

Methyl iodide

- 3. Operating Parameters Not given
- 4. Utilities Not given
- 5. <u>Waste Streams</u> The water effluent from the acid scrubber probably contains sodium iodide, caustic, methyl iodide, aniline, and traces of the secondary and tertiary amines. Methyl iodide and hydrogen iodide may be present in the gas effluent.
- 6. EPA Source Classification Code 3-01-034-01
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963) p. 420.

p-Benzoquinone



1. <u>Function</u> - p-Benzoquinone is manufactured by the oxidation of aniline as the sulfate salt with sodium dichromate or manganese dioxide mixed with sulfuric acid. Dilute sulfuric acid and approximately 25% of the total MnO₂ is charged to the oxidizing tank. This mix is cooled to 5-12°C, then a solution of the aniline and sulfuric acid is added to the tank. The remainder of the MnO₂ is added so that there is always an excess of MnO₂ in the tank. Cooling is a critical factor since this reaction is very exothermic. A variation of this process operates at 20-70°C and continuously at reduced pressure. After completion of the reaction the acidity is reduced by addition of a hydrated lime slurry and the p-benzoquinone is distilled with steam. The distillate is then chilled to form golden-yellow needles of a 99-100% purity product.

The non-volatile mineral salts are used as a source of manganese in fertilizer and animal feed supplements.

Often a marked increase in yield results if the substance contains an additional hydroxyl or amino group in the para position.

2. Input Materials - Basis: 1 kg p-Benzoquinone produced

Aniline - 0.85 kg

MnO₂ - 2.42 kg H₂SO₄ - 4.19 kg Water - 14.65 kg 3. Operating Parameters

Temperature: 5-12°C (41-54°F) initial or 20-70°F (68-158°F) in modified case Pressure: not given Catalyst: none

4. Utilities

Not given

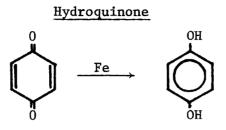
- 5. Waste Streams ammonia from distillation
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Ed., Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 415.

Ibid. Vol. 16 (1967), p. 907.

Chemical Technology, Barnes and Noble, New York, N.Y., Vol. 4 (1972), p. 402,405.

Carson, J., <u>Organic Reactions</u>, John Wiley & Sons, New York, N.Y., Vol. 4 (1949), p. 306



- 1. <u>Function</u> Hydroquinone is manufactured by reducing p-benzoquinone. This is done with the quinone in solution with iron dust and water at 60 - 76°C (140 - 149°F) and a slightly reduced pressure. The reaction mixture is filtered to remove iron oxide, and excess iron and the filtrate passed to crystallizers. In some processes the purewhite technical product obtained is purified by vacuum distillation. The distilled product is then dissolved in dilute sulfuric acid bath with the use of carbon, sodium bisulfite, or zinc dust as decolorizing agents. The solution is then filtered and a small amount of sodium hydrosulfite is added to the filtrate from which the hydroquinone crystallizes.
- 2. <u>Input Materials</u> per kg (lb) hydroquinone produced p-Benzoquinone - 1.25 kg (lb) Iron dust - 12.5 kg (lb) Water - 100 kg (lb)
- 3. Operating Parameters

Temperature: 60 - 65°C (140 - 149°F)

Pressure: slightly reduced

Catalyst: none

4. Utilities

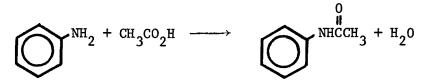
Electric power - not given Water - not given

- 5. <u>Waste Streams</u> possible sludge handling problems, starting material, and phenolic resins.
- 6. EPA Source Classification Code Code
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 11 (1966), p. 485-487.

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Acetanilide



 <u>Function</u> - Acetanilide can be manufactured in two major ways. The first uses a benzene solution of aniline and acetic acid and acetyl chloride. This solution is refluxed in a jacketed, enameled still until no free aniline remains. The reaction mixture is filtered and the crystals separating on cooling are recrystallized from hot water.

The second process employs aniline and approximately 100% molar excess of acetic acid. This solution is refluxed for 6 to 14 hours in a suitable still. The product is dropped into hot water and allowed to crystallize. If the acid is dilute the reaction is carried out under pressure at 150-160°C (302-320°F).

2. Input Materials

Process one

Aniline - 0.69 kg (lb)/kg (lb) acetanilide Acetic acid - 0.97 kg (lb)/kg (lb) acetanilide Benzene - as needed

Process two

Aniline - 0.69 kg (lb)/kg (lb) acetanilide Acetic acid - 0.76 kg (lb)/kg (lb) acetanilide

3. Operating Parameters

Temperature - 150-160°C (302-320°F) Pressure - Not given Catalyst - None Reaction time - 6-14 hrs

4. Utilities

Electric power - Not given Water - Not given

- 5. Waste Streams Benzene from refluxing operations and some acetic acid.
- 6. EPA Source Classification Code None
- 7. References

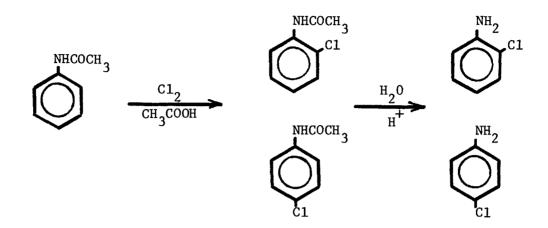
Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 151.

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 526.

Faith, W. L., et al., <u>Industrial Chemicals</u>, 3rd Edition, John Wiley and Sons, New York, N.Y., 1965, p. 9,10.

PROCESS NO. 18

Chloroanilines (from acetanilide)



 Function - Acetanilide is mixed with acetic acid and chlorine gas to produce a mixture of o- and p-chloroacetanilides. This mixture is then combined with water and acid to produce a mixture of o- and p-chloroanilines. The mixture can then be separated by steam distillation.

The production of m-chloroaniline is by the reduction of m-nitrochlorobenzene or by treating aniline in concentrated sulfuric acid with chlorine gas.

2. Input Materials

Acetanilide

Acetic acid

Chlorine

Water

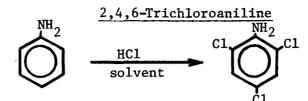
3. Operating Parameters

Temperature - not given Pressure - not given Catalyst - none

4. Utilities - not given

- 5. <u>Waste Streams</u> Possible chlorine gas from incomplete reaction in initial step and some acetic acid.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Astle, M. J., <u>Industrial Organic Nitrogen Compounds</u>, Rheinhold Publishing Co., New York, N.Y., 1961, p. 109. Migradichian, V., <u>Organic Synthesis</u>, Rheinhold Publishing Co., New York, N.Y., Vol. 2 (1957), p. 1555.



- 1. <u>Function</u> 2,4,6-Trichloroaniline can be manufactured by the direct chlorination of aniline according to the above reaction. In this reaction anhydrous hydrochloric acid in an anhydrous organic solvent is mixed with aniline to produce the 2,4,6-trichloroaniline, which is diluted with water, separated, and dried at 60°C/2.66 kPa.
- 2. Input Materials

Aniline	400	parts
Hydrochloric acid	157	parts
Solvent		

CC14	4000	parts
EtOH	80	parts

C1 ₂	1060	parts

3. Operating Parameters

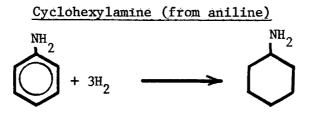
Temperature: 16°C (60.8°F) Pressure: not given Catalyst: none Reaction Time: 6 hours

- 4. Utilities Not given
- <u>Waste Streams</u> Aniline, CCl₄, EtOH, Cl₂, and HCl traces should be present in the waste streams.
- 6. EPA Source Classification Code None

7. <u>Reference</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 415.

U.S. Patent 2,675,409 (Apr. 12, 1954).



- <u>Function</u> Cyclohexylamine is produced commercially by reducing aniline with hydrogen and a ruthenium or a Raney nickel catalyst. The reduction employing the ruthenium catalyst takes place at approximately 220°C and up to 3.45 - 6.90 MPa. As of 1964, only one U. S. plant (Abbott) produced cyclohexylamine by this process, but it accounted for 28% of the total U. S. production.
- 2. Input Materials

Aniline

Hydrogen

Catalyst

3. Operating Parameters

Temperature - 220°C (428°F)

Pressure - 3.45-9.60 MPa (34-94.7 atm)

Catalyst - Raney nickel or ruthenium compound

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Possibly excess hydrogen and some aromatics may be given off by the process.
- 6. EPA Source Classification Code None

7. References

Astle, M. J., <u>Industrial Organic Nitrogen Compounds</u>, Rheinhold Publishing Co., New York, N.Y., 1961, p. 31.

Chemical Technology, Barnes and Noble, New York, N.Y., Vol. 4, (1972), p. 514.

Hahn, A. V., <u>The Petrochemical Industry: Markets and Economics</u>, McGraw-Hill Publishing Co., New York, N.Y., 1970, p. 431, 432.

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Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition,

Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 125.

Benzenesulfonic Acid



 Function - Three basic methods have been used to produce benzenesulfonic acid: sulfuric acid, oleum, and sulfur trioxide. Sulfur trioxide is considered to be the effective sulfonating agent regardless of the sulfur reactant used.

Sulfonation with sulfuric acid

a) Batch process - Benzene and sulfuric acid monohydrate are added to a sulfonator with agitation over a one hour period at an initial temperature of 75°C. The mixture is then heated to 105° for an hour and then held there for four hours.

b) Continuous process - Sulfuric acid is fed continuously to the sulfonator concomitantly with benzene which has been previously fed through a vaporizer-superheater. The reaction mass flows to the top of a plate column which acts as a second sulfonator. This stream passes downward countercurrent to another stream of benzene vapor. A sevenstage reactor operating at 180°C and a molar ratio of benzene to sulfuric acid of 10:1, has a residence time of 1.5 hr. The benzenesulfonic acid is discharge from the bottom of the tower while the benzene vapor and water are released at the top and collected in a condenser. The benzene is separated, dried, and reused.

Sulfonation with oleum

Liquid benzene is charged to a presulfonator and 9.5% oleum is fed in over a period of time, the temperature being controlled by the rate of

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addition of oleum. The reaction mass is then pumped to the vaporfeed sulfonators and raised to reaction temperature, ~100°C. Benzene vapor is fed in until the desired residual-acid level is attained. The reaction mass flows from the bottom of the reactor to storage. The excess benzene and water of reaction is scrubbed with caustic to remove acids and is then condensed; the benzene is dried and returned to the process.

Sulfonation with sulfur trioxide

Benzene is allowed to react with sulfur trioxide in liquid sulfur dioxide at -90°C. The liquid sulfur dioxide is evaporated until a temperature of 10-20°C is attained at which point benzene is added and the temperature is allowed to rise to 50-70°C. The sulfur dioxide is removed by an air stream.

In each process the benzenesulfonic acid can be crystallized from the sulfonation mass by cooling to $-10^{\circ}C$ (13°F) to give a low recovery of solid sulfonic acid.

2. Input Materials

Sulfonation with sulfuric acid

a) Batch process: benzene - 0.49 kg/kg product

 H_2SO_4 - 1.24 kg/kg product

b) Continuous process - benzene - 4.94 kg/kg product

sulfuric acid - 0.62 kg/kg product

Sulfonation with oleum

Benzene

01eum

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Sulfonation with sulfur trioxide
Benzene - 0.49 kg/kg product
Sulfur trioxide - 0.62 kg/kg product
Liquid sulfur dioxide
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Sulfur trioxide: sulfur dioxide = 1.8

3. Operating Parameters

Sulfonation with sulfuric acid

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a) Batch process - temperature - 65-105°C (149-221°F)
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pressure - not given

b) Continuous process - temperature - 180°C (356°F)

pressure - not given

Sulfonation with oleum

temperature - ~100°C (~212°F)

pressure - not given

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Sulfonation with sulfur trioxide
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Temperature: Stage 1 - 9°C (48°F) Stage 2 - 10-20°C (50-68°F) Stage 3 - 50-70°C (122-158°F)

Pressure: not given

Purification

Temperature - -10°C (14°F)

4. Utilities

Not given

5. <u>Waste Streams</u> - possible benzene vapors from leaks in system; diphenyl sulfone; H₂SO₄.

6. EPA Source Classification Code - None

7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1963), p. 403,404.

U. S. Patent 2,125,189 (July 26, 1938).

U. S. Patent 2,798,089 (July 2, 1957).

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Benzenedisulfonic Acids



- 1. <u>Function</u> The meta isomer of benzenedisulfonic acid is produced from the benzenesulfonic acid by direct sulfonation. In this process the monosulfonic acid is reacted with 65% oleum at 30-85°C for 6.5-7.5 hr. The para isomer cannot be produced by direct sulfonation. However, it is produced from the disodium salt of m-benzenedisulfonic acid by heating at 300°C under pressure, with a metal catalyst.
- 2. Input Materials

m-Benzenedisulfonic acid

Benzenesulfonic acid

65% oleum

p-Benzenedisulfonic acid

m-Benzenedisulfonic acid disodium salt

Catalyst

3. Operating Parameters

Benzenedisulfonic acid: temperature - 30-85°C (86-185°F)

pressure - not given

p-Benzenedisulfonic acid - temperature - 250-600°C (482-1112°F)

pressure - 405 kPa (4 atm)

catalyst - heavy metal (Hg, Ca)

4. Utilities

Not given

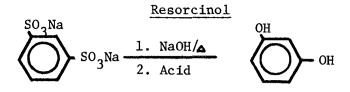
- 5. <u>Waste Streams</u> none identified but suspect SO₃, SO₂, benzene vapors.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 406.

Gilbert, E. E., <u>Sulfonation and Related Reactions</u>, Interscience Publishers, New York, N.Y., 1965, p. 69.

Groggins, P., <u>Unit Processes in Organic Synthesis</u>, 5th Ed., McGraw-Hill Book Co., Inc., New York, N.Y., 1958, p. 312.

British Patent 834,251 (May 4, 1960).



1. <u>Function</u> - Resorcinol can be made from m-benzenedisulfonic acid. The final sulfonation mixture from the manufacture of m-benzenedisulfonic acid is treated with 0.9 equivalents of a solution of sodium sulfite under agitation. The mixture is sent to another vessel containing a suspension of excess calcium carbonate in water, and the mixture is filtered. The filtrate, containing sodium sulfonate and calcium sulfonate, is treated with 0.1 equivalent of sodium carbonate. After the calcium carbonate precipitate is removed on another filter, the sodium m-benzenedisulfonate is obtained as a 20% solution. A steam heated drum dryer then concentrates the solution to 50%.

This dry salt is mixed by stirring with flaked caustic soda and fused at 360°C (679°F) in a gas-heated, sealed, cast-iron vessel. After cooling the mass is taken up in water. The solid sulfite is separated by filtration and the filtrate is acidified with hydrochloric acid. The free resorcinol is then extracted with diethyl ether in a continuous extractor.

2. Input Materials

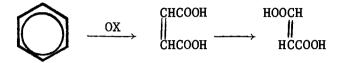
m-Benzenedisulfonic acid - 2.17 kg (1b)/kg (1b) product Sodium sulfite Calcium carbonate Water Sodium carbonate Caustic soda - 3.6 kg (1b)/kg (1b) product Hydrochloric acid

Diethyl ether

- 3. <u>Operating Parameter</u> Temperature: 360°C (679°F) Pressure: not given
- 4. <u>Utilities</u> Not given
- <u>Waste Streams</u> Various salts should be present in the sludge and SO_x should be emitted to the air.
- 6. EPA Source Classification Code None
- 7. <u>Reference</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 11 (1966) p. 475.

Fumaric Acid (from benzene)



1. <u>Function</u> - Fumaric acid is manufactured from maleic acid and by direct oxidation of benzene without isolating the maleic acid formed. Air and benzene are mixed and passed into a converter where oxidation takes place in the presence of $V_2O_5 + P_2O_5$ proprietary catalyst. The temperature of the reaction is kept near 400-450°C by heat-transfer coolants.

When fumaric acid is the desired product the effluent gases from the converter may be scrubbed with hydrochloric acid to effect the isomerization. Ammonium persulfate - ammonium bromide mixtures and 10-20% HCl may also be used to catalyze the isomerization of maleic acid to fumaric acid.

The fumaric acid precipitates from the aqueous medium and may be purified by recrystallization or sublimation.

2. Input Materials

Benzene - 0.71 kg/kg product Air

3. <u>Operating Parameters</u> - Converter:

Temperature - 400-450°C (752-842°F) Pressure - 101-446 kPa (1.0-4.4 atm) Isomerization: Temperature - ~100°C (212°F) Pressure - 101 kPa (1 atm) Catalyst - HC1 6-95

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste water may contain unreacted maleic acid and dilute hydrochloric acid, and fumaric acid not recovered by crystallization.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 12 (1967), p. 819-829.

A. L. Waddams, <u>Chemicals From Petroleum</u>, 3rd Ed., John Wiley & Sons, 1973, p. 224-225.

Nitrobenzene

+ HNO₃ + H₂SO₄ - O^{NO}2

1. <u>Function</u> - The usual method for the commercial manufacture of nitrobenzene is the direct nitration of benzene using mixed sulfuric and nitric acids. The reaction vessels are specially built cast-iron or steel kettles fitted with efficient agitators. The kettles are jacketed and generally contain internal cooling coils for proper temperature control of the strongly exothermic reaction. The batch equipment is normally sized for 454-680 kg quantities of benzene and operates on a time cycle of 2-4 hr.

In the typical batch process, the nitrator is charged with benzene and a heel of spent acid and the mixed acid (53-60% H_2SO_4 , 32-39% HNO_3 and 8% H_2O) is added slowly below the surface of the benzene. Although the ratio of reactants is expressed in different ways from plant to plant, using this concentration of mixed acid the weight ratio of mixed acid to benzene is usually 2.5:1. The temperature of the reaction is maintained at 50-55° C by adjusting the rate of feed of mixed acid, the rate of heat exchange, and the agitation of the mixture, and it is usually raised to 90° C toward the end of the nitration to promote comple-The reaction mixture is then run into a separator where tion. the spend acid settles out and is drawn off from the bottom of the unit. This spent acid is recovered or used as cycle acid to start subsequent runs after steam stripping to remove starting material. The crude nitrobenzene is drawn off the top of the separator and

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can be used directly in the manufacture of aniline. If pure nitrobenzene is required, the product is washed with water and dilute sodium carbonate and then distilled.

Newer plants use a continuous process, as typified by the Biazzi process, for the production of nitrobenzene. The sequence of operations is essentially the same as in the batch process but the main differences are the use of smaller reaction vessels, lower nitric acid concentrations, and higher reaction rates. A typical 114 ℓ continuous nitrator has a production capacity equal to a 568 & batch nitrator. Mixed acid of low nitric acid concentration and benzene sufficient to react with all of the nitric acid are mixed in the small stainless-steel nitrator fitted with a high-speed (600 rpm) agitator and a helical cooling coil. The reaction time is 15-20 min due to the rapid, efficient agitation. The reaction mixture is then drawn off from the side of the nitrator and allowed to separate for 10-20 min in a decanter. The washings are carried out in small vessels similar to the nitrator using high-speed mechanical agitation and are normally complete in 10 min.

2. Input Materials - Basis - 1 Mg Nitrobenzene

Benzene - 650 kg Sulfuric Acid - 721 kg Nitric Acid - 530 kg Water - 109 kg Sodium Carbonate - 10 kg

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3. Operating Parameters

Temperature:	45 to 95° C (113-203°F)
Pressure:	101 kPa (1 atm)
Reaction time:	2-4 hrs.

4. Utilities

Cooling Water - quantity not given Steam - quantitiy not given Electricity - quantity not given

5. Waste Streams

Reaction section - absorber vent (air) Benzene - 8.2 g/kg nitrobenzene NO_x - 0.09 g/kg nitrobenzene Nitrobenzene - nil

Acid concentration section - absorber vent (air)

NO₁ - 0.16 g/kg nitrobenzene

Major wastewater streams would come from the nitrobenzene purification section for washing crude nitrobenzene and would contain benzene and nitrobenzene.

6. EPA Source Classification Code - None

7. References

Anon., "Air Pollution From Nitration Processes," prepared for Office of Air Programs, Environmental Protection Agency, Contract No. CPA 70-1, March 1972.

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 7," "Chemical Engineering," June 24, 1974, p. 154, 155.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 13 (1967), p. 836, 837, 838.

$\underbrace{\bigcirc}^{\text{NO}_2}_{\text{HNO}_3 + \text{H}_2\text{SO}_4} \longrightarrow \underbrace{\bigcirc}^{\text{NO}_2}_{\text{NO}_3}$

- <u>Function</u> Dinitrobenzene is produced by nitrating nitrobenzene with a hot mixture of sulfuric and nitric acids. The process is essentially identical with the process for nitrobenzene (Process No. 25) except that the temperature is higher (140-180°C). The product is purified by recrystallization.
- 2. Input Materials

Nitrobenzene - 830 kg/Mg dinitrobenzene Sulfuric acid - 720 kg/Mg dinitrobenzene Nitric acid - 530 kg/Mg dinitrobenzene

3. Operating Parameters

Temperature - 90-100°C (194-212°F)

Pressure - 101 kPa (1 atm)

4. Utilities

Steam - quantities are not given Cooling water - quantities are not given Electricity - quantities are not given

5. <u>Waste Streams</u> - Small quantities of NO_x would be expected to be released to the air from reactor vents probably no more than 0.1 kg/Mg dinitrobenzene. Wastewater streams may be released from the purification step and may contain some spent acids, traces of mono-and dinitrobenzene, and some caustic soda used in the neutralization step.

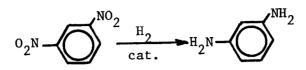
6. EPA Source Classification Code - None

7. References

Groggins, P., <u>Unit Processes in Organic Synthesis</u>, 5th Edition, McGraw-Hill Book Co., New York, N.Y., 1958, p. 113-115.

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 551.

m-Phenylenediamine



- Function m-Phenylanediamine is produced by the catalytic reduction of m-dinitrobenzene with iron and HCl as in the case of p-phenylenediamine (Process No. 30).
- 2. Input Materials

m-Dinitrobenzene

Iron

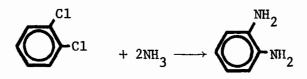
HC1

- 3. Operating Parameters not given
- 4. Utilities not given
- 5. <u>Waste Streams</u> No specific information was available, but iron, iron sulfides, ammonia, and ammonium polysulfides should be present in the waste streams.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y. Vol. II (1963) p. 90.

Ibid, Vol. 15 (1968) p. 216, 217.

o-Phenylenediamine



- Function o-Phenylenediamine is produced by the action of ammonia on o-dichlorobenzene. The product is made in an agitated, induction heated, high pressure autoclave with 316 stainless steel lining and is purified by vacuum distillation.
- 2. Input Materials

o-Dichlorobenzene

Ammonia

Catalyst (Cu⁺)

3. Operating Parameters

Temperature	lst Stage	180-190°C (356-374°F)
	2nd Stage	200-210°C (392-410°F)
Pressure:	Not given	
Reaction time	: 24 hrs	

4. Utilities

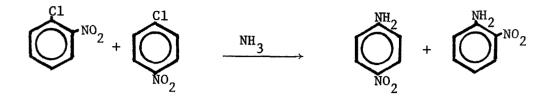
Not given

- Waste Streams Ammonia, hydrochloric acid, and copper chlorides should be present in the waste streams.
- 6. EPA Source Elassification Code

None

7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Ed., Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 361. o- and p-Nitroanilines (from o- and p-chloronitrobenzenes)



 <u>Function</u> o- and p-Nitroanilines are prepared commercially by ammonolysis of the appropriate chloronitrobenzene isomer. The process may be either batch or continuous.

The batch process will be described for the p-chloronitrobenzene but is identical for the o-isomer. Mixed isomers may be used since the physical properties of the isomers are sufficiently different so as to make separation of the o- and p-nitroanilines by either vacuum distillation or fractional crystallization entirely feasible.

In the batch method 1.892 m³ (500 gal) jacketed autoclaves are used. Molten p-chloronitrobenzene (227 kg; 500 lbs) is added to 1180.9 kg (2600 lbs) of 26°Bé (28%) ammonia and heated over a 3 hr period to 175°C at a pressure of 3.65-4.00 MPa (530-580 psi). These conditions are maintained for 16 hrs and then excess ammonia is vented to an absorption system until the autoclave pressure reaches 1.38 MPa (200 psi). The charge is transferred to an ammonia still and then to wooden crystallizing tubs, where it cools and is then centrifuged. Operating yields of 95% are obtained and ammonia losses amount to only about 6%.

In the continuous process, preheated aqueous ammonia is forced through an inlet pipe to the bottom of a vertical reaction column filled with p-chloronitrobenzene. The ammonia passes upward through an annular space and overflows through a central outlet pipe leading to an ammonia still. The product is drawn off and crystallized as in the batch process.

2. Input Materials

Chloronitrobenzene:	<u>Batch</u> 227 kg (500 lbs)	<u>Continuous</u> 150-200 parts
Ammonia (26° Bé):	1180.4 kg (2600 lbs)	900 parts

3. Operating Parameters

	Batch	Continuous
Temperature:	175°C (347°F)	225°C (437°F)
Pressure:	3.65-4.00 MPa	8.27 MPa (81.6 atm)

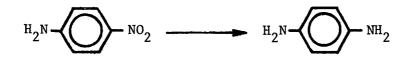
4. Utilities - Not given

5. <u>Waste Streams</u> - Chlorinated nitrobenzenes and nitrophenols may be present in the sludge and some ammonia is lost to the air.

6. EPA Source Classification Code - None

7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 352-353. p-Phenylenediamine



 <u>Function</u> - p-Phenylenediamine is produced by the catalytic reduction of p-nitroaniline with iron/HCl, iron/ammonium polysulfide/hydrogen, or iron/ferrous chloride.

A large wood vat is used in the process. Sufficient water is introduced to cover the agitator paddles (which operate at 40 rpm) and 453.6 kg (1000 lbs) iron borings are introduced. Then 45.4 kg (100 lbs) of 20° Be HCl is added, agitated and heated until a good paste of FeCl₂ is produced. 340.2 kg (750 lbs) of p-nitroaniline is introduced and 226.8 kg (500 lbs) fine iron is added.

Just prior to filtration, the batch is made alkaline with soda ash, then sodium bisulfite/sodium sulfide are added to precipitate soluble iron salts and prevent subsequent oxidation. The mixture is filtered on a large plate-and-frame filter. The filtrate is concentrated then dried in two-stage vertical evaporators and film evaporators. About 37.2 kg (82 lbs) of crude product are obtained per 45.4 kh (100 lbs) p-nitroaniline reduced.

2. Input Materials - Basis: 1 kg (1b) product

p-nitroaniline	1.28 kg (1b)
Iron	1.60 kg (1b)
HC1 (20° Be)	0.11 kg (1b)

3. Operating Parameters

Temperature: 230-250°C (446-482°F) Pressure: atmospheric

- 4. Utilities Not given
- 5. <u>Waste Streams</u> No specific information is given, but iron, iron sulfides, ammonia and ammonium polysulfides may be found in the waste streams.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963) p. 87-90. Ibid, Vol. 5 (1968) p. 217.

Aniline

$$\mathbb{N}^{NO_2}$$
 + $_{3H_2}$ \mathbb{N}^{H_2} + $_{2H_2O}$

- 1. <u>Function</u> Aniline is produced commercially by the reduction of nitrobenzene is a continuous, vapor-phase process in which nitrobenzene is vaporized in a stream of hydrogen and fed to a fluidized bed reactor containing a hydrogenation catalyst. The catalyst can be copper carbonate, cuprammonium nitrate, alumina, or sulfides of nickel, molybdenum, or tungsten. The unreacted hydrogen is recycled to the reactor. Reactor effluent goes to a separator, where two phases are formed. The organic phase contains water, and is fractionated in a two-tower system to remove heavy residue water from the aniline product.
- 2. Input Materials Basis 1 metric ton anilineNitrobenzene 1.35 Mg/Mg Aniline1350 kg (2,976 lbs) H_2 65 kg/Mg Aniline81 m³ (2,860 ft³)Copper carbonate0.7 kg (1.54 lbs)
- 3. <u>Operating Parameters</u> Temperature - 250-300°C (482-572°F) Pressure - 238 kPa (2.35 atm) Reaction time - 0.5 to 100 seconds Catalyst - Cuprammonium nitrate or sulfide (nickel, molybdenum, tungsten) or alumina

4. Utilities

Steam - quantity not given

5. <u>Waste Streams</u> - The separator aqueous layer, formed by the water of reaction, contains some aniline and may be discharged to the sewer. Sometimes this aniline is recovered by solvent extraction using the nitrobenzene.

Heavy residues and water from the fractionation tower may constitute an additional wastewater source.

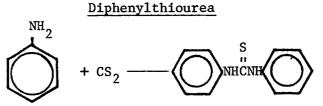
> Flow - 1.58 1/kg (190 gal/1000 lbs) COD - 13,400 mg/1 21.2 g/kg (1bs/1000 lbs) BOD₅ - 15 mg/1 0.02 g/kg (1bs/1000 lbs) TOC 12,150 mg/1 19.2 g/mg (1bs/1000 lbs)

- 6. EPA Source Classification Code None
- 7. References

Hahn, A. V., <u>The Petrochemical Industry: Market and Economics</u>,
McGraw-Hill Book Company, New York, N.Y., 1970, p. 503.
Austin, G. T., "The Industrially Significant Organic Chemicals Part 1," "Chemical Engineering," January 21, 1974, p. 132.
Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition,
Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 419.
Waddams, A. L., <u>Chemicals From Petroleum</u>, 3rd Ed., John Murray Ltd.,
London, Eng., 1973, p. 223.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition John Wiley and Sons, New York, N.Y., 1975, p. 113.

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corp., Park Ridge, N.J., 1974, p. 76.



- 1. <u>Function</u> Diphenylthiourea is produced by the reaction of aniline with carbon disulfide. A mixture of aniline, alcohol, carbon disulfide, and crystalline sulfur are heated to reflux for 5 to 6 hours. The mixture gradually solidifies. Excess carbon disulfide is distilled off. Excess aniline is removed with dilute hydrochloric acid. The diphenylthiourea is recrystallized from alcohol.
- 2. Input Materials

Aniline

Alcohol

Carbon disulfide

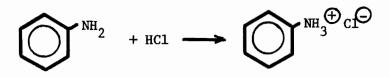
Sulfur (catalyst)

- 3. <u>Operating Parameters</u> Reflux 5 to 6 hours
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Expect traces of carbon disulfide to be present in air due to this process. Waste waters may contain dilute acids and salts from washings, as well as aniline, and oxidation products of aniline.
- 6. EPA Source Classification Code 3-01-034-01
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 414.

7. <u>References</u> (continued)

Houben Weyl, <u>Methoden der Organischen Chemie</u>, Vierte Auflage, Georg Thieme Verlag, Sttutgart, Bd. 9 (1955), p. 885. Aniline Hydrochloride



- <u>Function</u> Aniline hydrochloride is prepared by the direct reaction of aniline with hydrochloric acid. This is usually accomplished by two methods: a) by passing a stream of dry hydrogen chloride through an ethereal solution of aniline, or b) by neutralizing aniline at 100°C with concentrated hydrochloric acid. The product is purified by crystallization.
- 2. Input Materials

Aniline - 0.704 kg/kg product HCl - 0.276 kg/kg product Ethyl ether

- 3. Operating Parameters
 - a) Temperature ambient
 Pressure atmospheric
 - b) Temperature 100°C (212°C) Pressure - atmospheric
- 4. Utilities

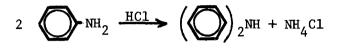
Not given

5. <u>Waste Streams</u> - No specific information available. An air emission containing traces of HCl and ether is possible from method (a). From method (b) aniline, HCl and traces of aniline hydrochloride are possible.

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- 6. EPA Source Classification Code 3-01-034-01
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 419. Diphenylamine



 Function - Diphenylamine is produced by heating aniline hydrochloride in an autoclave at 210-240°C and 730 kPa pressure. If a catalyst (0.5 weight % of amine) is used the aniline will condense with itself without the hydrochloride.

The product is then boiled with dilute hydrochloric acid to remove the unreacted aniline as the hydrochloride, and is distilled.

2. Input Materials

Aniline

Aniline hydrochloride

3. Operating Parameters

Temperature: 210-240°C (410-464°F)

Pressure: 730 kPa (7.2 atm)

4. Utilities

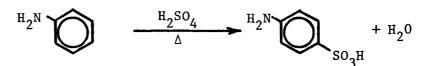
Steam: Quantities not given

- 5. <u>Waste Streams</u> No information available but it is likely that a waste water stream would be generated containing distillation bottoms; small amount of hydrogen chloride or aniline may be given off.
- 6. EPA Source Classification Code 3-01-034-01
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963) p. 413, 420. <u>Ibid</u>, Vol. 7 (1967), p. 40.

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 519.

Sulfanilic Acid



- 1. <u>Function</u> Sulfanilic acid (p-aminobenzene sulfonic acid) is prepared by placing the sulfuric acid in an iron pan fitted with a stirrer and the aniline is run in over 3-4 hours. The reaction mass is stirred for another 3 - 4 hours and then transferred to a heated cast iron oven fitted with a chimney. The temperature is kept at 230°C until no further sulfur dioxide is emitted. After cooling, the crude product can be dissolved in dilute caustic soda solution, filtered from the carbonaceous material, boiled to expell any free aniline, then acidified to yield the free acid (98% yield).
- 2. Input Materials

Aniline	1374 kg
Sulfuric acid	1597 kg

3. Operating Parameters

Temperature: 230°C (446°F)

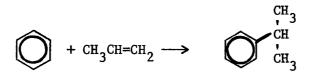
Reaction Time: 6 - 8 hours (before baking)

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Sulfur dioxide is emitted during the baking process and aniline vapors escape from the aniline recovery system. Some caustic soda sludge also should appear in the wastewater.
- 6. EPA Source Classification Code None
- 7. References

<u>Chemical Technology</u>, Barnes and Noble Books, New York, N.Y., 1972, Vol. 4, p. 590. Groggins, P., <u>Unit Processes in Organic Synthesis</u>, McGraw-Hill Book Co., New York, N.Y., 1958, p. 383.

Kirk-Othmer, <u>Encyclopedia Of Chemical Technology</u>, 2nd Ed., Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 424.

Cumene (alkylation)



- Function Benzene is alkylated in the vapor phase with propylene in the presence of a phosphoric acid catalyst to yield cumene. An excess of benzene is maintained to suppress dialkylation, oligomerization and other side reactions.
- 2. <u>Input Materials</u> Basis 1 metric ton cumene Benzene: 800 kg (1,764 lbs) Propylene: 430 kg (948 lbs)
- 3. <u>Operating Parameters</u> Temperature: 250°C (482°F) Pressure: 689 kPa (6.80 atm) Flow rates: not given Equipment: chamber type reactor Catalysts: phosphoric acid on kieselguhr Catalyst Consumption: 1.667 m³ cumene formed/kg catalyst
- 4. Utilities

Not given

5. <u>Waste Streams</u> - The principal waste water streams from the manufacture of cumene results from the recovery of cumene from the process stream. This stream contains some 1-4% of the product stream. The quantity of water carrying the wastes depends largely upon the use of propane to control bed temperature.

6. EPA Source Classification Code - None

7. References

Brownstein, A. M., U.S. Petrochemicals - Technologies, Markets, and Economics, The Petroleum Publishing Company, Tulsa, Oklahoma, 1972.

"1969 Petrochemical Handbook," "Hydrocarbon Processing," Nov., 1969, p. 167.

Gloyna, E. F., and Ford, D. L., "The Characteristics and Pollutional Problems Associated with Petrochemical Wastes," for FWPCA, Contract No. 14-12-451, Ada, Oklahoma, 1970.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 6 (1965), p. 544, 545.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 892.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> Processes, Technomic Publishing Co., 1975.

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 3,""Chemical Engineering," March 18, 1974, p. 91.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 294, 295.

PROCESS NO. 37

Phenol, Acetophenone, and Acetone (from cumene via hydroperoxide)

 $C_{6}H_{5}C(CH_{3})_{2}OOH \xrightarrow{H_{2}SO_{4}} C_{6}H_{5}OH + (CH_{3})_{2}CO$

 Function - As of January 1, 1975, almost 91% of synthetic phenol capacity was based on the cumene peroxidation process. Cumene is oxidized to cumene hydroperoxide as described in Process No. 294 and fed to an acidifier containing 5-25% sulfuric acid. The reactants are agitated at 45-65°C until the cumene hydroperoxide is cleaved to phenol and acetone.

After the reaction, the mixture is phase-separated to yield an oil layer containing cumene, phenol, acetone, α -methylstyrene (1.5%), acetophenone (0.8%), and tars. These are separated from each other by distillation or by a combination of distillation and extraction. The α -methylstryene can be hydrogenated to cumene and recycled or recovered as a by-product. Acetophenone is recovered as a by-product. Unconverted cumene can be removed after the oxidation step or recovered in the final distillation.

2. Input Materials

Cumene hydroperoxide (from cumene - 1.42 kg/kg phenol) Sulfuric acid

3. Operating Parameters

Temperature: 45 - 65°C (113-149°F) Pressure: not given

Utilities - Basis: 1.44 kg/sec capacity (100 M lb/yr) 4. Cooling water - 1.99 m³/sec (1.89 \overline{M} gph) Steam - 14.2 kg/sec (113,000 lb/hr) Electricity - process - 1778.4 MJ (494 KW) utilities - 626.4 MJ (174 KW) Nitrogen - 393 scm³/sec (50 scfh) Waste Streams* 5. Crude phenol surge vessel (water) Cumene - trace Acetone - 0.46 kg/Mg phenol Phenol - 0.08 kg/Mg phenol Single vessel mesityl oxide column (water) Mesityl oxide plus other contaminants - 19.9 kg/Mg phenol Hydrogenation column vent (air) Hydrogen - 15.0 g/Mg phenol Carbon monoxide - 20.0 g/Mg phenol Catalytic columns vent (air) Methylstyrene - trace Carbon monoxide - 0.22 kg/Mg phenol Phenol - 1.48 kg/Mg phenol Steaming column vent (air) No data given (assume phenol to be the major pollutant) - 0.5 - 1.0kg/Mg product Evaporator residue (solid) Acetophenone - 1.9 kg/Mg phenol Phenol - 0.75 kg/Mg phenol Polymeric matter - 110 kg/Mg phenol Cumylphenol - 0.85 kg/Mg phenol 6. EPA Source Classification Code 3-01-034-01 7. References Austin, G. T., "The Industrially Significant Organic Chemicals -Part 1", "Chemical Engineering", January 21, 1974, p. 130. Ibid., Part 8, July 22, 1974

* Includes Process No. 36

"1973 Petrochemical Handbook Issue", <u>Hydrocarbon Processing</u>, November, 1973, p. 158.

Hedley, W. H., <u>et al.</u>, <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Technomic Publishing Co., 1975.

Maleic Anhydride (from benzene)

 <u>Function</u> - A stream of benzene is vaporized in a mixer with an optimum amount of air. The vapors from the mixer pass then through a converter containing vanadium pentoxide on an inert carrier. Tubes that circulate mercury or fused salts serve to remove the heat of the reaction and thus control the temperature between 400 to 450°C.

The reaction gases from the reaction pass through a vapor cooler and then to a condenser. The bulk of the maleic anhydride is recovered in the condensers and contains some maleic acid. This is converted to the anhydride by vacuum or azeotropic distillation (using hydrocarbons).

As of 1973 all the maleic anhydride intentionally manufactured in the United States is produced via the oxidation of benzene. It is also obtained as a by-product in the manufacture of phthalic anhydride. Use of C_4 hydrocarbons as feedstock is planned by different companies. One plant (Ashland) is designed to use benzene but can be adapted to butane feedstock.

2. <u>Input Materials</u> - Basis - 1 metric ton maleic anhydride Air - 37.48 Mg/Mg (74,963 lb/ton) product - 15,600-21,750 m³ Benzene - 1.872 Mg/Mg (3,745 lb/ton) product - (550,909-768,094 ft³) Sodium perborate - 10.2 kg/Mg (20.2 lb/ton) product - 1,340 kg (2,954 lbs) Demineralized water - 23.66 kg/Mg (47.31 lb/ton) product

6-125

3. Operating Parameters

Temperature - 400-450°C (752-842°F) Pressure - 101 kPa (1 atm) Contact time - ~0.1 sec. Catalysts - V_2O_5 + MoO₃ (on aluminum turnings or diatomaceous earth)

4. <u>Utilities</u>

Basis - 13.6 Gg/yr (30 M 1b/yr) capacity

<u>Water</u>

Coolant - 88 dm³/s (1,400 gpm) Makeup cooling - 1.8 dm³/s (28 gpm) Boiler makeup - <63 cm³/s (<1 gpm)

Steam

Generated by reactor - 12.6 Mg/hr (27,800 1b/hr) Required - 1.3 Mg/hr (2,800 1b/hr) Net - 11 Mg/hr (25,000 1b/hr) Electricity - 11 GJ (3,000 kWh/hr) Nitrogen - 6.2 m³/hr (200 scfh)

5. Waste Streams

Recovery section - scrubber (air) Benzene - 131 kg/Mg (262 1b/ton product) Carbon monoxide - 780 kg/Mg (1,560 1b/ton) product Maleic acid - trace Purification section - anhydride vacuum column-bottoms (water) Maleic anhydride - 3.8 kg/Mg (7.5 1b/ton) High boilers (tar, fumaric acid, chromogenic compounds) - 27 kg/Mg (53 1b/ton) 5. Waste Streams (continued)

Purification section - anhydride vacuum column-overhead (water) Maleic acid - 0.6 kg/Mg (1.2 lb/ton)

- 6. EPA Source Classification Code None
- 7. <u>References</u>

Morse, Park L., "Maleic Anhydride", Report No. 46, Stanford Research Research Institute, Menlo Park, California, 1969.

Gloyna, E. F., and Ford, D. L., "The Characteristics and Pollutional Problems Associated with Petrochemical Wastes", Report of FQPCA, 1970. Austin, G. T., "Industrially Significant Organic Chemicals - Part 7," "Chemical Engineering," June 24, 1974, p. 150, 151.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 12 (1967), p. 828, 829. Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, Interscience, New York, N.Y., 1975, p. 514-8.

Chemical Week, May 9, 1973, p. 33.

Chemical Week, February 5, 1975, p. 13.

Succinic Acid (from maleic anhydride)

$$\begin{array}{c} \text{HC-C} & \stackrel{0}{\swarrow} & \stackrel{\text{H}_2}{\underset{\text{cat.}}{\text{cat.}}} \text{HOOC(CH}_2)_2 \text{COOH} \end{array}$$

- 1. <u>Function</u> Succinic⁰ acid is obtained from maleic anhydride by hydrogenation. Molten maleic anyhydride is charged to a hydrogenator. The vessel is purged and filled with hydrogen. A Raney-nickel catalyst is added as a slurry, agitation started, and the temperature is raised to 130 140°C (265 283°F). Hydrogen pressure of 17 megapascals (168 atm) is maintained for 4 6 hours. The product is then removed and distilled in two stages. The first removes any unreacted maleic anhydride under a vacuum as overheads. The second stage fed by the bottoms from the first removes the succinic acid under a vacuum as distillate overhead. The product is condensed, dried and sold as a white flake.
- 2. Input Materials

Maleic anhydride

Catalyst

Hydrogen

3. Operating Parameters

Temperature: 130 - 140°C (265 - 283°F)

Pressure: 17 MPa (167.8 atm)

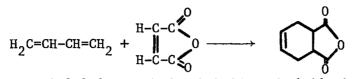
Reaction Time: 4 - 6 hours

- 4. Utilities Not given
- <u>Waste Streams</u> The maleic anhydride and some catalyst may be present in the waste streams.

- 6. <u>EPA Source Classification Code</u> None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, Second Edition, Interscience Publishers, New York, N.Y., Vol. 19 (1969), p. 143.

Tetrahydrophthalic Anhydride



- 1. <u>Function</u> cis-1,2,3,6-Tetrahydrophthalic anhydride is manufactured by the Diels-Alder reaction. 1,3-Butadiene reacts with maleic anhydride in benzene at room temperature (12 hours) and is then heated to 100°C for five hours in an autoclave. The product is crystallized from benzene-ligroin.
- 2. <u>Input Materials</u> Basis 1 kg (1b) product 1,3-Butadiene 0.458 kg (1b) Maleic anhydride 0.715 kg (1b) Benzene 1.14 1 inside reaction vat 1.43 1 outside reaction vat
- 3. Operating Parameters

Temperature: 20°C (67°F)

Pressure: not given

- 4. Utilities not given
- 5. <u>Waste Streams</u> Possible benzene emissions from purification of product are the only wastes from this reaction since the yield is quantitative.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y. Vol. 12 (1967) p. 825.

Adams, R., Organic Reactions, John Wiley and Sons, New York, N.Y., Vol. 4 (1948), p. 41.

Maleic Acid

$$+ 4 \frac{1}{2} 0_2 \xrightarrow{\frac{V_2 0_5}{COOH}} + H_2 0 + 2C0_2$$

 <u>Function</u> - Maleic acid is produced in conjunction with the manufacture of maleic anhydride (see Process 38). If maleic acid is to be the sole product, the gases from the reactor are absorbed in water to give a 40% solution. The solution is purified with activated carbon, concentrated, and crystallized.

A small amount of maleic acid is also obtained as a by-product in the manufacture of phthalic anhydride.

2. Input Materials

Benzene

Air

Water

3. Operating Parameters

Temperature: 400 - 500°C (752-932°F) Pressure: 101 kPa (1 atm) Contact time: ~0.1 sec Catalyst: V₂0₅

4. Utilities

Similar to those in Process

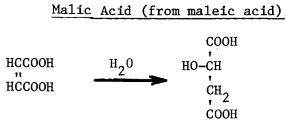
- <u>Waste Streams</u> Benzene vapors not recycled and maleic acid not recovered by crystallization; CO, CO₂ and hydrocarbons.
- 6. EPA Source Classification Code None

7. <u>References</u>

Lowenheim, F. A., Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 514-518.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 12 (1967), p. 829.

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 Function - R, S -Malic acid can be produced from maleic acid by hydration at elevated temperatures and pressures in the presence of catalysts. The reactors need to be corrosion-resistant.

The vapors from the gas-phase oxidation of benzene are dissolved in water to give a solution of maleic acid. The solution is treated 4 to 5 hr with oxygen at 70° C. After preliminary purification the solution passes through three Ti reactors at 185° C and 15 kg/cm², with residence time of 2.5, 1.6, and .85 hr. The resulting solution is cooled to 40° C to remove fumaric acid. The crude malic acid is purified further by recrystallization. Removal of traces of fumaric acid and mineral ions (Fe, Cu, Ca, Mg, Al) may be accomplished by the use of ionexchange resins.

2. Input Materials

Maleic acid Water Oxygen Catalyst - Co

3. Operating Parameters

Temperature - 185° C (365°F) Pressure 15 kg/cm² (1.47 MPa)

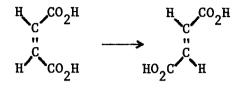
- 4. Utilities Not given.
- 5. <u>Waste streams</u> Waste waters essentially free of traces of byproducts and mineral ions with use of ion exchange resins.
- 6. EPA Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Vol. 12, Interscience Publishers, New York, N.Y., 1967 p. 843-846. Allied Chemical Corp. Neth. Appl. 6,516, 753, July 1, 1966. (C.A. 65-P16867d)

Ahlgreen, C. R. (to Allied Chemical Corp.) Belg. 670, 932, January 31, 1966 (C.A. 65-P13551C)

Allied Chemical Corp. Neth. Appl. 6,600,665 (1966). (C.A. 65-16867).

Fumaric Acid (from maleic acid)



- 1. <u>Function</u> Fumaric acid is manufactured by two main methods: (1) directly from benzene or (2) from maleic acid. The process employing benzene is discussed under Process No. 38. The process using maleic acid feed uses amine bases, mercaptans, heavy metal salts, mineral acids, disulfides, and other materials as catalysts. In common use are ammonium persulfate-ammonium bromide mixtures and 10 20% HC1. The conversion is carried out at atmospheric pressure at 40 60°C (103 139°F). Fumaric acid precipitates from the aqueous medium and after separation is dried and purified by recrystallization or sublimation.
- 2. Input Materials

Maleic acid

Catalyst

- 3. <u>Operating Parameters</u> Temperature: 40 - 60°C (103 - 139°F) Pressure: 101 kPa (1 atm)
- 4. Utilities Not given
- <u>Waste Streams</u> Unreacted maleic acid, HCl, and catalyst should be present in the waste streams.
- 6. EPA Source Classification Code None

7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 6," "Chemical Engineering," May 27, 1974, p. 102.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 12 (1967), p. 829.

Sittig M., <u>Chemicals from Aromatics</u>, Noyes Development Corp., Park Ridge, N.J., 1966, p. 28, 29. Cyclohexane

+ ^H2

- 1. <u>Function</u> Cyclohexane (35%) is produced from benzene by a liquid phase hydrogenation process. The reaction occurs at 220°C (428°F) and 3.5 MPa (34.5 atm) using a platinum or Ni catalyst containing a small amount of lithium salt supported on alumina. A typical plant incorporates several reactors for a stepwise operation. The recycled cyclohexane, hydrogen and make-up hydrogen pass through the beds in series, while the benzene passes through in parallel. This reduces the quantity of recycle cyclohexane and excess hydrogen required. The recycle cyclohexane absorbs the heat of hydrogenation, thus avoiding high bed temperatures and possible isomerization.
- 2. <u>Input Materials</u> Basis 1 metric ton cyclohexane Benzene - 0.98 kg (1b)/kg (1b) product 93.5 kg (2,061 lbs) Hydrogen - 65 kg (143 lbs) Catalyst - small
- 3. <u>Operating Parameters</u> Temperature - 220°C (428°F) Pressure - 3.5 MPa (34.5 atm)
- 4. Utilities 45 \overline{M} kg/yr (100 \overline{M} 1bs/yr), 350 days/yr

Electricity - 250 kW

Steam - kg/hr (1bs/hr) - consumed [4.2 MPa = 41.5 atm] - 4994 (11,000) generated - (1.2 MPa 11.8 atm) 6350 (14,000) Cooling water - ($\Delta T = 15^{\circ}$ C) 0.039 m³/s (618 gpm) HP steam required - 2.3 t/hr LP steam produced - 11.8 t/hr

5. <u>Waste Streams</u> - Outside of spent caustic wash $(2 \times 10^{-6} \text{ m}^3/\text{kg} = 0.24 \text{ gal}/10^3 \text{ lbs})$, the only major source of wastewater is the cooling water which amounts of 171-1717 g/m³ (200-2,000 gal/ton) of cyclohexane and which may contain 50-200 mg/l of COD. In the aromatics extraction, there are two major sources of wastewater: the extract water washing which contains aromatic hydrocarbons and the wastes from solvent regeneration which contain appropriate solvents. Both wastes may be minimized by the use of stripping columns.

Purge gas from the hydrogenation reactor may contain benzene, hydrogen, sulfur, and carbon monoxide.

- 6. EPA Source Classification Code None
- 7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals - Part 3," "Chemical Engineering," March 18, 1974, p. 91,92.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 6 (1965), p. 679.

Sittig, M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition, Noyes Development Corp., Park Ridge, N.J., 1969, p. 201.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical Processes</u>, Technomic Publishing Company, Westport, Conn., 1975.

7. <u>References</u> (Continued)

"1973 Petrochemical Handbook," "Hydrocarbon Processing," November, 1973, p. 116,117.

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corp., Park Ridge, N.J., 1974, p. 116. Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 299. Sittig, M., Chemicals from Aromatics, Noyes Development Corp., Park

Ridge, N.J., 1966, p. 4-9.

U.S. Patent 3,254,134 (May 31, 1966).

Adipic acid (from cyclohexane)

$$s \xrightarrow{ox} s \xrightarrow{OH} \xrightarrow{HNO_3} HOOC(CH_2)_4COOH$$

 <u>Function</u> - Adipic acid is obtained from cyclohexane in a two stage process. First stage involves air oxidation of cyclohexane to an alcohol-ketone mixture. The reaction carried out at 125-160°C and 404 kPa (4 atm.) uses a cobalt naphthenate or cobalt stearate catalyst.

The second stage oxidizes the alcohol-ketone mixture to adipic acid using 40 to 50% nitric acid. The reaction carried out at 50 - 150°C (122 - 302°F) and 345 - 1724 kPa (3.4 - 17.0 atm.) uses a catalyst made of ammonium meta-vanadate and copper.

The liquid product from the reactor is air stripped to remove nitrous oxides and steam distilled to remove nitric acid and lowboiling organics as overhead. The still bottoms are cooled to 40 - 50°C (104 - 122°F) and the adipic acid crystallizes. The crystals are dried to produce the adipic acid.

Adipic acid may also be made by air oxidation of cyclohexane.

2. Input Materials

Basis - 1kg (1b) adipic acid

- Cyclohexane 1.65 kg (lg)
 Air variable
 Catalyst 0.1 g (0.0001 lb)
- 2) Nitric acid 6.75 kg (1b)
 - Catalyst: Copper 15 g (0.015 1b) Ammonium meta-vanadate 5 g (0.005 1b) 6-140

3. Operating Parameters

- Temperature: 125 160°C (257 320°F)
 Pressure: 404 kPa (4atm)
- 2) Temperature: 50 150°C (122 302°F) Pressure: 345 - 1724 kPa (3.4 - 17.0 atm) Reaction time: 1 hour
- 4. Utilities Not given
- <u>Waste streams</u> Air pollution nitrous oxides and nitrogen dioxides from oxidizer; particulates from vent on product drying.

Water pollution - metallic catalyst residues and by-product organic acids.

- 6. EPA Source Classification Code None
- 7. References

Austin, G.T., "The Industrially Significant Organic Chemicals -Part 1," "Chemical Engineering," January 21, 1974, p. 131.

Hedley, William H., et. al., <u>Potential Pollutants from Petrochemical</u> Processes, Technomic Publishing Company, Westport, Conn., 1975.

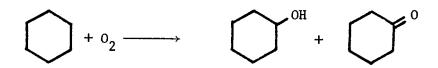
Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963) p. 411.

Sittig, M., "Pollution Control in the Organic Chemical Industry," Noyes Data Corporation, Park Ridge, New Jersey. 1974. p. 67, 68, 69, 70, 71. Faith, W.L., et. al., <u>Industrial Chemicals</u>, 3rd Ed., John Wiley and Sons, New York, N.Y., 1965, p. 46, 47.

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Cyclohexanol And Cyclohexanone (KA oil)



1. <u>Function</u> - Cyclohexanol is produced by oxidizing cyclohexane with air in the presence of a catalyst. The basic process takes place in the liquid phase by means of an oxygen-containing gas at a temperature of 120-250°C (248-482°F) and a pressure high enough to keep the cyclohexane from vaporizing, and in the presence of an oxidation catalyst such as cobalt naphthenate. This reaction produces a mixture of cyclohexanol and cyclohexanone. The two can be separated by conventional vacuumfractionating techniques.

A second technique which can be used if cyclohexanol is the desired product is the oxidation of cyclohexane over a boric acid catalyst. This process can result in alcohol-to-ketone yields as high as 10 to 1.

2. Input Materials - Basis - 1 metric ton cyclohexanone

Cyclohexane - 1010 kg (2227 lbs) Air - variable Catalyst (Mn + Co acetates) Metaboric acid - 5 kg (11 lbs) Zno - 0.75 kg (1.65 lbs)

3. <u>Operating Parameters</u> Temperature - 120-250°C (248-482°F) Pressure - Not given

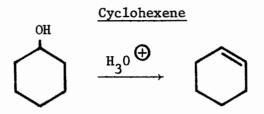
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Cyclohexane from separation process; residual crude from distillation; catalyst salts.
- 6. EPA Source Classification Code None
- 7. References

"1973 Petrochemical Handbook," "Hydrocarbon Processing," November, 1973 p. 118.

Austin, G. T., "The Industrially Significant Organic Chemicals - Part 3," "Chemical Engineering," March 18, 1974, p. 92.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 6 (1965), p. 684-686. Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition,

John Wiley and Sons, New York, N.Y., 1975, p. 304,305.



- 1. Function Cyclohexene can be manufactured by:
 - a) direct dehydration of cyclohexanol in presence of a catalyst;
 - b) dehydrohalogenation of the chlorocyclohexane or bromocyclohexane formed by halogenating cyclohexanol or cyclohexane.
- 2. Input Materials

Dehydration:

Cyclohexanol

Catalyst (Al₂0₃, H₃PO₄)

Dehydrohalogenation

Chloro- or bromo-cyclohexane

(from cyclohexanol or cyclohexane)

Dehydrohalogenating agent

3. Operating Parameters

Dehydration

(with H₃PO₄)

Initial temperature - 165-170°C

Final temperature - 200°C

Pressure - 101 kPa (1 atm)

Dehydrohalogenation

Catalyst - Zeolite impregnated with alkali oxide, or charcoal

impregnated with CuCl₂

- 3. <u>Operating Parameters</u> (continued) Temperature - 150-250°C Pressure - not given (nitrogen atmosphere) Catalyst-cyclic amidine in (CH₃)₂S0 Temperature - 80-90°C Pressure - not given
- 4. <u>Utilities</u> not given
- 5. <u>Waste Streams</u> In some continuous processes the Br₂ used to halogenate cyclohexane is recovered by absorbing the HBr in magnesia and oxidizing the resulting mass at 300°C.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

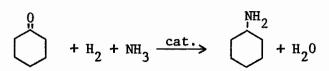
Houben Weyl - Methoden der Organischen Chemie, Vierte Auflage Bd. 5, T. 1b, George Thieme Verlag Stuttgart, 1972, p. 71, 160, 176-179.

French Patent 385,650 (January 15, 1965).

Belgian Patent 632,808 (November 25, 1963).

Organic Synthesis, John Wiley and Sons, New York, N.Y., Collective Vol. 2 (1943), p. 152.

Cyclohexylamine (from cyclohexanone)



 Function - Cyclohexylamine is manufactured by the reductive amination of cyclohexanone. This can be done in two ways both employing the same basic reaction with different operating parameters.

Process #1

Cyclohexanone is reduced with hydrogen in the presence of ammonia. A nickel catalyst supported on kieselguhr is activated by hydrogen at 427°C and used to promote the reaction which proceeds at 200°C and 31,088 kPa. One hundred percent conversion is achieved containing 81 wt.% cyclohexylamine.

Process #2

In this process cyclohexanone is reduced with hydrogen in ammonia over nickel. The operating parameters are at least 40°C and 769,359 kPa. Following the reaction the material is azeotroped with C_6H_6 then distilled to give a 99% pure product.

3. Input Materials

Process #1

Cyclohexanone - 1.23 kg/kg product

Ammonia - not given

Hydrogen - not given

Catalyst - not given

Process #2

Cyclohexanone - 1 kg/kg product Ammonia - 0.65 kg/kg product Hydrogen - 0.04 kg/kg product Catalyst - 0.11 kg/kg product Benzene

3. Operating Parameters

Process #1

Temperature: 200°C (392°F)

Pressure: 31.088 MPa (306.8 atm)

Catalyst: nickel

Process #2

Temperature: 40°C (104°F)

Pressure: 769.359 MPa (7,593 atm)

Catalyst: nickel

4. Utilities

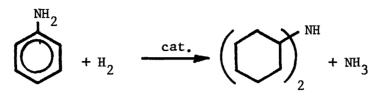
Not given

- <u>Waste Streams</u> possible hydrocarbon emissions from leaks in system; some nickel compounds and benzene may leak out.
- 6. EPA Source Classification Code None
- 7. References

French Patent, 1,446,554 (July 22, 1966).

British Patent, 1,050,589 (December 7, 1966).

Dicyclohexylamine (from aniline)



1. <u>Function</u> - Dicyclohexylamine is best prepared by the vapor phase catalytic hydrogenation of aniline over a nickel catalyst. The aniline (15 g/hr) is evaporated into a circulating hydrogen stream (425 1/hr) and the resulting mixture introduced into a reaction zone packed with a nickel-on-pumice (7 parts) catalyst. The vapors leaving the reaction zone are cooled to about 45°C, liquifying the dicyclo-hexylamine and a small amount of cyclohexylamine. The uncondensed vapors are cycled to the reactor after removing part of the ammonia and adding fresh aniline and hydrogen.

Dicyclohexylamine may also be prepared from cyclohexanone (via the cyclohexylamine produced) as in Process No.48 using a different set of operating parameters (101 kPa and 260°C).

<u>Input Materials</u> - Basis - 1 kg dicyclohexylamine
 Aniline, g 1,250

Catalyst: 7 parts nickel-on-pumice

3. Operating Parameters

Aniline feed, g/hr 15 Hydrogen feed, 1/hr 425 Temperature - not given Pressure - not given

4. Utilities

Not given

- 5. <u>Waste Streams</u> Basis 1 kg dicyclohexylamine There should be some aniline, hydrocarbons, and ammonia given off in addition to the 125 g cyclohexylamine and 11.4 g cyclohexanol.
- 6. <u>EPA Source Classification Code</u> None
- 7. <u>References</u>

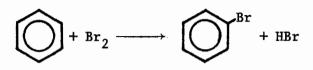
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Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 416.

German Pat. 805,518 (May 21, 1951).

U.S. Pat. 3,551,486 (December 29, 1970).

Bromobenzene



- <u>Function</u> Bromobenzene can be manufactured from benzene by reacting dry bromine with benzene in the presence of a catalyst such as Fe. This reaction takes place at 101 kPa (1 atm) and 80-100°C (175-212°F). Separation involves scrubbing to remove impurities and fractionating.
- 2. Input Materials

Bromine

Benzene

Catalyst

3. Operating Parameters

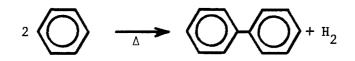
Temperature - 80-100°C (175-212°F)

Pressure - 101 kPa (1 atm)

Catalyst -- Fe

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Benzene from scrubbing and stripping operations, spent scrubbing sludge; unreacted iron and bromine.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 775,776. Biphenyl (from benzene)



- Function Biphenyl can be manufactured in 85-90% yield by the vapor phase non-catalytic reaction of benzene. Benzene is placed in a stainless steel, tubular coil reactor and heated to 600-800°C at 101 kPa.
- 2. Input Materials

Benzene

3. Operating Parameters

Temperature - 600-800 (1112-1472°F)

Pressure - 101 kPa (1 atm)

Reaction Time - 0.4-1.5 sec

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Some benzene, hydrogen, polyphenyls and benzene degradation products should be present in the waste streams.
- 6. EPA Source Classification Code None
- 7. References

U. S. Pat. 3,227,525 (January 4, 1966).

Sittig, M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition, Noyes Development Corp., Park Ridge, N.J., 1969, p. 275.

Diphenyl Oxide

- 1. <u>Function</u> Diphenyl oxide is produced in a continuous flow tubular reaction system. Aqueous NaOH, chlorobenzene, and recycled products (containing phenol and sodium phenoxide) are pumped through a Ni-lined heat exchanger which raises the temperature to 275-300°C. The temperature is raised to 400°C electrically and kept there for 10-30 min. during which time the reactants flow through the system. Two phases are obtained: 1) aqueous phenoxide, and 2) an oily layer which consists mainly of diphenyl oxide and unreacted chlorobenzene. This oily layer is distilled to produce the diphenyl oxide. The reaction must be carried out under sufficient pressure ([≥] 26.2 MPa) to prevent vaporization; otherwise, NaCl, NaOH, or phenoxide will deposit on the tube walls causing hot spots and excessive corrosion.
- 2. Input Materials

Chlorobenzene

Phenol

NaOH

3. Operating Parameters

Temperature: 1st Stage 275-300°C (527-572°F) 2nd Stage 400°C (752°F) Pressure: ≥ 26.2 MPa (258.6 atm) Reaction Time: 10-30 min.

4. Utilities

Not given

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- 5. <u>Waste Streams</u> Sodium hydroxide, sodium chloride, and sodium phenoxide should be present in the aqueous waste streams; chlorobenzene and phenol should also be emitted.
- 6. EPA Source Classification Code None
- 7. References

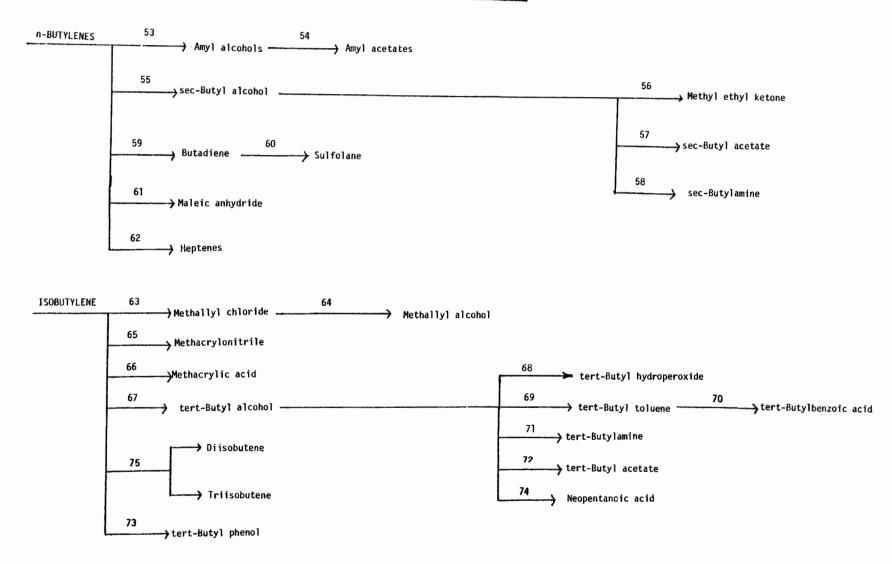
Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 15 (1968) p. 154.

Chemical Technology, Barnes and Noble Books, New York, N.Y., 1972,

p. 342.

SECTION II BUTYLENES

BUTYLENES



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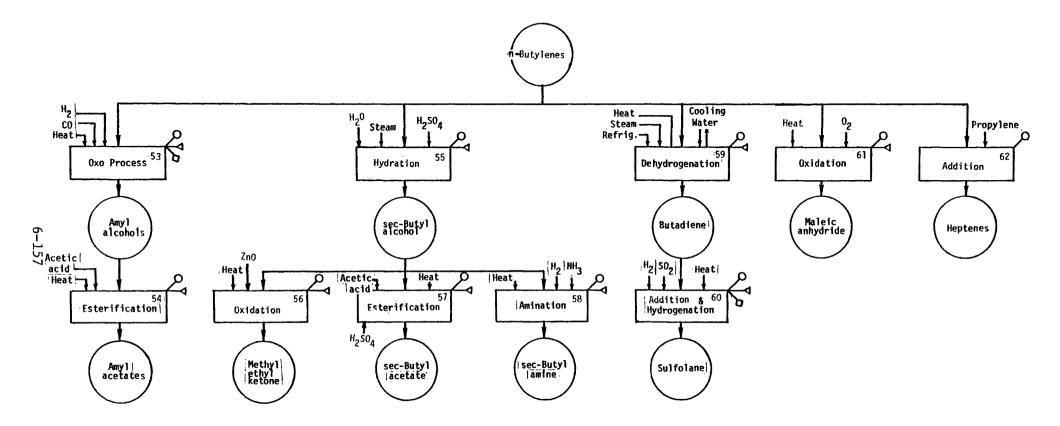


Figure 4. Butylenes Section Process Flow Sheet

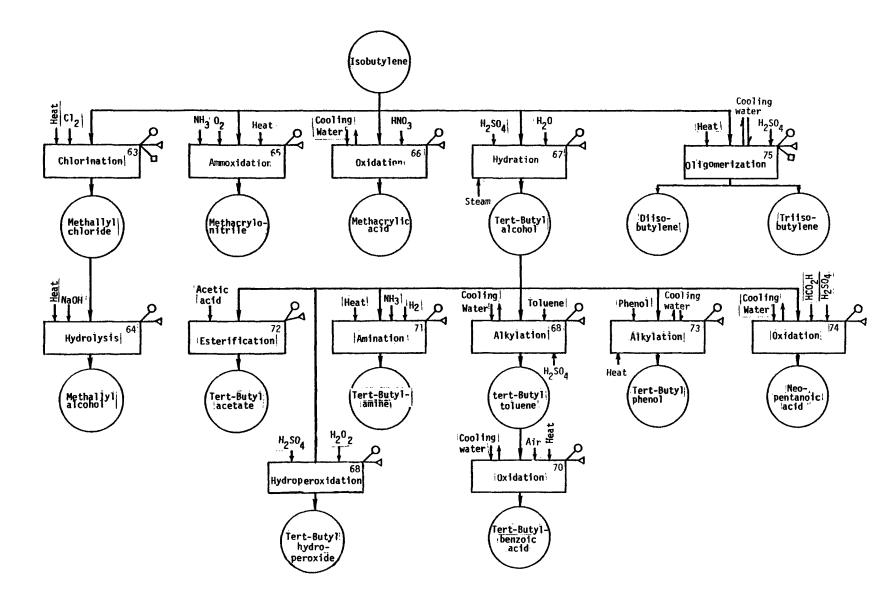


Figure 4. Butylenes Section Process Flow Sheet (Cont.)

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INDUSTRIAL ORGANIC CHEMICALS

Amyl Alcohols

$$\begin{array}{c} CH_{3}CH_{2}CH=CH_{2} \\ CH_{3}CH=CH-CH_{3} \\ CH_{3}-C_{1}=CH_{2} \\ CH_{3}-C_{1}=CH_{3} \\ CH_{3}-C_{1}=$$

- 1. <u>Function</u> The manufacture of oxo amyl alcohols entails the reaction of butylenes with carbon monoxide and hydrogen at high pressure and temperature in the presence of a catalyst, usually a cobalt carbonyl compound. The reaction produces a mixture of primary C₅ alcohols which are fractionated into 3 commercial grades: primary amyl alcohol being approximately 60% 1-pentanol, 35% 2-methyl-1-butanol, and 5% 3-methyl-1-butanol; 1-pentanol being about 99% 1-pentanol; commercial 2-methyl-1-butanol and 2% 1-pentanol.
- 2. Input Materials

Mixed butylenes - 1-Butene 2-Butene Methylpropene

Synthesis gas - CO

3. Operating Parameters

Pressure - 20.65 MPa (200 atm)

Temperature - 125-145°C (257-293°F)

4. Utilities

Not given

5. <u>Waste Streams</u> - Catalyst recovery section (air, water). Air vent discharges some carbon monoxide, butylenes and alcohols. Some catalyst recovery systems have a water waste stream which could contain small quantities of alcohols.

Purification section (air). Various by-products are formed in the oxo process, mainly dimeric alcohols and acetals. In fractionation the heavy ends may be sent for incineration while some of the light ends may be flared to the atmosphere.

- 6. EPA Classification Code None
- 7. References

Denney, R. G., "<u>Oxo Alcohols</u>," Report no. 21, Stanford Research Institute, Menlo Park, California, 1966.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 377,378.

Chemical Technology, Barnes and Noble, New York, N.Y., Vol. 4 (1972), p. 139.

 $\frac{\text{Amyl Acetates (from amyl alcohols)}}{\text{C}_{5}\text{H}_{11}\text{OH} + \text{CH}_{3}\text{COOH}} \xrightarrow{\text{H}_{2}\text{SO}_{4}} \text{CH}_{3}\text{COOC}_{5}\text{H}_{11} + \text{H}_{2}\text{O}$

- <u>Function</u> Commercial amyl acetate, a mixture of isomers, is prepared by the esterification of mixed amyl alcohols with acetic acid. Small amounts of sulfuric acid are used to catalyze the reaction. The crude product is purified by rectification. The principal isomers are isoamyl, normal, and secondary amyl acetates.
- 2. Input Materials

Amyl alcohols - 0.8 kg/kg product

Acetic acid - .505 kg/kg product

 Operating Parameters Temperature - 220-130°C (428-590°F)

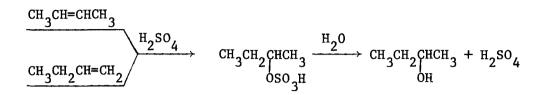
Pressure - 101 kPa (1 atm)

Catalyst - H_2SO_4

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Air and wastewater emissions from separator and other purification equipment may contain acetic acid, amyl alcohol, amyl acetate, traces of sulfuric acid, and various reaction by-products.
- 6. EPA Source Classification Code None
- 7. References

Goldstein, R. F., The Petroleum Chemicals Industry, 2nd Edition, John Wiley and Sons, New York, N.Y., 1958, p. 74,75.

sec-Butyl Alcohol



- <u>Function</u> In this process sec-butyl alcohol is produced by absorbing n-butenes in 70-85% sulfuric acid to form butyl hydrogen sulfate which is then hydrolyzed to sec-butyl alcohol and dilute sulfuric acid. The product is steam stripped from the dilute acid solution and purified by distillation.
- 2. Input Materials

n-Butenes - 900 kg/Mg alcohol Sulfuric acid

3. Operating Parameters

Sulfation: temperature - 15-30°C (55-78°F)

pressure - 698.8 kPa (100 psig) (7.8 atm)

Hydrolysis: temperature - 30-40°C (78-94°F)

pressure - 100 kPa

- 4. Utilities Not given
- 5. Waste Streams -

<u>Distillation column</u> (water) - Waste stream would contain some butyl alcohol. If the process includes a caustic wash, there will be some sodium hydroxide and sodium sulfate in the wastewater. Acid recovery section (water) - Sulfuric acid is wasted as tars build up.

- 6. EPA Source Classification Code None
- 7. References

Faith, W. L. et al., <u>Industrial Chemicals</u>, 2nd Edition, John Wiley and Sons, New York, N. Y., 1957.

Astle, M.J., <u>The Chemistry of Petrochemicals</u>, Reinhold Publishing Corporation, New York, 1956.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, Vol. 3 (1964).

Waddams, A.L., <u>Chemicals From Petroleum</u>, 3rd Ed., John Murray Ltd., London, 1973, p. 159.

4

Methyl Ethyl Ketone

$$\begin{array}{c} \operatorname{CH}_{3} \operatorname{CHCH}_{2} \operatorname{CH}_{3} & \xrightarrow{Zn0} & \operatorname{CH}_{3} \operatorname{CCH}_{2} \operatorname{CH}_{3} \\ \operatorname{OH} & & & \\ \end{array}$$

 Function - Methyl ethyl ketone (2-butanone, or MEK) is made from secbutanol by a process substantially the same as the acetone-from-isopropanol process. A catalyst of ZnO on pumice is used in a tubular reactor and the reactor temperature is maintained at 400-500°C.

Some MEK is obtained as byproduct from the oxidation of butane to acetic acid, some from the acetaldehyde process, and some from the acetaldehyde-to-acetic acid process.

2. Input Materials

sec-Butano1 - 1175 kg/metric ton MEK

Zn0

3. Operating Parameters

Temperature - 400-550°C (752-1022°F) Pressure - 200-300 kPa (15-30 psi) (1.97-2.96 atm) Catalyst - ZnO

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Scrubber (water): Wastewater stream would contain methyl ethyl ketone and reaction by-products.
- 6. EPA Source Classification Code None
- 7. References

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., (1975) p. 539-542.

7. <u>References</u> (continued)

Sittig, M., Organic Chemical Process Encyclopedia 1969, 2nd Edition, Noyes Development Corporation, Park Ridge, New Jersey, (1969).

sec-Butyl Acetate

$$\begin{array}{c} \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{CH}_{0} \to \operatorname{CH}_{3} \to \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{CH}_{3} \to \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{CH}_{3} \to \operatorname{CH}_{3}\operatorname{CH}_{3} \to \operatorname{CH}_{3} \to \operatorname{CH}_{$$

- 1. <u>Function</u> The esterification of sec-butyl alcohol with acetic acid with concentrated sulfuric acid as a catalyst yields sec-butyl acetate. This reaction is reversible and so the water of reaction and the ester product must be continuously withdrawn to increase the conversion going to the ester. The overhead is usually a mixture of alcohol, ester, and water which is separated and the ester purified by rectification.
- 2. <u>Input Materials</u> Basis 1 Mg ester sec-Butyl alcohol: 713 kg Acetic Acid: 550 kg H₂SO₄: 1-4 kg
- <u>Operating Parameters</u>
 Temperature: 89°C (192°F)

Pressure: 101 kPa (1 atm)

- 4. Utilities Not given
- 5. Waste Streams Separator

(Water) - 1% ester 3% alcohol 96% H₂0

(Air) - ester and alcohol vapors from air vent; some H_2SO_4

6. EPA Source Classification Code - None

7. <u>References</u>

Faith, W. L., et al., <u>Industrial Chemicals</u>, 3rd Edition, John Wiley and Sons, New York, N.Y., 1965, p. 176-178.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 8 (1966), p. 372.

Groggins, P. H., <u>Unit Operations in Organic Synthesis</u>, 5th Edition, McGraw-Hill Book Company, New York, N.Y., 1958, p. 730.

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 173-176.

sec-Butyl Amine

$$CH_3CH_2CHCH_3 + NH_3 \longrightarrow CH_3CH_2CHCH_3 + H_2O$$

OH NH2

- Function Sec-butyl amine is produced commercially by the catalytic addition of NH₃ to the corresponding alcohol, with separation of the mono-, di- and tri-substituted butyl amines.
- 2. <u>Input Materials</u> Basis 1 Mg mixed product Sec-butanol: 1.5 Mg (7.5 mole %) NH₃: 425 kg (45 mole %) H₂: (43 mole %)
- 3. Operating Parameters

Temperature: 350°C (662°F)

Pressure: 1.48 MPa (14.6 atm)

Flow rate: 1000/hr space velocity

Catalyst: Nickel

These conditions yield: 50 mole percent monoamine

20 mole percent diamine

30 mole percent triamine

- 4. Utilities Not given
- 5. <u>Waste Stream</u> CO_2 and formaldehyde by-products; unreacted alcohols, H₂, and NH₃ in vented gas streams.
- 6. EPA Source Classification Code None
- 7. References

Faith, W. L. et al., <u>Industrial Chemicals</u>, John Wiley and Sons, New York, N. Y., 1950, p. 47, 48. Sittig, M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition, Noyes Development Corp., Park Ridge, N. J., 1969, p. 127.

U. S. Patent 2,182,807 (December 12, 1939).

Butadiene (catalytic dehydrogenation of n-butenes)

$$n-C_4H_8 \xrightarrow{\text{Shell Catalyst 205}}_{621 - 677^{\circ}C}, 101 \text{ KPa} CH_2 = CHCH = CH_2 + H_2$$

 Function - n-Butenes which have been treated for isobutylenes and butanes removal are the exclusive feed for 15-20% of the butadiene manufactured in the U.S. Two commercial processes compete: one of which is based on the Dow Type B catalyst, the other on Shell Catalyst 205.

Shell Catalyst 205 (ferric oxide, chromium oxide, and potassium oxide) effects dehydrogenation to butadiene at temperatures of 621-677°C and atmospheric pressure. The preheated butene feedstock is mixed with superheated steam in a mole ratio of 1:8 and passed over the 81-91 cm. deep catalyst bed at a space velocity of 500 volumes of butenes at standard condition per hour, per volume, of catalyst space. Selectivity to butadiene is 73-75% with 26-28% conversion of n-butene per pass.

The more recently developed Dow Type B catalyst (calcium nickel phosphate stabilized with 2% chromium oxide) effects dehydrogenation at slightly lower temperatures (593-677°C) and higher pressures (170-255 kPa) than Shell Catalyst 205.

Selectivity to butadiene (90%) and butene conversion per pass (35-45%) are significantly higher with this catalyst, but larger quantities of diluent steam (1:20) and more frequent catalyst regeneration are required. Whereas Shell Catalyst 205 is regenerated only

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once a day for one hour, the Dow Type B Catalyst must be regenerated in fifteen minute cycles.

This catalyst also has a greater tendency to produce ketones and acetylenic by-products than Shell Catalyst 205. Although marketable quantities of acetone and methyl ethyl ketone may be obtained, their separation requires more extensive purification equipment.

The resulting butane/butene/butadiene mixture is separated by extractive distillation with aqueous furfural or acetonitrile. Butenes and butanes are collected overhead and recycled, while butadiene and residual acetylenics remain in the solvent bottoms. Since furfural cannot be used to separate butadiene from the 2-butenes, it is frequently advantageous to precede the extractive distillation with a feed splitter. This column takes most of the butanes and 2-butenes as bottoms, and passes the 1-butene/butadiene overhead into the furfural unit. Alternately, a final butadiene from the furfural solvent.

If acetonitrile is used as the extraction solvent, butanes and butenes separate almost quantitatively from butadiene and feed splitting is not required. However, a final water wash is necessary to remove the last traces of solvent from both the raffinate and product streams. Washing is not required to recover furfural due to the high boiling point of the solvent.

2. Input Materials

n-Butenes - (80-95%) Shell Catalyst 205 - 1.38-1.42 kg/kg product Dow Type B Catalyst - 1.14-1.18 kg/kg product

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Hydrogen - (acetylenics removal)

Furfural or acetonitrile

3. Operating Parameters

5. <u>Waste Streams</u> - Waste flows from butadiene production facilities were 417 m/Gg (100 gal/ton) of product with waste composition as follows (taken from one source only): pH: 8-9 TOC: 100 to 200 g/m³ Filtered COD: 250 to 375 g/m³ Suspended solids: 200 to 500 g/m³ Total solids: 3 to 4 kg/m³

The principal pollutant sources should be the quench waters containing tars, oils, and soluble hydrocarbons and the solvent extract and wash waters (if acetonitrile is used) containing acetonitrile and C_4 hydrocarbons. Some air emissions of furfural or acetonitrile may also occur.

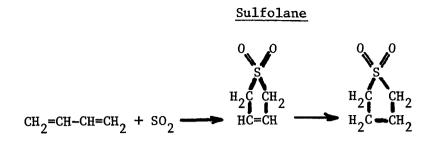
- 6. EPA Source Classification Code None
- 7. References

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical Processes</u>, Technomic Publishing Co., 1975.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 794-799.

Sittig, M., Organic Chemical Processes Encyclopedia - 1969, 2nd Edition Noyes Development Corp., Park Ridge, N.J., 1969, p. 118.

U. S. Pat. 3,200,166 (August 10, 1965).



1. <u>Function</u> - Sulfolane is produced by the cyclic addition of sulfur diox 3 to butadiene to form sulfolene. The reactions is carried out in a Cr-steel tube (1300 x 100 mm) filled with catalyst. The crude product is treated with a chloride of lime suspension (to remove any mercaptans found) and then distilled. The sulfolene is then hydrogenated to sulfolane.

Steps must be taken to keep peroxides from entering the reaction with the reactants because undesirable polymeric by-products will result.

2. Input Materials

Catalyst	20% Cr ₂ 0 ₃	3.70 kg	Butadiene	467	kg/Mg
0	.58% к ₂ 0		so ₂	553.4	kg/Mg
79	.42% A1 ₂ 0 ₃		^H 2	17.3	kg/Mg

- Operating Parameters
 Temperature 500°C (932°F)
- 4. Utilities

Steam - quantities not given

- <u>Waste Streams</u> Possible waste streams should contain some SO₂, nickel, catalyst, and some polymeric byproducts.
- 6. EPA Source Classification Code

None

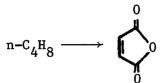
7. References

Drake, L. R., et. al., <u>J. Amer. Chem. Soc.</u>, <u>68</u>, p. 2521 (1946). U.S. Patent 2,420,834 (May 20, 1947).

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Ed. Interscience Publishers, New York, N.Y., Vol. 19 (1969) p. 250.

INDUSTRIAL ORGANIC CHEMICALS

Maleic Anhydride



- 1. <u>Function</u> Butenes are oxidized to maleic anhydride at a temperature of 350°C and a pressure of 276-450 kPa (25-50 psig). A catalyst is used for this oxidation which consists of the oxides of molybdenum, vanadium, and phosphorous (in a ratio of 9:3:1), supported on silica gel. The maleic anhydride is solvent extracted from the reaction gases and purified by vacuum distillation or sublimation.
- 2. Input Materials

Butenes

Air

Catalyst (oxides of Mo, V, P on silica gel)

3. Operating Parameters

Temperature: 350°C

Pressure: 276-450 kPa (2.7 - 4.4 atm)

Contact time: 1.5 sec.

4. Utilities

Cooling water - quantities not given

Steam - quantities not given

5. <u>Waste Streams</u> - Recovery section - air emissions containing butenes, carbon oxides and traces of maleic acid Purification section - waste water stream from bottoms containing maleic anhydride and high boilers. Another waste water stream from overhead containing maleic acid.

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6. EPA Source Classification Code - None

7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 12 (1967), p. 828, 829.

Morse, P. L., <u>Maleic Anhydride</u>, Report No. 46, Stanford Research Institute, Menlo Park, California, 1969.

U.S. Patents 3,156-705 - 3,156,707 (1964).

Heptenes

$$CH_2 = CHCH_3 + C_4H_8 \longrightarrow C_7H_{14}$$

1. <u>Function</u> - Heptenes are a cut fractionated from the gasoline mixture that is produced by polymerizing C_3-C_4 refinery gases.

In general, the yield of heptenes is about 25% based on propylene and 33% based on n-butene and isobutene. However, these figures vary considerably, depending on the reaction conditions and the feed composition.

2. Input Materials

C₃ Refinery gas Propylene: 1.7 kg/kg heptene C₄ Refinery Gas Butylenes: 1.71 kg/kg heptene

3. Operating Parameters

Temperature: 200-240°C (392-464°F)

Pressure: 1.52-2.53 MPa (15-25 atm)

Catalyst: H₃PO₄

4. Utilities

Not given

- 5. <u>Waste Streams</u> Since all the fractions of the gasoline mixture product are utilized, there are no wastes from this process. However, any number of olefins may be released to the atmosphere in small quantities by process leaks.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Goldstein, R. F., <u>The Petroleum Chemicals Industry</u>, 2nd Edition, John Wiley and Sons, New York, N.Y., 1958, p. 125.

Waddams, A. L., <u>Chemicals from Petroleum</u>, 3rd Edition, John Murray Ltd., London, England, 1973, p. 137, 144.

Methallyl Chloride

$$CH_2 \stackrel{\text{CH}_2=\text{C}-\text{CH}_3}{\underset{\text{CH}_3}{\text{H}_3}} + C1_2 \longrightarrow CH_2 \stackrel{\text{C}-\text{C}-\text{C}}{\underset{\text{C}}{\text{H}_2}} C1 + HC1$$

 Function - Isobutylene and chlorine are mixed in a ratio of 2:1 at 70-80°C to yield methallyl chloride. The main mechanism of this reaction is an allylic substitution.

The crude product is recovered by distillation with the overhead being approximately 95% methallyl chloride.

2. Input Materials

- 3. <u>Operating Parameters</u> Temperature: 70-80°C (158-176°F)
- 4. Utilities

Steam: quantity not given

- 5. <u>Waste Streams</u> Distillation column: heavy ends may be incinerated some Cl₂ and HCl vapors may be present in the waste streams.
- 6. EPA Source Classification Code

None

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol 3 (1964), p. 840, 841.

Faith, Clark, & Keyes, <u>Industrial Chemicals</u>, 2nd Edition, J. Wiley & Sons, Inc., New York, 1950.

Methally1 Alcohol

 $CH=C-CH_2C1 + NaOH \longrightarrow CH=C-CH_2OH + NaC1$ CH_3 CH_3

- <u>Function</u> Methallyl alcohol is produced from methallyl chloride by hydrolysis with caustic solution.
- 2. <u>Input Materials</u>

Methallyl chloride NaOH (10%)

3. Operating Parameters

Temperature: 145-155°C (293-311°F) Pressure: 1.5 MPa (19.8 atm) Reaction Time: < 15 minutes

- 4. Utilities Not given.
- <u>Waste Streams</u> Wastewater streams would have some NaOH, NaCl, alcohol, and chloride.
- 6. EPA Source Classification Code None.
- 7. References

Goldstein, R. F., <u>The Petroleum Chemicals Industry</u>, 2nd Edition, John Wiley and Sons, New York, N. Y., 1958, p. 171.

Astle, M. J., <u>The Chemistry of Petrochemicals</u>, Reinhold Publishing Corp., New York, N. Y., 1956, p. 69.

Methacrylonitrile

$$CH_3 \xrightarrow{-C=CH_2} + NH_3 \xrightarrow{air} N \equiv C-C=CH_2$$

 $CH_3 \xrightarrow{CH_3} CH_3$

- Function Methacrylonitrile is produced by the amminoxidation of isobutylene. Isobutylene, ammonia, and air are fed to a fluid-bed catalytic reactor operating at 800-900°C. The reactor effluent is scrubbed and the product recovered by distillation.
- 2. Input Material

Isobutylene - 1 kg/kg product Ammonia - 0.5 kg/kg product Air - 20 kg/kg product

3. Operating Parameters

Temperature: 800-900°C (1472-1652°F)

Catalyst: oxide of Co, Mn, or Mo

4. Utilities

Cooling water: 470 kg/kg product Steam: 6.5 kg/kg product Refrigeration: capacity not given Process water: 100 kg/Mg product Electricity: capacity not given

5. Waste Streams

Reaction section - absorber off-gas to flare (air)

Methacrylonitrile - 5 kg/Mg product

Carbon monoxide - 200 kg/Mg product

Isobutylene - 100 kg/Mg product

Ammonia - trace

Purification section - off-gas from drying column to flare (air) Hydrogen cyanide - 1 kg/Mg product

Reaction section - neutralizer (water)

Wastewater contains ammonium sulfate

Purification section - stripper (water)

Wastewater may contain by-products such as acetonitrile

- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kent, J. A., Editor, <u>Riegel's Handbook of Industrial Chemistry</u>, Van Nostrand Reinhold Company, New York, N. Y., 1974, p. 810.
Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition,
Interscience Publishers, New York, N. Y., Vol. 13 (1967), p. 333,
342.

$(CH_3)_2 C = CH_2 \xrightarrow{HNO_3} CH_2 = C - COOH$

1. <u>Function</u> - Methacrylic acid is produced by the thermally activated reaction of isobutylene with nitric acid or mixtures of this acid with $N_2^0_4$. The initial oxidation proceeds at low temperatures (0-5° C), and in several intermediate stages the oxidation products are converted to α -hydroxyisobutyric acid, which is then dehydrated to methacrylic acid.

A plant was built in Pensacola, Florida, by Escambia Chemical Corporation to use this process. There were some economic problems with the process and its present status is unknown.

2. Input Materials

Isobutylene

Nitric acid

3. Operating Parameters

Initial oxidation stage: temperature - 0-5°C (32-41°F) Subsequent oxidation stages: temperature - higher but unknown

- 4. <u>Utilities</u> Chilling water quantities not given
- 5. <u>Waste streams</u> No data available. It is presumed that some isobutylene and oxidation products would be released to the atmosphere through leaks and vents.
- 6. EPA Source Classification Code None

7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 842. Anon., Chemical Week, 90(26), 17 (1962).

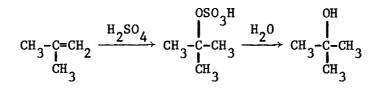
Fr. Pat. 1,335,166 (July 8, 1963).

U.S. Pat. 2,847,453 (Aug. 12, 1958).

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INDUSTRIAL ORGANIC CHEMICALS

tert-Butyl Alcohol



 Function - Isobutylene is absorbed in sulfuric acid to form t-butyl hydrogen sulfate which is subsequently hydrolyzed with water to t-butyl alcohol and dilute sulfuric acid. The product is steam stripped from the acid solution and purified by distillation.

The process is similar to that for sec-butyl alcohol except for the sulfuric acid being less concentrated (60-65% vs 75-80%) to minimize polymerization reactions.

2. Input Materials

Isobutylene - 850 kg/Mg alcohol

Sulfuric acid - recycled

3. Operating Parameters

Sulfation: Temperature - 30-45°C (86-113°F) Pressure - not given

Hydration: Temperature 30-40°C (86-104°F)

Pressure - not given

4. Utilities - Not given

5. Waste Streams -

Distillation column (water) - Some t-butyl alcohol will be present in the waste water. If caustic washing is included the waste water stream will contain some sodium hydroxide and sodium sulfate. Acid recovery section (water) - As tars build up some sulfuric acid is wasted in the effluent stream.

6. EPA Source Classification Code - none

7. References

Astle, M.J., <u>The Chemistry of Petrochemicals</u>, Reinhold Publishing Corporation, New York, 1956.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, Vol. 3 (1964), p. 827.

tert-Butyl Hydroperoxide

$$\begin{array}{c} \begin{array}{c} {}^{CH_{3}}_{H_{3}}c - \stackrel{CH_{3}}{c} - OH + H_{2}O_{2} \\ \stackrel{H_{2}SO_{4}}{\longrightarrow} H_{3}C - \stackrel{CH_{3}}{c} - OOH + H_{2}O \\ \stackrel{H_{3}}{\longrightarrow} H_{3}C - \stackrel{CH_{3}}{C} - OH + H_{2}O \end{array}$$

1. <u>Function</u> - The formation of t-butyl hydroperoxide can be achieved by three different methods. First, the alkylation of hydrogen peroxide by alkyl sulfates, chlorides or alcohols in the presence of sulfuric acid. Second, the oxidation of an appropriate hydrocarbon, in this case isobutane, in the presence of a chain initiator (HBr), and third, the oxidation of an appropriate Grignard reagent with oxygen saturated ether. The method of choice is the alkylation of hydrogen peroxide with t-butyl alcohol in the presence of sulfuric acid.

The t-butyl alcohol, 30-50% hydrogen peroxide, in equimolar quantities, and sulfuric acid are combined in a water-imiscible solvent (chloroform or methylene chloride) having a boiling point lower than that of t-butyl hydroperoxide. The reaction is carried out at 60° C with very rapid stirring, necessary because of the dual phase system, for a short period of time (1/2 - 1 hour). The reaction mixture is rapidly cooled and the organic solvent evaporated under reduced pressure. The yields are 70-80% of a 97% pure product. The t-butyl hydroperoxide may be purified by vacuum distillation provided the pressure is maintained at 100 mm or less at which point the boiling point (53°C) is below the decomposition temperature (73°C) of the hydroperoxide.

6-188

2. Input Materials

t-Butyl alcohol

30% Hydrogen peroxide

70% Sulfuric acid

Methylene chloride or chloroform

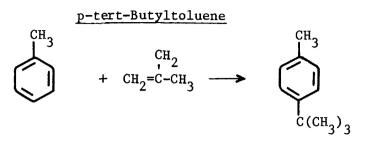
3. Operating Parameters

Temperature - 60°C (140°F) Pressure - 100 kPa (1 atm) Catalyst - sulfuric acid

- 4. Utilities Not given
- <u>Waste Streams</u> Vent streams from the reaction vessel and purification system contain organic solvent vapors. Wash water, sulfuric acid, t-butyl alcohol and some t-butyl hydroperoxide.
- 6. EPA Source Classification Code None
- 7. References

"Encyclopedia of Polymer Science and Technology, Vol. 9, Interscience Publishers, New York, New York, 1968, p. 815.

U. S. Patent 2,573,947 (1951 Shell Development Co.).



- 1. <u>Function</u> Toluene is alkylated with isobutylene or tert-butyl alcohol in the presence of sulfuric acid. The alcohol dehydrates readily in the acidic conditions of this process. The alkylation proceeds very cleanly if temperatures are controlled to no more than 75 to 80°C. The product is washed in a caustic scrub to remove the last traces of acid catalyst.
- 2. Input Materials

Isobutylene or tert-butyl alcohol

Toluene

Sulfuric acid

3. Operating Parameters

Temperatures: 75 to 80°C (167-176°F)

Pressure: 101 kPa (1 atm)

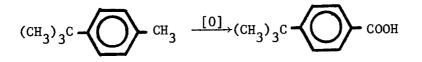
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Wastewater stream from caustic scrubbing would contain spent caustic and traces of product.
- 6. EPA Source Classification Code None
- 7. References

Schlatur, M. J. and Clark, R. D., <u>J. Amer. Chem. Soc</u>., Vol. 75 (1953), p. 361-369.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 3 (1964), p. 873.

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p-tert-Butylbenzoic Acid



- 1. <u>Function</u> The stable character of the tert-butyl side chain on tert-butyltoluene toward oxidation leads to the production of tert-butylbenzoic acid by air oxidation. In this process, a cobalt catalyst is used and a temperature of 110-180°C with a pressure of about 450-625 kPa (4.4-6.2 atm). Water is removed as soon as it is formed. Generally, the tert-butylbenzoic acid is isolated by crystallization or by extraction and crystallization.
- 2. Input Materials

tert-Butyltoluene: 850 kg/Mg acid

Air: approximately 2 Mg/Mg acid

3. Operating Parameters

Temperature: 110-180°C (230-356°F) Pressure: 450-625 kPa (4.4-6.2 atm) Catalyst: a cobalt compound

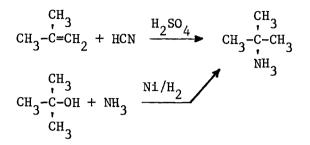
4. Utilities

Steam - quantities not given

- 5. <u>Waste Streams</u> The water of reaction removed from the process would probably carry small quantities of both product and reactant.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 436.

tert-Butylamine



- <u>Function</u> Two routes are used to produce tert-butylamine: (1) isobutylene or tert-butyl alcohol is reacted with HCN in the presence of sulfuric acid at a temperature of 25°C; the alcohol dehydrates readily in acid and reacts the same as isobutylene with the HCN; (2) tert-butyl alcohol is reacted with ammonia at 190°C in the presence of a nickel catalyst and hydrogen.
- 2. Input Materials
 - Isobutylene or tert-butyl alcohol
 Hydrogen cyanide

Sulfuric acid

(2) tert-Butyl alcohol

Ammonia

Hydrogen

- 3. Operating Parameters
 - (1) Temperature: must be carefully controlled to around 25°C (77°F) to prevent polymerization
 - (2) Température: 190°C (374°F)
- 4. Utilities Not given

- 5. <u>Waste Streams</u> No specific information available but purification would give wastewater streams containing spent catalyst and products in small amounts. Vents in process 2 could allow some ammonia and hydrogen to escape to the atmosphere.
- 6. EPA Source Classification Code None

7. References

Faith, W. L. et al., <u>Industrial Chemicals</u>, 2nd Edition, John Wiley and Sons, New York, N. Y., 1957, p. 53, 54.

tert-Butyl Acetate

$$\begin{array}{c} H_{3}C-C=CH_{2} \\ H_{3}C-C=CH_{2} \\ CH_{3} \end{array} + CH_{3}COOH \rightarrow H_{3}C-C-OOCCH_{3} \\ H_{3}C-C-C-OOCCH_{3} \\ CH_{3} \end{array}$$

- 1. <u>Function</u> Reacting isobutylene with glacial acetic acid in the liquid phase over a silica catalyst impregnated with V₂O₅ and K₂SO₄ at 93.3°C (200°F) and 1.72 MPa (17.0 atm) yields tert-butyl acetate. Exxon Corporation is the only company which reported production of the acetate to the U.S. Tariff Commission.
- 2. <u>Input Materials</u>

Glacial acetic acid

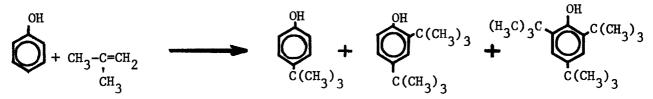
- 3. <u>Operating Parameters</u> Temperature 93.3°C (200°F) Pressure 1.72 MPa (17.0 atm)
- 4. Utilities

Not given

- 5. <u>Waste Streams</u> Purification would give a wastewater stream which could contain small amounts of acid, acetate, alcohol, and catalysts.
- 6. <u>EPA Source Classification Code</u> None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 8 (1965), p. 342.

p-tert-Buty1phenol



 <u>Function</u> - Isobutylene reacts quite readily with phenol in the presence of any of a wide range of acidic and Friedel-Crafts catalysts to give, successively, the mono-, di-, and tri-tertbutylphenols.

Under acidic condition, tert-butyl alcohol dehydrates readily and yields the same alkylated phenols as the isobutylene. High temperatures favor dealkylation and trisubstituted tert-butyl-phenols.

2. Input Materials

Isobutylene or tert-butyl alcohol

Pheno1

Acidic (50% H_2SO_4) or Friedel-Crafts catalysts

3. Operating Parameters

Temperature: controlled to 70°C (158°F), then taken to 150°C (302°F) Pressure: atmospheric Reaction Time: 1 hr

4. Utilities

Not given

5. <u>Waste Streams</u> - No specific information available but it is probable that purification procedures would give wastewater streams containing traces of mixed isomeric butylphenols, isobutylene polymers, and H₂SO₄ or Friedel-Crafts catalysts.

6. <u>EPA Source Classification Code</u> - None

7. <u>References</u>

Kirk-Othmer, Encyclop dia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963) p. 904.

Neopentanoic Acid (pivalic acid)

$$\begin{array}{c} \begin{array}{c} CH_{3} \\ H_{3}CH_{3}CH_{3} \\ CH_{3} \end{array} & \begin{array}{c} H_{2}SO_{4} \end{array} & \begin{array}{c} HCO_{2}H \\ \hline \end{array} & \begin{array}{c} HCO_{2}H \\ CH_{3}C-COOH \end{array} & \begin{array}{c} CH_{3} \\ CH_{3} \end{array} & \begin{array}{c} CH_{3}C-COOH \\ CH_{3} \end{array} & \begin{array}{c} CH_{3} \end{array} & \begin{array}{c} CH_{3}C-COOH \end{array} & \begin{array}{c} (A) \end{array} \end{array}$$

$$CH_{2} = \overset{CH_{3}}{C-CH_{3}} + CO \xrightarrow{H_{2}SO_{4}} CH_{3}\overset{CH_{3}}{\underset{CH_{3}}{C-CO_{2}}H} (B)$$

 Function - Neopentanoic acid is made by two different processes. In one process (A) tert-butyl alcohol is reacted with sulfuric acid and formic acid at a temperature of 20-25°C. The product is purified by distillation.

The other process (B) involves the carboxylation of isobutylene with carbon monoxide in aqueous sulfuric acid. The isobutylene and acid catalyst are pumped to a pressurized reaction vessel where a CO rich gas is bubbled through the mixture to form a tertiary carbonium ion. After degassing, the complex is hydrolyzed with water to spring the acid catalyst for recycle. The crude acid is treated to remove the last traces of catalyst and then purified by distillation.

2. Input Materials

(A) tert-Butyl alcohol

Formic acid

Sulfuric acid

(B) Isobutylene

Carbon monoxide

Dilute H₂SO₄

3. Operating Parameters

- (A) Temperature: 20-25°C (68-77°F)
 Pressure: Not given

4. Utilities

Steam - Not given

Electrical power - Not given

5. Waste Streams

(A) Distillation bottom ends could give a wastewater stream containing small quantities of product and catalyst.

(B) Reactor off-gas will contain CO and isobutylene vapors. Water from springing of catalyst could give rise to a wastewater stream carrying some acid catalyst and crude product.

6. EPA Source Classification Code - None

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 8 (1965), p. 853,854.

Sittig, M., Chemicals From C₄ Hydrocarbons, Noyes Development Corp., Park Ridge, N.J., 1966, p. 88,89.

Di- And Tri-Isobutenes

- <u>Function</u> The isobutene in a C₄ stream (free of butadiene) is absorbed in 50-65% sulfuric acid at 10-20°C and then heated to 80-100°C to coproduce diisobutylene and triisobutylene in the ratio of 80% to 20%. The oligomers separate as an upper layer which is separated, washed, and purified by distillation.
- 2. Input Materials

Isobutene

H₂SO₄ (recycled)

3. Operating Parameters

Temperature: extraction - 10-20°C (50-68°F) polymerication - 100°C (212°F) time - 0.5 hour

- 4. Utilities Not given
- <u>Waste Streams</u> Caustic washes (water) Waste stream contains sodium hydroxide, sodium sulfate, and organic by-products such as butyl alcohol.

Distillation column produces heavy ends.

- 6. EPA Source Classification Code None
- 7. References

McKetta, J. J., Editor, <u>Advances in Petroleum Chemistry and Refining</u>, Interscience Publishers, New York, N. Y., Vol. 7 (1963), p. 285-321.

Goldstein, R. F., <u>The Petroleum Industry Today</u>, 2nd Edition, John Wiley and Sons, New York, N. Y., 1958, p. 125.

SECTION III

SOURCES OF CRESYLIC ACIDS

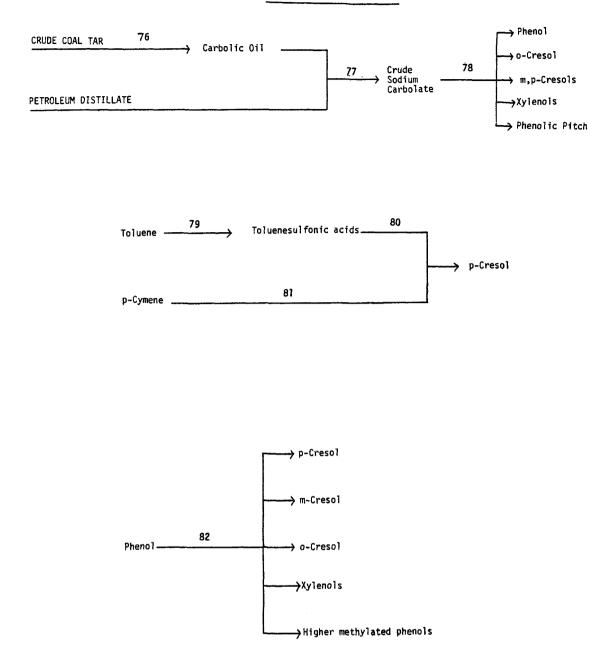


Figure 5. Sources of Cresylic Acids Chemical Tree

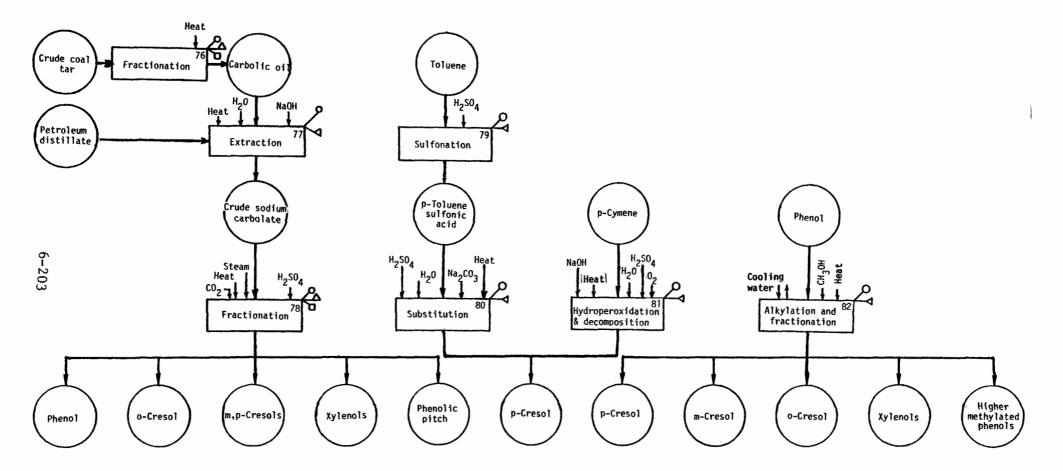


Figure 6. Sources of Cresylic Acids Process Flow Sheet

Carbolic Oil

1. <u>Function</u> - As produced, crude coal tar is of value only as a fuel. Today, at least 85% of the tar produced is distilled. The two main objectives in the primary distillation of crude tar are to obtain a pitch or refined-tar residue of the desired softening point and to concentrate those components which are subsequently to be recovered. In the case of continuous vertical-retort tar, the main aim is to concentrate the phenol, cresols, and xylenols in the carbolic oil fraction. The amount of "phenolic bodies" in coal tar depends on the carbonization process used. Coke-oven by-product tars contain between 1 and 7% of "phenolic bodies", the average being close to 3%. Gasworks tars derived from the carbonization of bituminous coal in continuous vertical retorts have an average tar acid content of 15% and low-temperature tars may contain as much as 25%.

Primary distillation of coal tar in the U. S. is done in "Recycle Continuous Stills". Crude tar, after screening and doping with alkali, is pumped through a series of heat exchangers and a waste-heat coil and then injected into the lower section of a dual flash chamber where it meets hot pitch overflowing from the upper section. The water and light-oil vapors released in the lower section pass up through a liquid seal into the upper part. The mixture of dehydrated tar and pitch is pumped from the base of the distillation column, through the furnace coil and, at a temperature of 360°C enters the upper chamber of the distillation column, where the oil vapors flash off assisted by the injection of superheated steam. These vapors and the vapors

from the lower section issue from the top of the distillation column into the base of the side-stream fractionating column. The pitch, which accumulates at the base of the upper section of the distillation column, is partly withdrawn as product and partly allowed to overflow into the lower section where it mixes with the crude tar before recycle through the furnace coils.

2. Input Materials

Crude coal tar

Steam

Alkali

3. Operating Parameters

Temperature - 360°C (680°F)

Pressure - not given

4. Utilities

Steam - quantities not given

 <u>Waste Streams</u> - Small quantities of hydrocarbons would be expected to escape to the air from distillation columns.

3.38 1/kg (405.3 gal/10 ³ 1b)	3.38 1/kg
2,570 mg/1g	
8.68 g/kg (1b/10 ³ 1b)	
833 mg/1	
2.81 g/kg (1b/10 ³ 1b)	
3,010 mg/1	
10.16 g/kg (1b/10 ³ 1b)	
	2,570 mg/lg 8.68 g/kg (1b/10 ³ 1b) 833 mg/l 2.81 g/kg (1b/10 ³ 1b) 3,010 mg/l

6. EPA Source Classification Code - None

7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 6 (1965), p. 434.

<u>Ibid</u>, Vol. 19 (1969), p. 653.

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corp., Park Ridge, N. J., 1974, p. 108-113.

INDUSTRIAL ORGANIC CHEMICALS

PROCESS NO. 77

Crude Sodium Carbolate

1. <u>Function</u> - Since only phenol, the cresols, and the lower-boiling xylenols are of commercial value, only those fractions obtained on the primary distillation of crude tar which distill between 185° and 240°C are treated for tar acid extraction. These oils (carbolic oil) are contacted with a slight excess of 8-10% caustic soda solution at the minimum temperature which will prevent crystallization of the naphthalene which is also usually a major component. Extraction may be carried out in stirred vessels, in packed or unpacked towers, in mixersettler units, or simply by mixing the two streams by a gear pump.

The other major source of cresols in the U.S. is from petroleum. The petroleum-based cresols are obtained from spent caustic liquor used to wash petroleum distillates.

2. Input Materials

Carbolic oil Petroleum distillates NaOH

н,0

- <u>Operating Parameters</u>
 Temperature not given
 Pressure atmospheric
- 4. Utilities not given
- 5. <u>Waste Streams</u> Caustic soda may be released in wastewater streams; small quantities of non-acidic hydrocarbons released to the air or wastewater streams.

6. EPA Source Classification Code - None

7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 6 (1965), p. 434.

INDUSTRIAL ORGANIC CHEMICALS

PROCESS NO. 78

Phenol, o-Cresol, m,p-Cresol, Xylenols and Phenolic Pitch

1. Function - Crude sodium carbolate is treated with live steam, sometimes after extraction with a phenol and base-free coal-tar naphtha or light creosote oil. The purified carbolate is then contacted countercurrently with a gas containing CO, in packed towers. The springing medium may be flue gas containing 10-14% CO₂ or a richer gas containing 30-35% CO_2 . Conditions in the springing towers are generally adjusted so that the aqueous phase leaving this stage contains 2-3% of the available alkali as bicarbonate. After springing, the two layers are separated by decantation and the tar acid layer, which contains about 20% water, is retreated with the CO_2 - containing gas to convert any residual carbonate to bicarbonate. Alternatively, the crude wet tar acids may be partially dehydrated by treating with concentrated sulfuric The partly dried tar acids are first distilled to yield water acid. containing some phenol (this fraction is recycled to the extraction stage), a main fraction of "once-run tar acids", and a residue of phenolic pitch. The main fraction is fractionated in two or three continuous columns to yield phenol, o-cresol, m,p-cresol mixture and xylenols.

The same procedure may be used in treating the crude sodium carbolate from petroleum sources or an additional oxidation step may be introduced to remove any mercaptans.

2. Input Materials

Crude sodium carbolate

CO2 H2SO4 Steam

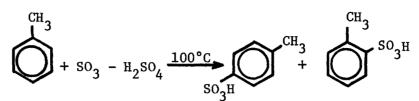
3. Operating Parameters

Temperature - not given

pressure - not given

- 4. Utilities not given
- 5. <u>Waste Streams</u> Caustic soda may be released in wastewater; small quantities of phenolic bodies released to the air from distillation columns.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 6 (1965), p. 434. Toluenesulfonic Acids



1. <u>Function</u> - The sulfonation of toluene produces all three isomers (o, m and p). The para isomer is formed as the temperature of the reaction is increased. Sulfonating with oleum at low temperature produces a mixture of ortho and para sulfonic acids, the ortho isomer predominating. These isomers are separated either by converting to the sulfonyl chloride derivative (ortho-viscous oil; para-solid) or by crystallization.

The pure meta isomer is produced by sulfonating p-toluidine and diazotization of the product. The predominately para-isomer is made by raising the reaction temperature to 100°C.

- 2. <u>Input Materials</u> Basis: 1 kg of toluenesulfonic acid Toluene - 0.53 kg Oleum - >0.46 kg.
- 3. Operating Parameters

Temperature:	100°C (212°F)
Pressure:	100 KPa (1 atm)
Catalyst:	None

4. Utilities - Not given

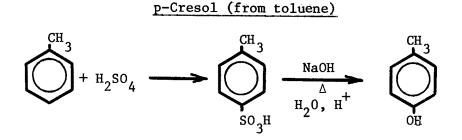
5. <u>Waste streams</u> - No specific information was available. The usual sulfonation process is enclosed to prevent the emission of acid mists. Air pollution by mists can occur when storage vessels are loaded. The distillation may result in toluene vapor emissions.

There will be a wastewater stream containing neutralized acid, probably as sodium sulfate. Some organic material will also be discharged into the waste stream (toluene and toluene sulfonic acid). The wastewater will arise from three sources: (1) air pollution control devices (scrubber); (2) condensate from the distillation; (3) diluted acid from the reactor.

- 6. EPA Source Classification Code None
- 7. References

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Monsanto Research Corporation, Dayton, Ohio, Technomic Publishing, Co., Inc., Westport, Conn., 1975, p. 330.

Brooks, B. T., S. K. Kurtz and L. S. Schmerling, <u>"The Chemistry</u> of Petroleum Hydrocarbons," Vol. III, Reinhold Publishing Corp., New York, N.Y., 1955.



- 1. <u>Function</u> Only a small tonnage of p-cresol is produced synthetically by sulfonation of toluene. The sulfonation product is predominantly p-toluene sulfonic acid with a small amount of the o-isomer. Fusion with caustic soda and caustic potash at 330-360°C yields the alkali salts of the cresols from which they are recovered by neutralization and pure p-cresol is recovered by fractionation.
- 2. Input Materials

Toluene

Sulfuric acid

NaOH or Na₂CO₃

Water

3. Operating Parameters

Not given

4. Utilities

Not given

5. <u>Waste Streams</u> - Small quantities of sulfuric acid and cresol would be expected to escape in waste waters and air.

Flow 10.8 1/kg (1291 gal/10³ 1b) COD 23,800 mg/1 256 g/kg (1b/10³ 1b) BOD₅ 11,400 mg/1 123 g/kg (1b/10³ 1b) TOC 5,020 mg/1 54 g/kg (1b/10³ 1b)

6. EPA Source Classification Code - None

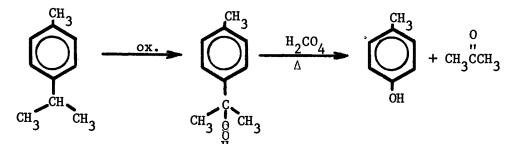
7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 6 (1965), p. 434.

Ibid, Supplement Volume (1971), p. 271

U.S. Patent 2,225,564 (Dec. 17, 1940).

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corp., Park Ridge, N.J., 1974, p. 113-116. p-Cresol (from p-cymene)



- 1. <u>Function</u> A small amount of p-cr^Hesol is also produced synthetically by oxidation of p-cymene. The general tight supply of naval stores (from which p-cymene is isolated) and the recent high cost does not make this an economical starting material for the synthesis of p-cresol. The Hercules Powder Co. has alkylated toluene with propylene in the presence of AlCl₃ to give a mixture of cymenes rich in the mand p- derivatives. This mixture is treated with an oxygen-containing gas at 25-35°C in the presence of aqueous alkali and the resultant mixture of hydroperoxides is decomposed into cresols and acetone by treatment, in an alcohol solvent, with sulfuric acid at 65-85°C.
- 2. Input Materials

p-Cymene 0₂ Alkali H₂0 Methanol 3. <u>Operating Parameters</u>

> Hydroperoxidation - 25-35°C (77-95°F) Decomposition - 65-85°C (149-185°F)

Pressure - Atmospheric

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste water contains sodium hydroxide, p-cresol and acetone. The air vents may emit p-cymene and acetone.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

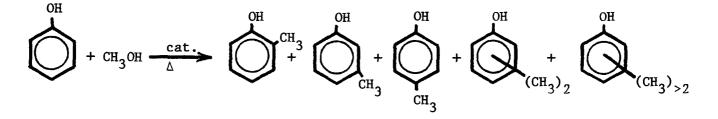
Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 6 (1965), p. 434.

Ibid., Supplement Volume (1971), p. 271.

Brit. Patent, 754,872 (Aug. 15, 1956).

p-Cresol, m-Cresol, o-Cresol, Xylenols

and Higher Methylated Phenols



1. <u>Function</u> - Vapor-phase methylation of phenol with methanol over an aluminum catalyst yields, according to the conditions, different methylated phenol products. Careful control of the temperature and selection of different acidity silica - alumina catalysts permits some selectivity in methylation products. The ratio of mono- to poly-methylated products can be controlled by the ratio of methanol to phenol. The methyl group needed for the methylation of phenol may be derived from many different sources, e.g., methyl halides, methyl ethers, methyl amine. Co-catalysts may also be used to increase the selectivity in methylation. In 1965 Koppers Company started the first synthetic cresol plant which was soon followed by Consolidated Coal Co.

The pure cresols may be separated in a continuous fractional distillation. The similarity in the b.p. of the m- and o- isomers precludes their separation by this means. Azeotropic distillation with benzyl alcohol, selective solvent extraction or solid complex formation between the reagent and one of the cresol isomers are some of the techniques used in their separation.

2. Input Materials

Pheno1

Methano1

3. Operating Parameters

Alkylation - Temperature from 175°C to 375°C depending upon the products desired.

4. <u>Utilities</u>

Not given

- 5. <u>Waste Streams</u> Small quantities of phenol and methanol would be expected to escape in waste water as well as air.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, Vol. 6 (1965), p. 434.

Ibid., Supplement Volume (1971) p. 271.

British Patent 602,257 (May 24, 1948).

SECTION IV ETHYLENE

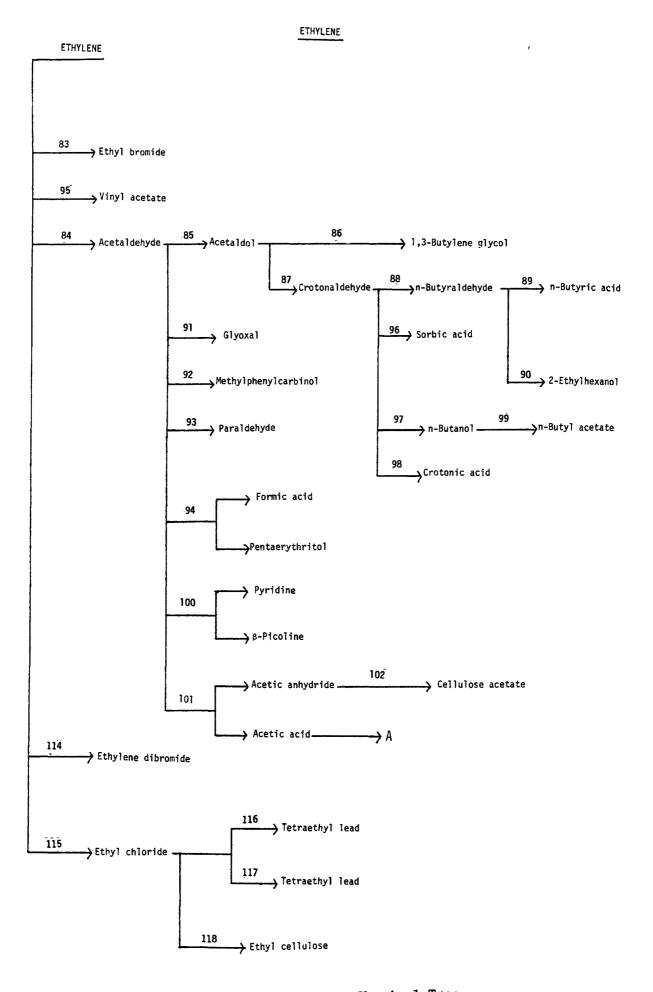


Figure 7. Ethylene Section Chemical Tree

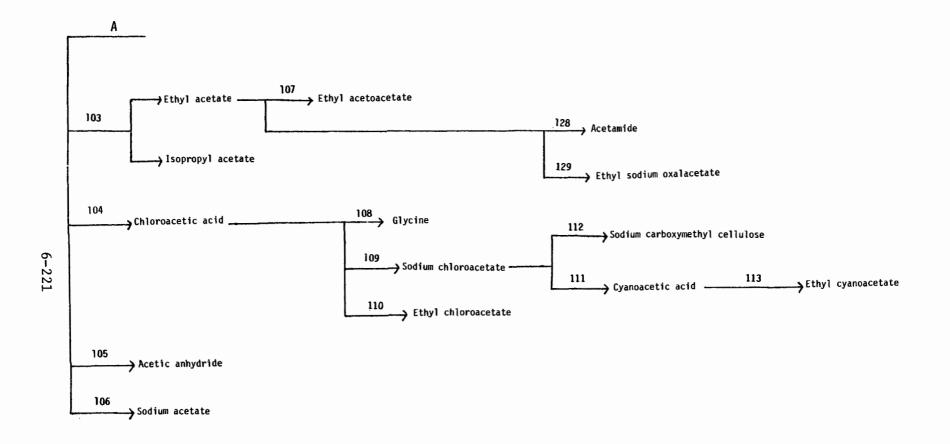


Figure 7. Ethylene Section Chemical Tree (Cont.)

ETHYLENE

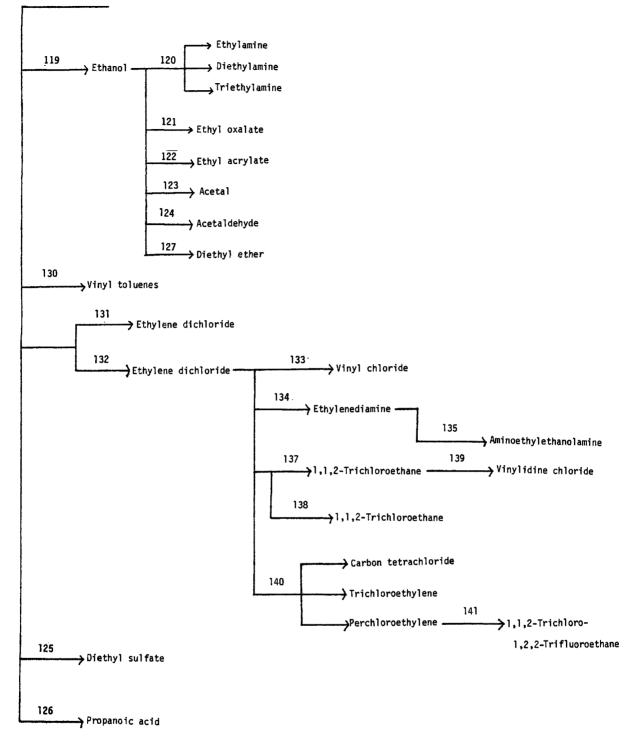


Figure 7. Ethylene Section Chemical Tree (Cont.)

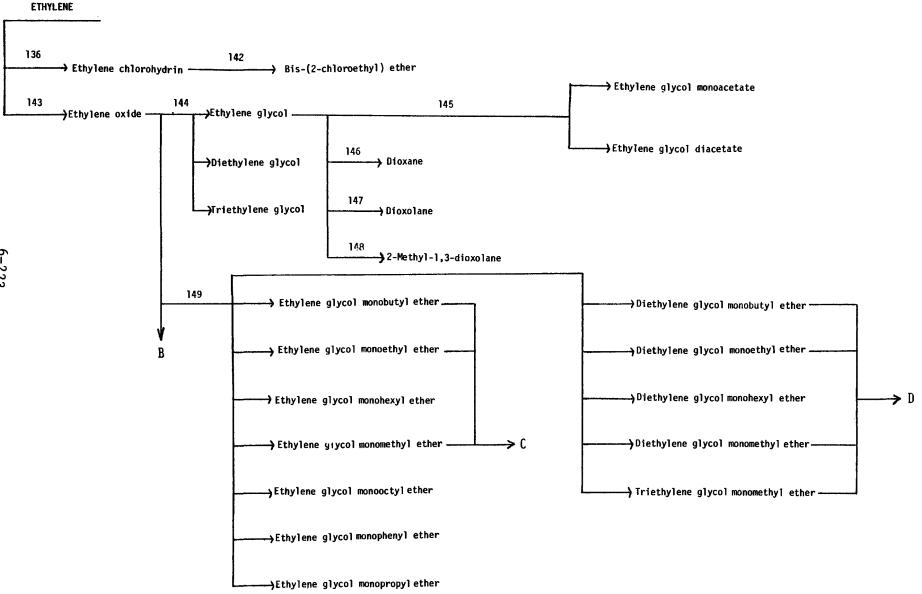


Figure 7. Ethylene Section Chemical Tree (Cont.)

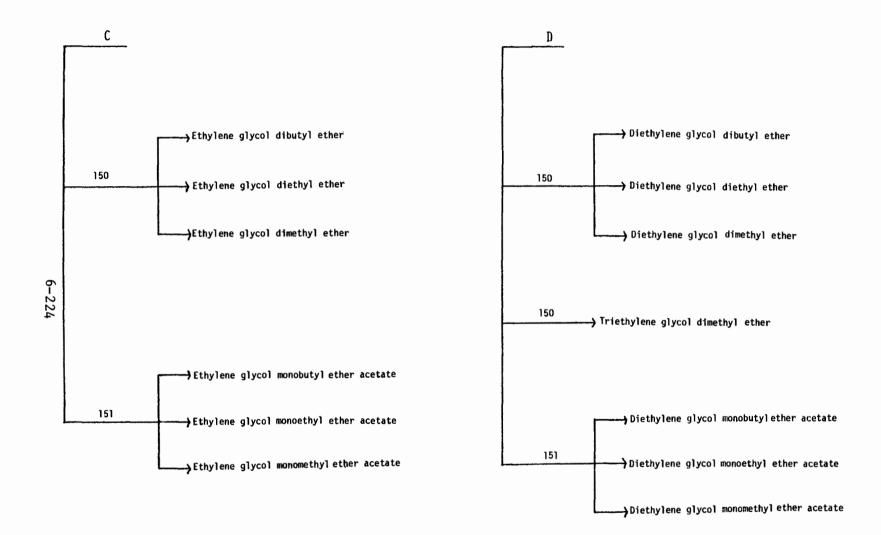


Figure 7. Ethylene Section Chemical Tree (Cont.)

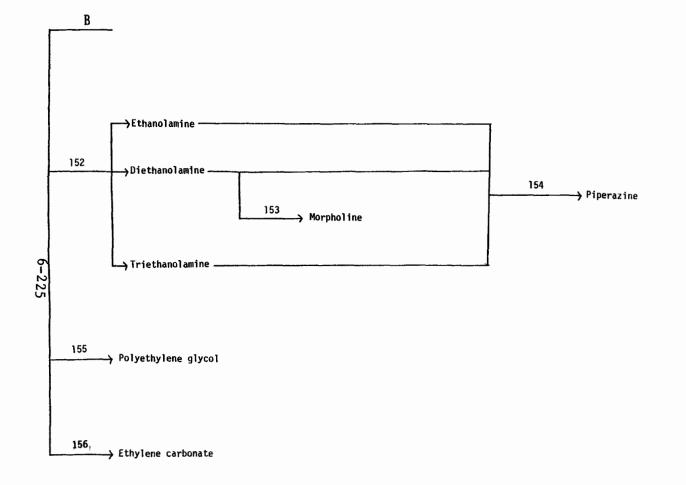


Figure 7. Ethylene Section Chemical Tree (Cont.)

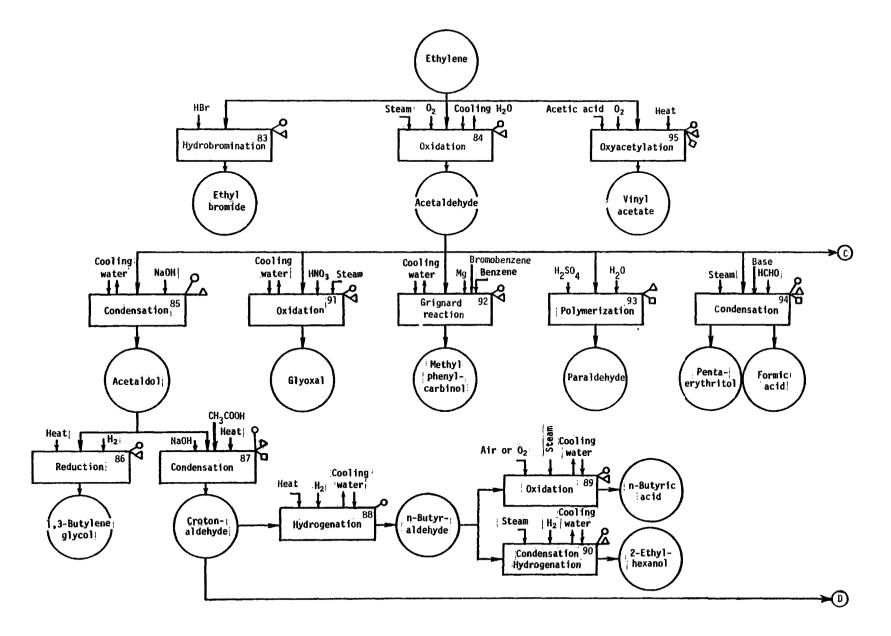


Figure 8. Ethylene Section Process Flow Sheet

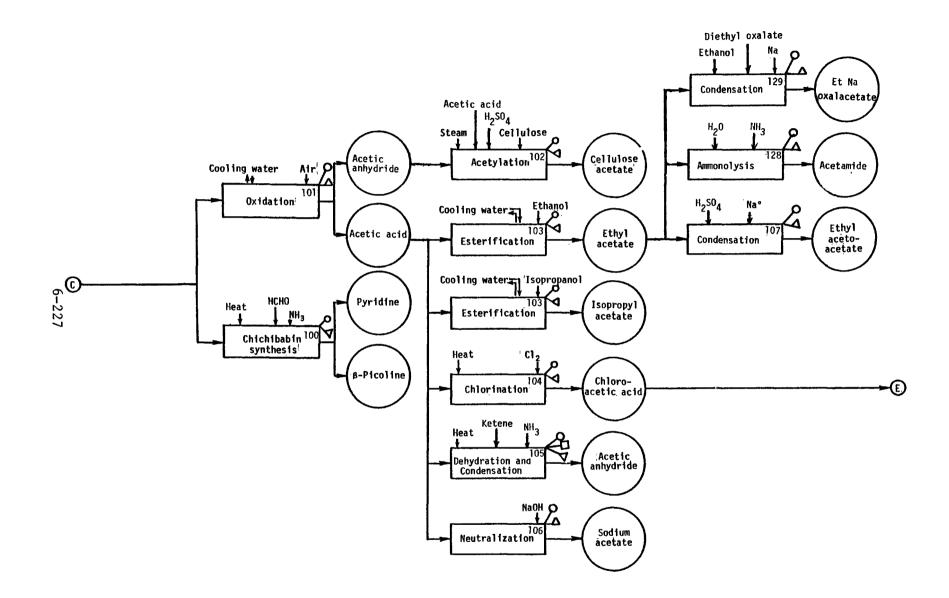


Figure 8. Ethylene Section Process Flow Sheet (Cont.)

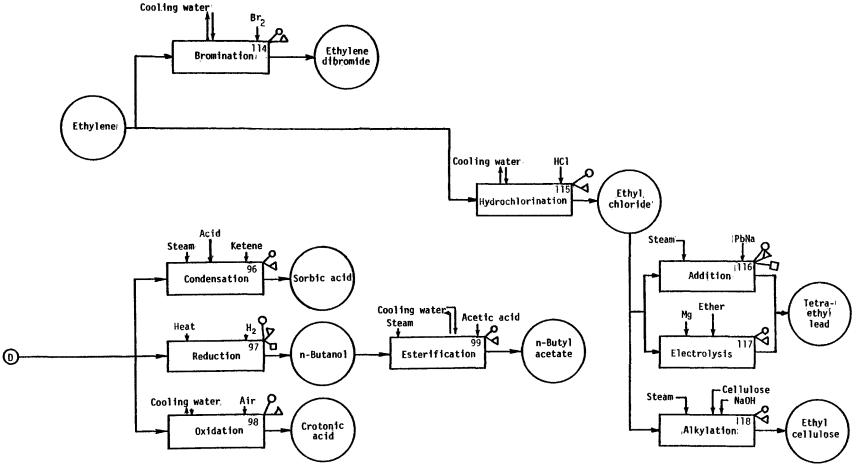


Figure 8. Ethylene Section Process Flow Sheet (Cont.)

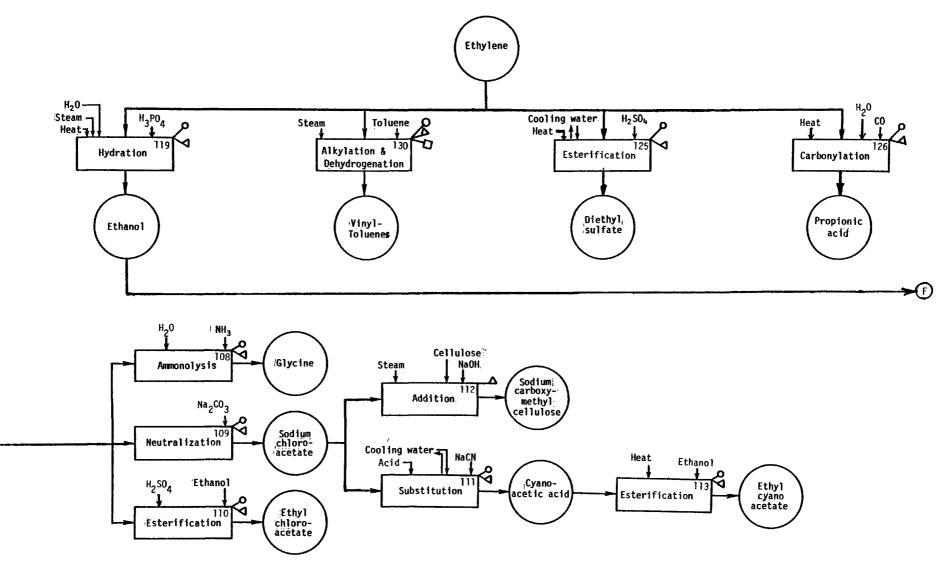


Figure 8. Ethylene Section Process Flow Sheet (Cont.)

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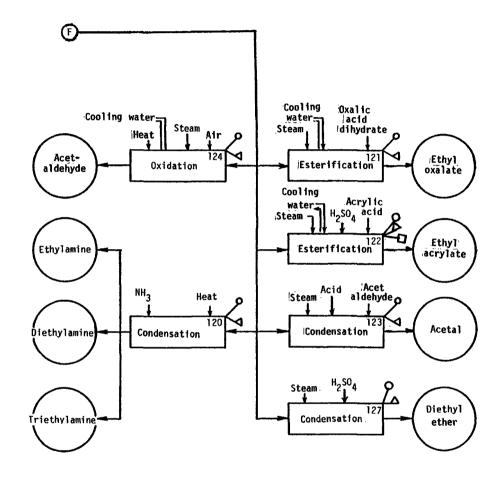


Figure 8. Ethylene Section Process Flow Sheet (Cont.)

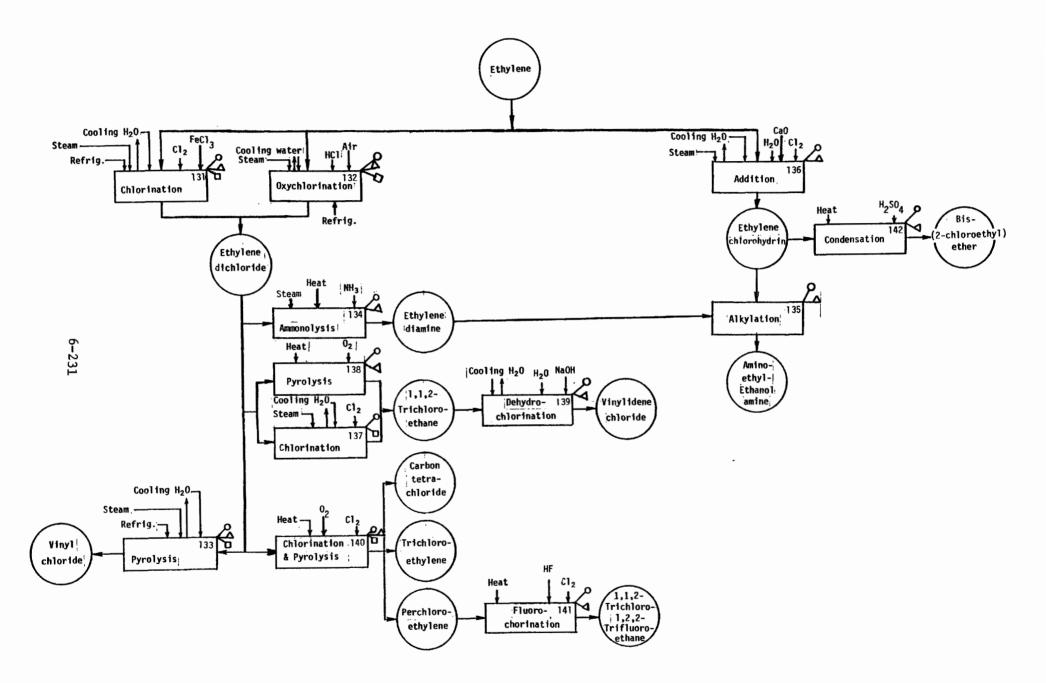


Figure 8. Ethylene Section Process Flow Sheet (Cont.)

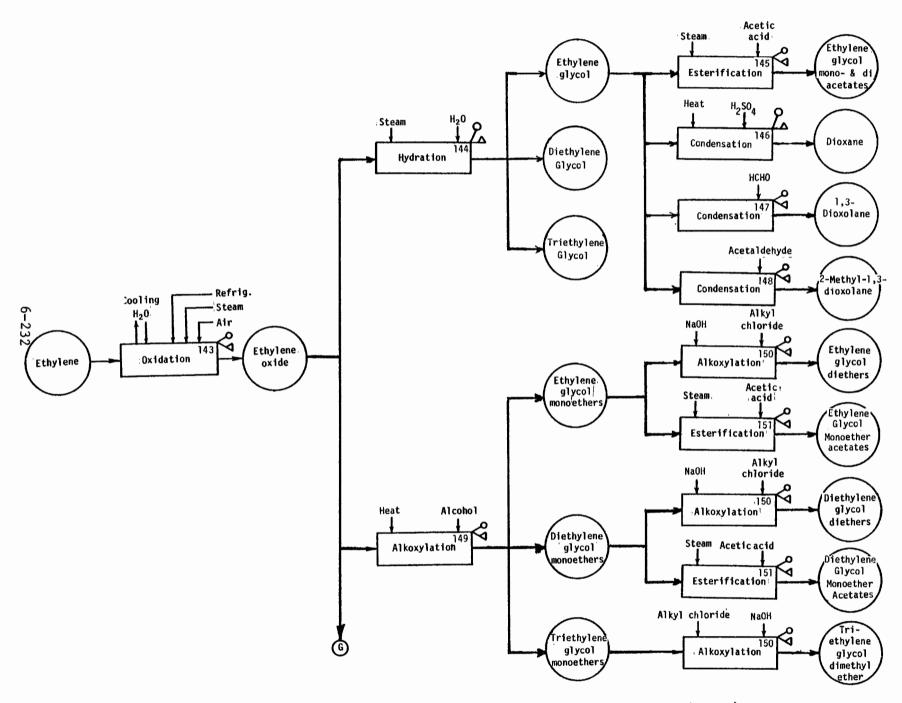


Figure 8. Ethylene Section Process Flow Sheet (Cont.)

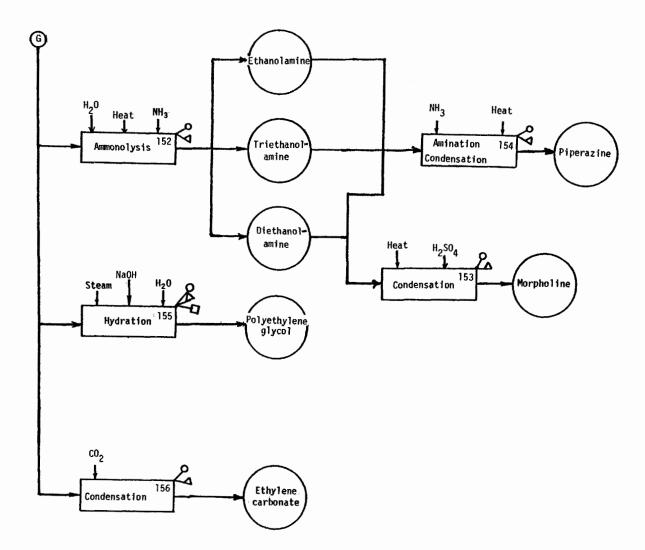


Figure 8. Ethylene Section Process Flow Sheet (Cont.)

Ethyl Bromide (from ethylene)

 $CH_2 = CH_2 + HBr \longrightarrow CH_3 CH_2 Br$

- <u>Function</u> In recent years, ethyl bromide has been produced by the vapor-phase reaction of high-purity ethylene and hydrogen bromide. The reaction is catalyzed by gamma radiation from cobalt-60. It may also be prepared from ethanol and HBr.
- 2. Input Materials

Ethylene

Hydrogen bromide

3. Operating Parameters

Temperature: Not given Pressure: Not given Catalyst: Cobalt-60, as a source of gamma radiation

4. Utilities

Not given

- 5. <u>Waste Streams</u> Information on this process was too limited to evaluated its potential pollutant sources, but HBr and ethylene may leak out of the system.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 774.

Shreve, R. N., <u>Chemical Process Industries</u>, 3rd Ed., McGraw-Hill Book Co., New York, N.Y., 1967, p. 793.

References (continued)

Hahn A. V., <u>The Petrochemical Industry:</u> <u>Markets and Economics</u>, McGraw-Hill Book Co., New York, N.Y., 1970 p. 316.

Acetaldehyde (Wacker process)

 $C_{2}H_{4} + 1/2 \quad 0_{2} \longrightarrow CH_{3}CHO + heat (244 kJ/mole)$

 <u>Function</u> - The Wacker process employs an aqueous catalyst solution of palladium chloride, promoted by copper chloride.

The catalyst acts as the oxygen carrier and causes selective conversion of ethylene to acetaldehyde. The reaction steps essentially are:

Reaction: $C_2H_4 + 2CuCl_2 + H_20 \xrightarrow{PdCl_2} CH_3CH0 + 2HC1 + 2CuCl$ Regeneration: $2CuCl + 2HC1 + 1/20_2 \longrightarrow 2CuCl_2 + H_20$

There are two basic process variations, depending upon such factors as oxygen cost, utilities prices, and available ethylene purity. In the single-stage process, pure oxygen is employed as the oxidant. The reactor effluent is condensed and water-scrubbed. Unreacted gas is recycled into the reactor. By-products and water are separated from the acetaldehyde product by distillation. Both the reaction and regeneration are effected at the same time.

In the two-stage process, the oxidant is air. The reaction is carried out with catalyst solution and ethylene in one reactor, and the regeneration is carried out with air in a separate reactor. Lower purity ethylene can be used with this version of the process. However, this process forms more by-products and requires high operating pressures.

The production of acetaldehyde by vapor phase oxidation of propane rich LPG is considered obsolete.

2. Input Materials (per metric tonne acetaldehyde)

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		Single-stage	Two-stage
	Ethylene 99.8 vol. %, kg	670	670*
	Oxygen, Nm ³	275	-
	Catalyst: PdCl ₂ , g	0.9	0.9
	$CuCl_2 + 2H_20$, g	150	150
	HCl (100%) used as 30% a solvent, kg	queous 4	15
3.	Operating Parameters		
	Temperature, °C(°F)	130(266)	-
	Pressure, kPa (atm)	294 (2.90)	784-883 (7.74-8.71)
4.	<u>Utilities</u>		(/./+-0./1)
	Cooling water (25°C), m ³	300	200
	Cooling water (12°C), m ³	-	12
	Process water, m^3	6	-
	Deionized water, m^3	3	-
	Steam, metric ton	1.6	1.2
	Electric power, MJ (kWh)	754 (210)	300**
	Credit for nitrogen (pro gas), Nm ³ (637 kPa)	tection -	900
5.	<u>Waste Streams</u> - Purifica	tion section - acetaldehyde	scrubber vent
	to flare (air).		
	Ethane:	2.2 kg/Mg acetaldehyde	
	Ethylene:	27.4 kg/Mg acetaldehyde	
	Acetaldehyde:	trace	
	Methane:	trace	
	Methyl chloride:	trace	

^{*} Ethylene of lower purity results in slightly higher consumption ** Including air compression

.

Purification section - acetaldehyde stripper vent to flare (air)Methyl chloride:8.65 kg/Mg acetaldehydeAcetaldehyde:trace

A typical Wacker process discharges about 4.4 m³ (1,200 gallons) of waste per ton of product. The chlorinated aldehydes are the principal contaminants in the waste streams which have a COD of approximately 10 cg/m³ (10,000 mg/1).

The two-stage process yields relatively small amounts of a rather concentrated waste water which must be pretreated before normal biodegradation. The single-stage yields considerably more of a more dilute waste water suitable for biodegradation.

6. EPA source classification code - None

7. References

Morse, P. L., "Acetaldehyde," Report No. 24, Stanford Research Institute, Menlo Park, California, April 1967.

Gloyna, E. F., and Ford, D. L., "The Characteristics and Pollutional Problems Associated with Petrochemical Wastes," for FWPCA, Contract No. 14-12-461, February 1970.

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 1," "Chemical Engineering," January 21, 1974, p. 127.

"1975 Petrochemical Handbook," "Hydrocarbon Processing," <u>54</u>, November 1975, p. 100.

Jira, R., et al., "Hydrocarbon Processing," 55, March 1976, p. 99.

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corporation, Park Ridge, N.J., 1974, p. 50,52.

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N.Y., 1975, p. 1,2.

Acetaldol,

- Function Acetaldol is made from acetaldehyde via liquid-phase condensation at 10-25°C in the presence of dilute alkali. This process results in a 95% yield with about a 60% conversion.
- 2. Input Material

Acetaldehyde: 1.05 kg/kg acetaldol, 107 kg/hr $H_2^{0: 20 \text{ kg/hr}}$ NaOH (20 g/l): 16 l/hr

3. Operating Parameters

Temperature: 10-25°C (50-77°F) Pressure: not given Catalyst: 10% NaOH

pH: 4-5 (by HCO_2H)

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Wastewater streams from acetaldehyde strippers may contain acetaldehyde, acetaldol, and dilute sodium hydroxide.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 1 (1963), p. 82. Ibid, Vol. 6 (1964), p. 446

British Patent 630,904 (October 24, 1949).

INDUSTRIAL ORGANIC CHEMICALS

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PROCESS NO. 86
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1,3-Butylene Glycol (reduction of acetaldol)

 $\begin{array}{c} \text{CH}_{3}\text{,}\text{CHCH}_{2}\text{CHO} & \xrightarrow{\text{H}_{2}} & \text{CH}_{3}\text{,}\text{CHCH}_{2}\text{CH}_{2}\text{OH} \\ \text{OH} & \text{OH} \end{array}$

 <u>Function</u> - 1,3-Butylene glycol is produced by the catalytic hydrogenation of acetaldol. The hydrogenation can be effected with copper, platinum oxide, or several other catalysts, but preferably with Raney nickel. Pressures and temperatures of 4.83 MPa and 65 -120°C are used.

Low-boiling materials are stripped off under reduced pressure from the hydrogenation product. The residue is then filtered to remove precipitated salts and catalyst, and is redistilled at low pressure to give pure 1,3-butylene glycol.

- 2. <u>Input Materials</u> Basis 1.68 kg 1,3-butylene glycol Acetaldol (70%, 30% H₂0): 2.67 kg Hydrogen: 2.07 MPa (20.4 atm) Ni catalyst: 0.500 kg
- 3. Operating Parameters

Temperature: 65 - 120°C (149-248°F) Pressure: 4.83 MPa (47.7 atm) Catalyst: Raney nickel, copper, platinum oxide Reaction Time: 0.5 - 2 hrs

- 4. Utilities not given
- 5. <u>Waste Streams</u> No specific information was available. Waste gas from the strippers may contain quantities of ethanol, n-butanol,

and other by-products, including 2,4-dimethyl-1,3-dioxane. Wastewater streams from filtering operations probably contain various salts and traces of catalyst. Heavy ends from distillation columns going to waste streams are mainly dibutylene glycols and their butyl ethers. Traces of acetaldehyde, acetaldol, and 1,3-butylene glycol are probably present in all waste streams.

6. EPA Source Classification Code - None

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 10 (1966), p. 664. Hancock, C. K., and Henson, D. D., "Industrial and Engineering Chemistry," Vol. 45 (1953), p. 629-632.

Crotonaldehyde

2 CH₃CHO $\xrightarrow{10\% \text{ NaOH}}$ CH₃CHOHCH₂CHO $\xrightarrow{\text{H}_30^{\bigoplus}}$ CH₃CH=CHCHO

- <u>Function</u> Crotonaldehyde is most commonly made by the aldol condensation of acetaldehyde followed by dehydration. After the initial condensation has proceeded to 60% of completion, the acetaldol is treated with acetic or phosphoric acid and passed through a dehydration column at 95°C. Unreacted acetaldehyde is recovered and crotonaldehyde is separated overhead in almost quantitative yield.
- 2. Input Materials

Acetaldol - 1.625 kg/kg crotonaldehyde

- 3. <u>Operating Parameters</u> Temperature - 10-25°C (50-77°F) Pressure - not given Catalyst - 10% NaOH
- 4. Utilities not given
- 5. <u>Waste Streams</u> There may be a wastewater stream. The likely pollutants are acetaldehyde, acetaldol, crotonaldehyde, and by-products. Heavy ends from distillation columns are usually incinerated.
- 6. EPA Source Classification Code None
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 2", "Chemical Engineering," February 18, 1974, p. 126.

7. References

Hedley, W. H., et. al., <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Technomic Publishing Co., 1975.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 6 (1965), p. 446.

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 365.

Faith, W. L., et. al., <u>Industrial Chemicals</u>, 3rd Ed., John Wiley & Sons, New York, N.Y., 1965, p. 300, 301.

Waddams, A. L., <u>Chemicals From Petroleum</u>, 3rd Ed., John Murray Ltd., London, England, 1973, p. 79. n-Butyraldehyde (hydrogenation of crotonaldehyde)

 $CH_3CH=CHCHO + H_2 \longrightarrow CH_3CH_2CH_2CHO$

 Function - In the production of n-butyraldehyde, crotonaldehyde is vaporized and passed through a converter with hydrogen. The converter tubes are packed with an activated nickel catalyst on an asbestos carrier.

Steam on the outside of the tubes is used to bring them to the reaction temperature, and is later replaced by water to carry heat away from the exothermic reaction.

The exit gases from the converter pass through condensers, and the hydrogen, which may be several times the theoretical amount, is recycled. The crude butyraldehyde is purified by fractionation.

2. Input Materials

Crotonaldehyde

Hydrogen

3. Operating Parameters

Temperature - 220-260°C (428-500°F)

Pressure - 207 kPa (2,04 atm)

Catalyst - Activated nickel supported on asbestos or copper chromite Space velocity - 400/hr

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Some crotonaldehyde and n-butyraldehyde may escape to the atmosphere during processing and purification. No specific information was available, however.

- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 870,871.

U. S. Patent 2,825,743 (March 4, 1958).

Sittig, M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition, Noyes Development Corp., Park Ridge, N.J., 1969, p. 132.

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n-Butyric Acid (oxidation of n-butyraldehyde)

 $CH_3CH_2CH_2CHO + 1/2 O_2 \longrightarrow CH_3CH_2CH_2COOH$

 <u>Function</u> - Some butyric acid is prepared commercially by the oxidation of n-butyraldehyde. In this process, air or oxygen is passed into n-butyraldehyde in the presence of a catalyst such as manganese butyrate or a cobalt salt.

Yields of about 90% are possible over a wide range of temperatures.

2. Input Materials

n-Butyraldehyde - 0.91 kg/kg butyric acid

Air or oxygen

3. Operating Parameters

Temperature: 30-50°C (86-122°F)

Pressure: not given

Catalyst: 0.5% manganese butyrate

Cobalt salts

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Although no information was available, some n-butyraldehyde and butyric acid are probably present in the reactor off-gas. Process slops may also be a source of these pollutants, as well as reaction by-products.
- 6. EPA Source Classification Code None

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 880.

<u>Chemical Technology</u>, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 426.

Goldstein, R. F., <u>The Petroleum Chemicals Industry</u>, 2nd Edition, John Wiley and Sons, New York, N.Y., 1958, p. 331.

2-Ethylhexanol (from n-butyraldehyde)

$$2CH_{3}CH_{2}CH_{2}CH_{2}CHO \longrightarrow CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CHO + H_{2}O$$

$$\downarrow^{H_{2}}CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}OH$$

$$CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}OH$$

1. Function - 2-Ethylhexanol is produced by the aldol condensation of n-butyraldehyde, which can be derived from propylene via the oxoprocess or from acetaldehyde via ethylene. The oxo process is the preferred route. The C_{g} aldehyde formed is then hydrogenated to 2-ethy1hexano1.

In the aldox process, dimerization is allowed to proceed without the separation of the C_{L} aldehydes. The C_{L} and C_{R} aldehydes from the oxo step are hydrogenated at a temperature of approximately 150°C and a pressure of 180 atm (18 MPa) in the presence of a nickel catalyst. Gas-liquid separation yields 2-ethylhexanol with isobutyl alcohol as a byproduct.

2. Input Materials - Basis: 1 metric tone 2-ethylhexanol

n-Butyraldehyde - 1300 kg Hydrogen - 360 m^3 Nickel catalyst - 1 kg

3. Operating Parameters

Aldolization:	Hydrogenation:	
Temperature - 60-130°C	(140-266°F)	Temperature - 150° (302°F)
Pressure - 0.3-1.0 MPa	(2.96-9.87 atm)	Pressure - 18 MPa (180 atm)

- <u>Utilities</u> 0.72 kg/sec capacity Cooling water - 32 dm³/sec Steam - 0.45 kg/sec at 1.14 MPa Power - 447 KW capacity
- 5. <u>Waste Streams</u> Light hydrocarbons from hydrogenation 113.5 kg/Mg. High boiling oxygenated compounds from the condensation of aldehydes and alcohols. Butyraldehyde 58.5 kg/Mg product.
- 6. EPA Source Classification Code None
- 7. References

Hedley, W. H., et al., "Potential Pollutants from Petrochemical Processes," Technomic Publishing Co., 1975.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 14 (1963), p. 373-389.

Waddams, A.L., <u>Chemicals From Petroleum</u> 3rd Edition, John Wiley & Sons, (1973) p. 205.

Lowenheim, F. A. and Moran, M. K., <u>"Industrial Chemicals</u>," 4th Edition, John Wiley & Sons, New York, N.Y., (1975), p. 413-417. Glyoxal (oxidation of acetaldehyde)

сн₃сно _____ сносно

- <u>Function</u> Recently, glyoxal has been produced by the nitric acid oxidation of acetaldehyde in an autoclave. Previously the catalytic vapor-phase oxidation of ethylene glycol had been the standard commercial process. The product is washed with NaHSO₃ and precipitated from EtOH/H₂O.
- 2. <u>Input Materials</u> Basis 0.70 kg glyoxal Acetaldehyde: 0.783 kg SeO₂ (or HNO₃): 28 g
- 3. <u>Operating Parameters</u> Temperature: 80°C (176°F) Reaction Time: 2 hrs
- 4. Utilities not given
- 5. <u>Waste Streams</u> The information available on current production techniques was not sufficient to warrant a discussion of possible pollutant sources. As in all oxidation processes, reactants, products, and by-products may be emitted as a result of process slops.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 1 (1963), p. 80. <u>Ibid</u>, Vol. 10 (1966), p. 646.

Riley, H. L., et al., <u>J. Chem. Soc.</u>, <u>1932</u>, p. 1875-1883.

Methyl Phenylcarbinol (from acetaldehyde)

 $C_6H_5Br + Mg \longrightarrow C_6H_5MgBr$

 $C_6H_5MgBr + CH_3CHO \longrightarrow C_6H_5CH(CH_3)OMgBr$ $C_6H_5CH(CH_3)OMgBr + H_2O \longrightarrow C_6H_5CH(CH_3)OH + MgOH$

- <u>Function</u> One method of synthesizing methylphenylcarbinol involves the addition of acetaldehyde to a Grignard reagent prepared from bromobenzene.
- 2. Input Materials

Acetaldehyde

Bromobenzene

Ether (solvent)

Magnesium

Water

3. Operating Parameters

Temperature: reflux temperature of solvent

Pressure: 101 kPa (1 atm)

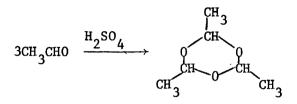
- 4. Utilities Not given
- <u>Waste Streams</u> Air ether and bromobenzene vapors.
 Water magnesium salts solid - unreacted Mg turnings and tarry materials.
- 6. EPA Source Classification Code None

7. References

Horning, E. C., <u>Organic Synthesis</u>, John Wiley and Sons, New York, N.Y., Collective Vol. III (1955), p. 200-201.

INDUSTRIAL ORGANIC CHEMICALS

<u>Paraldehyde</u>



- 1. <u>Function</u> In the presence of sulfuric acid, acetaldehyde rapidly polymerizes to paraldehyde, the trimer. The crude trimer is washed with water to remove monomer and the acid catalyst, and dried. Distillation separates the pure paraldehyde. In the absence of acid catalyst the trimer suffers no depolymerization on distillation or storage. Acetaldehyde can be regenerated readily by heating gently and distilling the paraldehyde in presence of acid catalyst.
- 2. Input Materials

Acetaldehyde - 1.05 kg/kg paraldehyde

2. Operating Parameters

Temperature (distillation) - 124°C (255°F)

Pressure - 101 kPa (1 atm)

Catalyst - H₂SO₄

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste water probably contains traces of acetaldehyde and sulfuric acid.
- 6. EPA Source Classification Code None

7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 81.

K. C. Frisch, <u>High Polymers</u>, Vol. XXVI, "Cyclic Monomers," John Wiley & Sons, 1972, p. 124.

Brandrup, J. and Goodman, M. <u>Macromolecular Synthesis</u>, Vol. 3, John Wiley & Sons, New York, N.Y., 1967, p. 74.

Pentaerythritol

$$CH_{3}CHO + 2HCHO \xrightarrow{OH} CH_{2}(CH_{2}OH)CHO + HCHO$$

$$CH_{2}(CH_{2}OH)CHO + 2HCHO \xrightarrow{OH} CH(CH_{2}OH)_{2}CHO + HCHO$$

$$CH(CH_{2}OH)_{2}CHO + 2HCHO \xrightarrow{OH} C(CH_{2}OH)_{3}CHO + HCHO$$

$$C(CH_{2}OH)_{3}CHO + HCHO + OH \xrightarrow{O} C(CH_{2}OH)_{4} + HCOO$$

1. <u>Function</u> - Pentaerythritol is made by reacting formaldehyde and acetaldehyde in molar ratios ranging from 4:1 to 10:1. The reaction is carried out in the presence of lime or caustic soda at near ambient temperatures and pressures.

The reaction sequence involves three identical aldol condensations in which the alkali acts as a catalyst, followed by a cross-Canizzaro reaction in which the condensation takes place.

Sodium carbonate is added to the reaction mixture to precipitate calcium ions in solution. The reaction mixture, which contains pentaerythritol, polypentaerythritols, sodium formate, and suspended calcium carbonate, is then filtered and passed through ion exchange and fractional distillation columns to obtain the final product. The yield is high, with about 88% of the product occurring as pentaerythritol, 10% as dipentaerythritol, and most of the remainder as tripentaerithritol. The sodium formate is commonly treated with sulfuric acid to give formic acid as a by-product.

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- 2. <u>Input Materials</u> Basis 1 metric ton pentaerythritol Acetaldehyde - 383 kg (844 lbs) Formaldehyde - 3175 kg (7000 lbs) Calcium hydroxide or sodium hydroxide 1050 kg (2315 lbs) Sodium carbonate Acid (formic) - 600 kg (1323 lbs)
- 3. Operating Parameters

Temperature: 15-50°C (59-122°F) Pressure: 101 kPa (1 atm) Catalyst: Ca(OH)₂ or NaOH Reaction Time: 3.5 hrs

4. <u>Utilities</u>

Not given

5. <u>Waste Streams</u>

Calcium carbonate precipitator (solid)

Calcium carbonate

Triple effect evaporator and vacuum crystallizer (air)

Air streams may contain unreacted acetaldehyde and formaldehyde,

as well as some organic, side products (methanol and ethanol).

Vacuum crystallizer (water)

Water streams contain sodium formate which is usually recovered as formic acid. Inorganic sodium salts are then the final waste product.

- 6. <u>EPA Source Classification Code</u> None
- 7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 7," "Chemical Engineering," June 24, 1974, p. 155, 156.

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7. <u>References</u> (continued)

Hedley, W.H., et a., <u>Potential Pollutants from Petrochemical</u> Processes, Technomic Publishing Co., 1975.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 590, 591.

U.S. Patent 2,612,526 (September 30, 1952).

Sittig, M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition, Noyes Development Corp., Park Ridge, N.J., 1969, p. 508.

Lowenheim, F. A. and Moran, M.K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 598, 599. Vinyl Acetate (vapor-phase reaction of ethylene)

 $CH_2 = CH_2 + 1/2 0_2 + CH_3 COOH \longrightarrow CH_3 COOCH = CH_2 + H_2 0$

 <u>Function</u> - The most common route to vinyl acetate involves a vaporphase oxyacetylation using ethylene, acetic acid, and oxygen. The reaction takes place at 175-200°C and 485-965 kPa (70-140 psi) over a supported palladium catalyst. The conversion per pass is about 10% ethylene, 20% acetic acids, and 60% oxygen.

The reaction mixture is partly condensed after leaving the reactor and separated into liquid and gas phase. The gases are recycled via scrubbers in which vinyl acetate and carbon dioxide are removed. The liquid condensate is fed to the distillation train where light ends, mainly acetaldehyde, water, and polymers are removed from the purified vinyl acetate. Acetic acid is recycled to the reactor.

The overall yield is 91% vinyl acetate, 8% carbon dioxide, and 1% by-product, with better than 99% recovery of ethylene and acetic acid. The liquid-phase route to vinyl acetate from ethylene has not been a success.

2. Input Materials

Ethylene - 0.36 kg/kg vinyl acetate Acetic acid - 0.77 kg/kg vinyl acetate Oxygen - 0.20 kg/kg vinyl acetate

3. Operating Parameters

Temperature - 175-200°C (347-392°F)

Pressure - 70-140 psi - 483-965 kPa (4.8-9.5 atm)

Catalyst - supported palladium catalyst with small amount of potassium acetate (485-965 kPa)

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste gases from the scrubbers may contain traces of ethylene, acetic acid, vinyl acetate, acetaldehyde, and other by-product gases. Heavy ends from distillation columns include polymers and mixed aldehydes.
- 6. EPA Source Classification Code None
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 9," "Chemical Engineering," August 5, 1974, p. 98.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 862-867.

Waddams, A. L., <u>Chemicals from Petroleum</u>, 3rd Edition, John Wiley and Sons, New York, N.Y., 1973, p. 111.

PROCESS NO. 96

Sorbic Acid (from crotonaldehyde)

$$CH_{3}CH=CHCHO + CH_{2}=C=0 \longrightarrow H-[OCHCH_{2}CO]_{n}H \xrightarrow{H^{\oplus}} CH_{3}CH=CH-CH=CH-CO_{2}H$$

$$CH$$

$$CH$$

$$CH$$

$$CH$$

$$CH$$

$$CH$$

$$CH$$

 <u>Function</u> - Crotonaldehyde and ketene react in the presence of a catalyst to form a polyester of 3-hydroxy-4-hexenoic acid.

The polymer intermediate may be isomerized to sorbic acid in acid or alkaline media. The crude sorbic acid is purified by codistillation under vacuum with an organic solvent having the same general distillation range.

Sorbic acid may also be manufactured by oxidation of 2,4-hexadienal.

2. Input Materials

Crotonaldehyde

Ketene

3. Operating Parameters

Temperature: not given

Pressure: not given

Catalysts: Reaction step - usually zinc carboxylic salts. Isomerization step - acid or base.

- 4. <u>Utilities</u> Not given
- 5. <u>Waste Streams</u> Waste water streams from the purification section may include acid or base catalysts, spent reaction catalysts, and distillation solvents in addition to traces of crotonaldehyde and sorbic acid.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 18 (1969), p. 590-591. n-Butanol (from crotonaldehyde)

$$CH_3CH=CHCHO \xrightarrow{H_2} CH_3CH_2CH_2CH_2OH$$

 <u>Function</u> - The reduction of crotonaldehyde to n-butanol accounts for approximately 20% of the n-butanol produced in the United States. The reduction is accomplished by the vapor phase hydrogenation over a reduced nickel-chromium catalyst at 180°C and 207 kPa.

Precursor steps may include ethanol or ethylene to acetaldehyde, acetaldehyde to acetaldol, and acetaldol to crotonaldehyde.

2. Input Materials

Crotonaldehyde - 1.04 kg/kg n-butanol

Hydrogen

- 3. <u>Operating Parameters</u> Temperature - 180°C (356°F) Pressure - 207 kPa (30 psi) (2 atm) Catalyst - Nickel-Chromium
- 4. Utilities Not given
- 5. <u>Waste Streams</u> The wastewater stream from the stripper may contain some n-butanol and crotonaldehyde. Heavy ends from distillation columns are usually incinerated.
- 6. EPA Source Classification Code None
- 7. References

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical Processes</u>, Technomic Publishing Co., 1975. 7. References (continued)

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 826.

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 658-660.

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Crotonic Acid

 $CH_3CH=CHCHO + 1/20_2 \longrightarrow CH_3CH=CHCOOH$

 Function - Crotonic acid is prepared commercially by the catalytic oxidation of crotonaldehyde with air. The catalyst is a copper acetate-cobalt acetate mixture, about 0.5 - 1.0% by weight of the total charge, and the temperature is held between 35 - 50°C.

Percrotonic acid may be an immediate product of this process. In the continuous process, crotonaldehyde and catalyst solution are combined with an inert organic diluent such as benzene, methyl acetate, acetone, or methyl ethyl ketone in about equal volume and pumped into the oxidation kettle. Air is bubbled in, while the crude product is drawn off continuously. The diluent and unreacted crotonaldehyde are distilled off and returned to the process, while the crude crotonic acid is fractionated under reduced pressure.

2. Input Materials - Basis - 157 parts crotonic acid

Crotonaldehyde: 226 parts Air Organic diluent (MeOAc): 245 parts Catalyst [Cu(OAc)₂]: 2.70 parts

[Co(0Ac)₂]: 0.45 parts

3. Operating Parameters

Temperature: 35 - 50°C (95-122°F) Pressure: not given Catalyst: Copper acetate - cobalt acetate

- 4. <u>Utilities</u> The principal pollutant source from this process should be the waste stream from the purification section, containing acetic acid, formic acid, other reaction by-products, and traces of crotonaldehyde, crotonic acid, organic diluent, and spent catalyst.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

U.S. Patent 2,413,235 (December 24, 1946).

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 6 (1965), p. 454, 455. British Patent 595,170 (November 27, 1947).

n-Butyl Acetate

$$CH_{3}COOH + C_{4}H_{9}OH \xrightarrow{H_{2}SO_{4}} CH_{3}COOC_{4}H_{9}$$

1. <u>Function</u> - Butyl acetate's manufacture involves the classic reaction between butanol and dilute acetic acid, catalyzed by 0.1% H₂SO₄. Butyl acetate, which boils at 126.5°C forms with butanol and water, a ternary azeotrope which boils (89.4°C) below a binary azeotrope that butyl acetate forms with butanol. The ternary azeotrope separates into two layers on condensing - 81% ester, 13% butanol, and 6% water in the tops and 1% ester, 3% butanol, and 96% water in the bottoms. These fortunate circumstances ease removal of the water-of-reaction, so that low concentrations of acetic acid in water work extremely well as feed to the process.

A 10% excess of the stoichiometric requirement of butanol is fed to this reaction.

2. Input Materials

n-Butanol - 0.98 kg/kg (1,969 lb/ton) n-butyl acetate Acetic acid - 0.81 kg/kg (1,620 lb/ton) n-butyl acetate

3. Operating Parameters

Temperature: 90°C (194°F) Pressure: not given Catalyst: 0.1% H₂SO₄

4. Utilities

Not given

5. Waste Streams

Separator (water)

The separator may discharge a water stream containing n-butyl acetate, n-butanol, acetic acid, and sulfuric acid and may be treated to recover some of these materials. Separator (air)

The separator air vent could emit n-butyl acetate and n-butanol vapors.

Purification section

No information was available on this section, but the same types of pollutants would be expected.

6. EPA Source Classification Code - None

7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 2," "Chemical Engineering," February 18, 1974, p. 126.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> Processes, Technomic Publishing Co., 1975.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 173, 174.

INDUSTRIAL ORGANIC CHEMICALS

Pyridine and β -Picoline

1. <u>Function</u> - Pyridine and beta-picoline are co-produced by the vapor phase reaction of acetaldehyde, ammonia, and formaldehyde. The formaldehyde is usually added in excess to inhibit the formation of alpha- and gamma-picoline, but mixtures of formaldehyde and methanol are also used.

In both process variations, the reactants are vaporized and passed through a fluid-catalyst-type reactor containing a fluidized catalytic bed of silica-alumina catalyst. The reaction is carried out at 250 - 500°C and atmospheric pressure.

The crude product is fractionated to obtain pyridine and 3picoline. Typical yields based on acetaldehyde feed are 35% for pyridine and 27% for beta-picoline.

- 2. <u>Input Materials</u> Basis 47 parts pure mixed product acetaldehyde: 62 parts (6.37 kg/kg pyridine; 7.01 kg/kg 3-picoline) ammonia: 1 part formaldehyde: 67 parts methanol (in some process variations): 32 parts
- 3. Operating Parameters

Temperature: 250 - 500°C (482-932°F) Pressure: 101 kPa (1 atm.)

Catalyst: Alumina-silica (13% Al₂0₃, 87% SiO₂)

4. Utilities - not given

- 5. <u>Waste Streams</u> Waste gases from the purification section may contain formaldehyde, ammonia, acetaldehyde, various amine byproducts, and methanol, if used.
- 6. EPA Source Classification Code None
- 7. References

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U.S. Patent 2,807,618 (September 24, 1957).

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 16 (1968), p. 781, 785.

Acetic Anhydride and Acetic Acid

 $\begin{array}{c} \mathrm{CH}_{3}\mathrm{CHO} + \mathrm{O}_{2} \ (\texttt{air}) \longrightarrow \mathrm{CH}_{3}\mathrm{COOOH} \\\\ \mathrm{CH}_{3}\mathrm{COOOH} + \mathrm{CH}_{3}\mathrm{CHO} \longrightarrow (\mathrm{CH}_{3}\mathrm{CO})_{2}\mathrm{O} + \mathrm{H}_{2}\mathrm{O} \\\\\\ \mathrm{CH}_{3}\mathrm{COOOH} + \mathrm{CH}_{3}\mathrm{CHO} \longrightarrow 2\mathrm{CH}_{3}\mathrm{COOH} \end{array}$

 Function - Acetic acid and acetic anhydride are prepared primarily by the catalytic oxidation of acetaldehyde. In this process, the peracetic acid formed by the initial oxidation is allowed to react with an excess of acetaldehyde to form the anhydride, as well as acetic acid.

Copper, cobalt, or manganese acetate catalysts give selectivity to anhydride formation. Entraining agents such as ethyl acetate further enhance this conversion by removing the water of reaction.

2.	<u>Input Materials</u> - Basis -	<u>l kg (ton) acetic anhydride</u>	
	Acetaldehyde, kg (1bs)	1.10 (2,200)	1.20 (2,400)
	Catalyst, g (lbs)	3.30 (6.6) (MnAc ₂)	1.0 (2) $\left(\frac{CuAc}{CoAc}\right)$
	Air, m^3 (ft ³)	0.251 (8,040)	variable
	Diluent (less recovery), kg (lbs)		1.65 (3,300)
3.	Operating Parameters		
	Temperature, °C (°F)	55-80 (131-176)	50-70 (122-158)
	Pressure, kPa (atm)	843-517 (4.77-5.10)	414 (4.09)
	Reaction time, hrs	12	

- 4. <u>Utilities</u> Basis 4,536 (100 M̄ kg/yr) Water cooling, m³/min - 25.3 (6,690) Water makeup, m³/min (gpm) - 1.25 (330) Power,kW - 1,665 Steam, kg/hr (lbs/hr) - 2.06 x 10⁴ (45,420)
- 5. Waste Streams

Reaction section - off-gas scrubber vent Methane - 1.8 g/kg (3.6 lbs/ton) acetic acid Carbon monoxide - 3.3 g/kg (6.5 lbs/ton) acetic acid Higher acids Total waste flow - 4.17 m³/kg (10³ gallons/ton) product Organics - >15 g/1

	<u>Plant 1</u>	<u>Plant 2</u>
Flow	4.17 m ³ /kg	0.085 m ³ /kg
COD	186 mg/1 0.78 g/kg	306,100 mg/1 26.18 g/kg
BOD ₅	84 mg/1 0.35 g/kg	64,000 mg/1 5.44 g/kg

6. EPA Source Classification Code - None

7. References

Austin, G. T., "The Industrially Significant Organic Chemicals - Part 1," "Chemical Engineering," January 21, 1974, p. 128.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical Processes</u>, Technomic Publishing Co., 1975, p. 158,183.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 8 (1965), p. 408. 7. References (continued)

Faith, W. L. et al., <u>Industrial Chemicals</u>, 3rd Ed., Wiley & Sons New York, N.Y., 1965, p. 18-19.

Kent, J. A., <u>Riegel's Handbook of Industrial Chemistry</u>, 7th Ed., Van Nostrand Reinhold Co., New York, N.Y., 1974, p. 790.

Sittig, M., <u>Acetic Acid and Anhydride</u>, Noyes Development Corporation, Pearl River, N.Y., 1965, p. 29-31.

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corp., Park Ridge, N.J., 1974, p. 54.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N.Y., 1975, p. 8,9,16,17.

INDUSTRIAL ORGANIC CHEMICALS

Cellulose Acetate

 $[c_{6}H_{7}O_{2}(OH)_{3}]_{n} + 3n(CH_{3}CO)_{2}O \longrightarrow [c_{6}H_{7}O_{2}(OOCCH_{3})_{3}]_{n} + 3nCH_{3}COOH$

 Function - Cellulose acetate is produced by the catalytic acetylation of high-quality cellulose, usually 98-99% α - cellulose. This rather complicated batch process may be explained in terms of several subprocedures.

Pretreatment

The cellulose is first dried to a fixed optimum moisture content. A pretreating reagent, acetic acid, is then added to swell the cellulose and permit the acetylation reagent to diffuse into the fiber more rapidly. The time of pretreatment varies from 15 minutes to several hours.

Acetylation

The acetylation mixture consists of acetic anhydride, acetic acid (cellulose acetate solvent), and sulfuric acid catalyst. The amount of acetic anhydride used is slightly in excess of that required to react with the moisture in the cellulose and to form the triester.

For many applications, the cellulose acetate formed must be deesterified to some extent. This is accomplished by adjusting the water content to 5-10% and allowing hydrolysis to occur in the presence of sulfuric acid catalyst. When the desired ester content is reached, hydrolysis is arrested by neutralizing the sulfuric acid, usually with sodium acetate.

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Precipitation and Purification

The product is precipitated by dilution with water to some point just short of precipitation followed by mixing with an excess of aqueous acetic acid solution with vigorous agitation. The freshly precipitated product is purified by washing with water until all traces of acid are removed.

Stablization

For the most part, product instability is due to the presence of sulfate ions in solution and trace amounts of sulfate esters. These are removed by adding magnesium ion and boiling in slightly acidified water. The stable product is then centrifuged and dried. Acetic Acid Recovery

All wash liquors containing an appreciable amount of acetic acid are combined to give an aqueous solution containing 18-20% acetic acid. Glacial acetic acid is obtained by concentrating this liquor.

<u>Input Materials</u> - Basis - 1 metric ton cellulose acetate Cellulose - 700 kg (1543 lbs) Acetic Acid - 3250 kg (7165 lbs) Acetic Anhydride - 2000 kg (4409 lbs) Sulfuric Acid (catalyst) - 100 kg (220 lbs) Water

Sodium acetate or sodium bicarbonate

3. Operating Parameters

Temperature: Pretreatment - 40-50°C (104-122*F) Acetylation - 5-45°C (41-113°F) Hydrolysis - 25°C (77°F) Drying - 95°C (203°F) Pressure: slightly above atm.

Catalyst: 1% H₂SO₄

Reaction Time: 15-30 min.

4. Utilities

Not given

5. <u>Waste Streams</u> - The stills used to recover acetic acid and other solvents are major sources of waste water. The wastes contain considerable amounts of degraded cellulose and sulfuric acid. About 12-15 cubic meters of waste waters are generated per Mg (12-15 gal/1000 lb) of product with a solids loading of 200 g/m³ depending upon the relationship of flake to fiber production.

Solvent handling operations are the principal potential sources of emissions to the air in the processing of cellulose acetate. Various solvents may be involved.

- 6. EPA Source Classification Code None
- 7. References

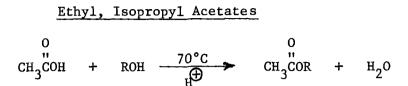
Austin, G. T., "The Industrially Significant Organic Chemicals -Part 2," "Chemical Engineering," February 18, 1974, p. 127, 128.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> Processes, Technomic Publishing Co., 1975. Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 4 (1964) p. 633-635.

U.S. Patent 3,040,027 (June 19, 1962).

Sittig, M., Organic Chemicals Process Encyclopedia - 1969, 2nd Edition, Noyes Development Corp., Park Ridge, N.J., 1969, p. 156.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N.Y., 1975 p. 239, 240.



 <u>Function</u> - Lower aliphatic acetates, such as ethyl and isopropyl acetate, are manufactured commercially by batch and continuous processes. The continuous process is favored for large volume production.

<u>Batch Process</u> - The esterification chamber (reactor) is a cylindrical tank or pot, heated by closed coil steam pipe. The acetic acid (8%), ethanol (95%), and catalyst (usually sulfuric acid) are charged in the ratio of 10:10:0.33. The mixture is heated by steam, and the vapors are fed to the base of a fractionating tower. The temperature at the top of the column is maintained at the boiling point of the ternary azeotrope of ethyl acetate (83%), ethanol (9%), and water (8%). The reflux from this tower is returned to the reactor. The vapors from the top of the column are sent to a reflux condenser, part of the condensate is returned to the column as reflux, and the rest is sent to storage.

The ultimate product of the batch process is the azeotrope ethyl acetate/ethanol/water. The azeotrope is satisfactory for many downstream commercial processes. However, others require pure ethyl acetate which is separated from the ternary azeotrope by the method used in the continuous process.

<u>Continuous Process</u> - The sulfuric acid/excess ethanol/acetic acid mixture is brought to equilibrium with agitation and heating. It

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is then pumped to a receiving tank. The mixture is used in the reflux condenser as a heat exchange fluid. The heated mixture is then introduced near the tope of a reaction column. The temperature at the top of the column is maintained at ethanol reflux temperature. Live steam is introduced at the base of the column. An additional feed of recovered alcohol is introduced simultaneously near the bottom of the column. Vapors from the reaction column containing approximately 10% water, are condensed and sent to a recovery column. The excess water and sulfuric acid are removed at the bottom of the reaction column. The acetic acid is consumed completely because there is always an excess of ethanol due to the constant removal of ethyl acetate and water.

The recovery column removes the excess alcohol from the ternary mixture and returns it to the reaction column. The ternary mixture, refluxing at the top of the recovery column, is condensed and recycled (to the bottom) until it approaches the composition of the constant-boiling ternary. The constant boiling ternary from the top of the recovery column is then sent to a mixing coil where water is added to form two layers. The layers are sent to a separator. The lower layer is sent back to the recovery column below the level of the feed plate, but above the base of the column.

The upper layer is sent to a second recovery column. The vapors are condensed and returned to the mixing coils. Ethyl acetate of 95-100% purity is taken from the bottom of the second recovery column. This product is then fractionated to obtain highpurity ethyl acetate and a small amount of constant boiling mixture which is returned to the first recovery column.

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Ethyl acetate can be made by vapor phase esterification by reaction of ethylene with acetic acid, or by dehydrogenation of ethyl alcohol. These are not used commercially at present with the olefins below C_4 , insofar as is known. Ethylacetate is also recovered as a by-product in polyvinyl alcohol production.

2. Input Material

95% ethanol 8% acetic acid/92% water 50-66° Be sulfuric acid Water Steam

3. Operating Parameters

Batch process - top plate of fractionating tower - 70°C (158°F) est. reaction chamber temperature - 80°C (176°F) top plate of recovery column - 78°C (172°F) catalyst - 50-66° Be sulfuric acid equipment - cylindrical tank, steam coil, perforated steam pipe, fractionating stills, bellcap column, pumps, condensers Continuous process - top plate reaction column - 80°C (176°F) bottom of recovery column - 100°C (212°F) catalyst - 50-66° Bé sulfuric acid equipment - stirred reactors, steam-heated reaction column, reflux condensers, total condensers, mixing coils, separating tanks, receivers, cooling coils

- 4. Utilities Not given.
- 5. Waste Streams

<u>Batch Process</u> - Dilute sulfuric acid stream from separation column sent to sewer and liquid leaks from pump seals. Possible vapor leaks from reactors, separation columns and condensers. No solid wastes. <u>Continuous Process</u> - Dilute sulfuric acid from recovery column sent to sewer. Possible vapor leaks from reactors, reaction column, recovery columns, condensers, and fractionating columns. Liquid leaks from pump seals. No solid wastes.

- 6. EPA Source Classification Code None.
- 7. References

Keyes, D. B., "Esterification Processes and Equipment", "Ind. Eng. Chem.", Vol. 24 (1932), p. 1096-1103.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 8 (1965), p. 313.

Sittig, M., <u>Organic Chemical Process Encyclopedia - 1969</u>, 2nd Edition, Noyes Development Corp., Park Ridge, N. J., 1969, p. 299.

U. S. Patent 2,787,636 (April 2, 1957).

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N. Y., 1975, p. 350, 351.

Chloroacetic Acid

 $CH_3COOH + C1_2 \longrightarrow C1CH_2COOH + HC1$

- Function In the U.S., virtually all chloroacetic acid is produced by the direct chlorination of acetic acid. Catalysts such as sulfur and red phosphorus are used at temperatures of 85-120°C. The yield is about 95% based on acetic acid. Since HCl is a reaction by-product, glass-lined or specially designed corrosion-resistant equipment is used.
- 2. Input Materials

Basis - <u>1 metric ton chloroacetic acid</u> Acetic Acid - 688 kg (1517 lbs) Chlorine - 813 kg (1792 lbs) Red Phosphorus - 6.8 kg (15 lbs)

3. Operating Parameters

Temperature: 85-120°C (185-248°F)

Pressure: not given

Catalyst: Sulfur, red phosphorus

Chlorine Flow: 9-27 kg

4. Utilities

Not given

5. <u>Waste Systems</u> - Waste water streams from HCl absorbers and scrubbers may contain chlorine, hydrogen chloride, spent caustic, and chlorinated by-products. Vapors from reactors and the purification section may be expected to contain quantities of unreacted acetic acid,

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chloroacetic acid, and reaction by-products, as well as some chlorine and HC1. However, no specific information was available.

6. EPA Source Classification Code - None

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y. Vol. 8 (1965), p. 816,417.

Faith, W. L., et al., <u>Industrial Chemicals</u>, John Wiley & Sons, Inc. New York, N.Y., 1965, p. 257,258.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N.Y., 1975, p. 254,255. Acetic Anhydride (from acetic acid and ketene)

 $CH_3COOH \longrightarrow CH_2CO + H_2O$

 $CH_2CO + CH_3COOH \longrightarrow (CH_3CO)_2O$

 <u>Function</u> - One method of producing acetic anhydride is the reaction of ketene and acetic acid. Ketene is first prepared by the catalytic cracking of acetic acid at 700° - 750°C. Triethyl phosphate is the usual catalyst. As reaction gases leave the converter, ammonia gas (1 kg/4.2 kg TEP) is injected into the stream to prevent reversion if the ketene is the product.

The reaction product passes from the pyrolysis tube to a coolingseparation system where the water from unreacted acetic acid are removed. The ketene is then reacted with acetic acid in two absorption towers at 30 - 40 °C to produce acetic anhydride in yields approaching 90% based on acetic acid.

About half of the acetic anhydride produced in the U.S. is made by the Celanese Process. Acetic acid is cracked at somewhat lower temperatures (<700°C) to an equimolar mixture of ketene and acetic acid. After water is removed by flashing with benzene, the two reaction products combine to yield acetic anhydride.

2. <u>Input Materials</u> - Acetic acid - 1.25 kg/kg acetic anhydride 1350 mg/metric ton acetic anhydride

Ammonia gas - 16.8 kg/kg acetic anhydride

Benzene

Triethyl Phosphate - 0.25 kg/kg acetic anhydride

- 3. Operating Parameters Ketene production Temperature - 700°-750°C (1292-1382°F) Pressure - 26.7 kPa (0.26 atm) Catalyst - Triethyl Phosphate <u>Anhydride Production</u> Temperature - 30-40°C (86-104°F) Pressure - Not given
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Vent from gas scrubber system (air: This stream may contain methane, ethylene, and ketene, and they are normally fed to the burner to be used as fuel. Acetic anhydride column and acetic acid column: Heavy ends from these columns are generally incinerated. Gas scrubber system (water): Water streams may contain sodium hydroxide and sodium acetate. Some benzene expected in waste streams from the Celanese process.

6. EPA Source Classification Code - None

7. References

Austin, G. T., "The Industrially Significant Organic Chemicals Part 1," "Chemical Engineering," January 21, 1974, p. 129.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical Processes</u>, Technomic Publishing Co., 1975.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 8 (1965), p. 408.

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 17,18.

PROCESS NO. 106

Sodium Acetate (from acetic acid)

 $CH_3COOH + NaOH \longrightarrow CH_3COONa \cdot 3H_2O$

- <u>Function</u> Sodium acetate is made on a commercial scale by reacting alkali with acetic acid.
- 2. Input Materials

Acetic acid

Sodium hydroxide

- Operating Parameters
 Not given
- 4. <u>Utilities</u>

Not given

- 5. <u>Waste Streams</u> Separator waste streams are probably the main pollutant sources in this process. Waste water streams may contain quantities of acetic acid and sodium hydroxide, and acetic acid may be present in the off-gas.
- 6. EPA Source Classification Code None
- 7. References

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 277.

Ethyl Acetoacetate (from ethyl acetate)

 $2CH_3COOC_2H_5 + 2Na \longrightarrow$

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CH_3C(ONa)CHCOOC_2H_5 + NaOC_2H_5 + H_2
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 $2CH_3C(ONa)CHCOOC_2H_5 + H_2SO_4 \longrightarrow$

```
2CH_3COCH_2COOC_2H_5 + Na_2SO_4
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 <u>Function</u> - Ethyl acetoacetate is most conveniently prepared by allowing high-purity ethyl acetate to react with metallic sodium or sodium ethoxide.

The sodium derivative is then neutralized with sulfuric acid. The yield is better than 90% after separation and vacuum distillation of the crude ester.

2. Input Material

Ethyl acetate - 1.50 kg/kg ethyl acetoacetate

Sodium

Sulfuric acid

- 3. <u>Operating Parameters</u> Not given
- 4. <u>Utilities</u>

Not given

5. <u>Waste Streams</u> - Waste water from the separators may contain varying amounts of organic and inorganic sodium salts (sodium ethoxide, sodium sulfate, ethyl sodioacetate, etc.), ethyl acetate, ethyl acetoacetate, and reaction by-products. Scrubbers may be used to remove excess sulfuric acid, and should also contribute to waste water pollution. Emissions from reactor, separation, and scrubber vents may contain any of the volatile reactants, products, and byproducts.

- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963) p. 158.

<u>Chemical Technology</u>, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 499. Glycine (ammonolysis of chloroacetic acid)

 $C1CH_2COOH + 2NH_3 \longrightarrow NH_2CH_2COOH + NH_4C1$

- <u>Function</u> Glycine is prepared on a commercial scale by adding an excess of aqueous ammonia to chloroacetic acid. Ammonium salts such as ammonium carbonate are often added to reduce the pH of the solution and inhibit conversion to the secondary and tertiary amine. Yields are generally good.
- 2. Input Materials basic 0.450 kg glycine

Chloroacetic acid: 0.500 kg in 0.400 ℓ H₂O Aqueous ammonia (30%): 1.00 ℓ Ammonia salts (or hexamethylene tetramine): 2.200 kg (NH₄)₂CO₃ H₂O: 0.500 ℓ

3. Operating Parameters

Temperature: 40-90°C (104-194°F) Pressure: 101 kPa (1 atm) Reaction Time: 4-20 min.

- 4. Utilities Not given.
- 5. <u>Waste Streams</u> Wastewater from separators may contain ammonia, several ammonium salts, and traces of chloroacetic acid, glycine and other amine by-products. In ammonia recovery, some air emissions may occur, but no specific information was available.
- 6. EPA Source Classification Code None.
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 2 (1963), p. 350.

Cheronis, N. D., and K. H. Spitzmueller, <u>J. Org. Chem.</u>, <u>6</u>, 349 (1941). 6-290 U. S. Patent 3,215,736 (November 2, 1965).

Sittig, M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition, Noyes Development Corp., Park Ridge, N. J., 1969, p. 350.

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Sodium Chloroacetate (from Chloroacetic Acid)

 $CH_{3}COOH + C1_{2} \xrightarrow{Fe^{+3}} C1CH_{2}COOH \xrightarrow{Na_{2}CO_{3}} C1CH_{2}COONa$

- 1. <u>Function</u> Acetic acid is chlorinated in the presence of iron, H_2SO_4 , or PCl₃ at 85-120°C to yield monochloroacetic acid in 95% yield. Even though the chlorine in chloroacetic acid is readily displaced from aqueous solutions of either itself or its alcoholic salts, the sodium chloroacetate is prepared by heating chloroacetic acid in Na₂CO₃ to 50°C, then cooling to room temperature.
- 2. Input Materials

Acetic acid Chlorine Iron, H₂SO₄ or PC1₃ Sodium carbonate

3. Operating Parameters

Temperature:	lst Step	85-120°C	(185-248°F)
	2nd Step	50°C	(122°F)

Pressure: not given Reaction time: not given

4. Utilities

Not given

5. <u>Waste Streams</u> - Excess chlorine, ferric chloride, and HCl should be in the waste streams from the first step and CO₂, and carbonic acid should be present from the second step. 6. EPA Source Classification Code

None

7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 8 (1965), p. 415, 417. <u>Organic Synthesis</u>, John Wiley and Sons, New York, N.Y., Coll. Vol. II (1943), p. 376.

Ethyl Chloroacetate

$$C1CH_2COOH + C_2H_5OH \longrightarrow C1CH_2COOC_2H_5 + H_2O$$

- 1. <u>Function</u> Ethyl chloroacetate is produced by the direct esterification of chloroacetic acid with absolute ethanol. Two moles of chloroacetic acid react with an excess of absolute ethanol (~ 3 moles) in the presence of 25g of concentrated sulfuric acid. The mixture is refluxed for six hours. The crude product is isolated and purified by conventional methods.
- <u>Input Materials</u>
 Chloroacetic acid
 Ethanol

- 3. <u>Operating Parameters</u> Temperature: Reflux Pressure: 101 kPa (1 atm) Catalyst: H₂SO₄
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Traces of volatile reactants and products may be detected in air. Waste waters from washing crude product will contain sulfate salts, and traces of reactants and products. By-products may be present in waste waters from the purification by distillation.
- 6. EPA Source Classification Code None

7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition,
Interscience Publishers, New York, N.Y., Vol. 8 (1965), p. 372.
Blatt, A. H., <u>Organic Synthesis</u>, Collective Vol. II, John Wiley &
Sons, New York, N.Y., 1943, p. 263.

Cyanoacetic Acid

 $\texttt{C1CH}_2\texttt{CO}_2\texttt{Na} + \texttt{NaCN} \xrightarrow{} \texttt{NCCH}_2\texttt{COONa} + \texttt{NaCl} \xrightarrow{} \texttt{H}_3 \overset{\bigoplus}{\longrightarrow} \texttt{NCCH}_2\texttt{COOH}$

- Function Cyanoacetic acid is made by reacting the sodium salt of chloroacetic acid with sodium cyanide solution. Neutralization of the resulting mixture yields cyanoacetic acid.
- 2. Input Materials

Chloroacetic acid - 1.24 kg/kg cyanoacetic acid Sodium cyanide

- 3. <u>Operating Parameters</u> Not given
- 4. Utilities

Not given

- 5. <u>Waste Streams</u> Information available was insufficient to identify pollutant sources in this process. However, waste water streams from various processing equipment may contain chloroacetic acid, sodium cyanide, cyanoacetic acid, and reaction by-products. Air vents may release any of the volatile reactants or products.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 8 (1965), p. 417.

Hahn, A. V., <u>The Petrochemical Industry: Market and Economics</u>, McGraw-Hill Book Co., New York, N. Y., 1970, p. 165. Sodium Carboxymethyl Cellulose

 $C_6H_7O_2(OH)_3$ + NaOH \longrightarrow $C_6H_7O_2(OH)_2ONa$ + H_2O

 $C_6H_7O_2(OH)_2ONa + C1CH_2COONa \rightarrow C_6H_7O_2(OH)_2OCH_2COONa + NaCl$

 <u>Function</u> - Sodium carboxymethyl cellulose is produced by a two-step process, involving the addition of sodium hydroxide and sodium chloroacetate to cellulose.

Only 13-50% of the available hydroxyl group react to yield alkali cellulose, the properties of the final product being quite dependent on this fraction.

The alkali cellulose formed is then combined with sodium chloroacetate at 35-45°C to yield the final product.

After drying, the crude product contains considerable amounts of sodium chloride and other diluents, such as sodium glycolate. If necessary, these impurities may be removed by washing with methanol or ethanol.

2. Input Materials

Cellulose 1 part Sodium hydroxide - 10 parts Sodium chloroacetate - 1.5 parts Methanol or ethanol

3. Operating Parameters

Temperature: 35-45°C (95-113°F) Pressure: 101 kPa (1 atm)

4. Utilities - Not given.

- 5. <u>Waste Streams</u> Wastewater streams from washing operations may contain unreacted sodium hydroxide, alkali cellulose, sodium chloroacetate, or chloroacetic acid, and reaction by-products, such as sodium glycolate. Methanol or ethanol may also be present.
- 6. EPA Source Classification Code-None.
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 8", July 22, 1974, p. 112.

U. S. Patent 3,322,798 (May 30, 1976).

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 4 (1964), p. 644, 645.

Sittig, M., Organic Chemical Process Encyclopedia - 1960, 2nd Edition, Noyes Development Corp., Park Ridge, N. J., 1969, p. 601.

Ethyl Cyanoacetate

$$C1CH_2COOH + Na_2CO_3 \xrightarrow{10^{\circ}C} C1CH_2COONa + CO_2 + NaOH$$

 $\text{C1CH}_2\text{COONa} + \text{NaCN} \xrightarrow{\sim 90^{\circ}\text{C}} \text{NCCH}_2\text{COONa} + \text{NaCl} \xrightarrow{\text{H}_30^{\bigoplus}} \text{NCCH}_2\text{COOH}$

$$\text{NCCH}_2\text{COOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{H}_2\text{SO}_4}_{\text{reflux}} \text{NCCH}_2\text{COOC}_2\text{H}_5$$

 Function - Ethyl cyanoacetate is manufactured by esterification of cyanoacetic acid with ethyl alcohol. The cyanoacetic acid is formed via the reaction of sodium chloroacetate with sodium cyanide.

The crude ester (washed, dried) is purified by distillation under reduced pressure.

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2. Input Materials
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Chloroacetic acid

Water

Na₂CO₃ (neutralize chloroacetic acid)

NaCN

HC1 (to liberate cyanoacetic acid)

C2H5OH

3. Operating Parameters

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Temperature: Neutralization C1CH<sub>2</sub>COOH - 10°C (50°F)
Formation - sodium cyanoacetate - ~90°C (194°F)
Esterification - reflux temperature
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- 4. Utilities Not given
- 5. <u>Waste Streams</u> Excess NaCN reacts with HCl to give HCN, which is vented to the air. Waste waters may contain salts, dilute acids, traces of alcohol, and of ethyl cyanoacetate.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 12 (1967), p. 853-854.

Gilman, H., <u>Organic Synthesis</u>, 2nd Edition, 5th Printing, John Wiley and Sons, New York, N.Y., Collective Vol. I, 1948, pp. 254-256. Ethylene Dibromide

$$CH_2 = CH_2 + Br_2 \longrightarrow BrCH_2CH_2Br$$

- 1. <u>Function</u> Ethylene dibromide is produced by the reaction of ethylene and bromine. The reaction takes place in earthenware or glass vessels, the ethylene being passed into the bromine. After any free acid is neutralized, the product is purified by fractionation. The yield is approximately 90% of the theoretical.
- 2. <u>Input Materials</u> Per kg product (2.2 lbs) Ethylene - 1.166 kg (2.57 lbs) Bromine - 0.933 kg (2.06 lbs)
- 3. Operating Parameters

Temperature 10-100°C (50-212°F)

Pressure 101 kPa (1 atm)

Reaction Time 16 hrs (batch)

2 hrs (continuous)

4. Utilities

Not given

- 5. <u>Waste Streams</u> No information was available, but waste streams from distillation columns and other processing equipment may contain traces of reactants, reaction products (ethylene dibromide and by-products), and free acid neutralization products.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 5,""Chemical Engineering," April 29, 1974, p. 146. 7. References (continued)

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 771.

Sittig, M., Chemicals from Ethylene, Noyes Development Corporation, Pearl River, N.Y., 1965, p. 36, 37.

Ethyl Chloride (from ethylene)

$$CH_2 = CH_2 + HC1 \xrightarrow{A1C1_3} C_2H_5C1$$

 Function - Eighty-eight percent of the ethyl chloride produced in the U.S. is made by the liquid-phase reaction of dilute ethylene and hydrogen chloride.

The reaction is carried out at normal temperature and pressure in an 0.2% solution of aluminum chloride in ethyl chloride. The yield is approximately 90% of the theoretical.

2. Input Materials

Basis - 1 kg ethyl chloride

Ethylene - 0.488 kg

Hydrogen chloride - 0.625 kg

Catalyst - 5 g

3. Operating Parameters

Temperature:	35-40°C (95-104°F)
Pressure:	372 kPa (3.67 atm)
Catalyst:	0.2% A1Cl ₃ solution

4. Utilities

Not given

- 5. <u>Waste Streams</u> Emissions from air vents and wastewater streams may include ethylene, hydrogen chloride gas, hydrochloric acid, CH₄, CO₂, ethyl chloride, and trace amounts of catalyst.
- 6. EPA Source Classification Code None

7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 5,""Chemical Engineering," April 29, 1974, p. 144, 145.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 5 (1964), p. 144.

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corp., Park Ridge, N.J., 1974, p. 133, 134.

Sittig, M., Organic Chemical Processes, The Noyes Press, Inc., Pearl River, N.Y., 1962, p. 55.

PROCESS NO. 116

Tetraethyl Lead (via lead amalgam)

 $4CH_3CH_2C1 + 4PbNa \longrightarrow Pb(CH_2CH_3)_4 + 3Pb + 4NaC1$

 <u>Function</u> - The major reaction for the production of tetraethyl lead involves the addition of lead amalgam to ethyl chloride at 65-75°C and 345-414 kPa (50-60 psig). The lead amalgam used is about 90% lead and 10% sodium.

The yield based on sodium feed exceeds 90%. Some sodium is lost to side reactions, which form hydrocarbons. The tetraethyl lead formed is steam distilled and purified. The lead sludge is reprocessed.

2. Input Materials

Ethyl chloride

Lead amalgam 90% lead - 0.75 kg/kg tetraethyl lead 10% sodium - 0.32 kg/kg tetraethyl lead

3. Operating Parameters

Temperature - 65-75°C (149-167°F)

Pressure - 345-414 kPa (3.40-4.09 atm)

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Hydrocarbons formed by combination and disproportionation of ethyl radicals are normally vented during reaction period. The effluents from washings may contain small amounts of oxidizing agents, reaction products and sodium chloride from the washings of the lead sludge.
- 6. EPA Source Classification Code None

7. References

Austin, G. T., "The Industrially Significant Organic Chemicals - Part 8," "Chemical Engineering," July 22, 1974, p. 114.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition,

Interscience Publishers, New York, N.Y., Vol. 12 (1967), p. 290-293.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N.Y., 1975, p. 502-508.

INDUSTRIAL ORGANIC CHEMICALS

PROCESS NO. 117

Tetraethyl Lead (via electrolysis)

 $\mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{C1} + \mathrm{Mg} \longrightarrow \mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{MgC1}$

 $2CH_3CH_2MgC1 + 2CH_3CH_2C1 + Pb \longrightarrow (CH_3CH_2)_4Pb + 2MgC1_2$

- 1. <u>Function</u> The newer electrolysis process is used <u>mainly</u> to produce <u>tetramethyl lead</u> but is suitable for the manufacture of other lead alkyls. The process consists of two major steps: 1) Synthesis of a Grignard reagent from magnesium and ethyl chloride in anhydrous mixed ethers such as THF and diethylene glycol; and 2) Electrolysis of the solution of the Grignard reagent where the ethyl radicals migrate to an anode of lead pellets and combine to form tetraethyl lead. Magnesium migrates to the cathode (steel wall of the cell) and reacts with excess ethyl chloride to give magnesium chloride.
- 2. Input Materials

Ethyl chloride

Magnesium

Lead

Tetrahydrofuran

Diethylene glycol dibutyl ether

3. Operating Parameters

For Grignard reagent formation: Temperature - 350°C (662°F)

Pressure - 69-138 kPa (0.68-1.36 atm)

4. Utilities - Not given

- <u>Waste Streams</u> No information available. Possible emissions from recycling and purification of solvents.
- 6. EPA Source Classification Code None
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals - Part 8," "Chemical Engineering," July 22, 1974, p. 114, 115.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 12 (1967), p. 290-293.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N.Y., 1975, p. 502-508.

Ethyl Cellulose

 $R_{cell} \rightarrow R_{cell} \rightarrow R_{cell} \rightarrow R_{cell}$ OH · NaOH

 $R_{cell} OH \cdot NaOH + C_2H_5Cl \longrightarrow$

 $R_{cell} OC_2H_5 + NaCl + H_2O$

1. <u>Function</u> - On a commercial scale, ethyl cellulose is made by the liquid-phase reaction of alkali cellulose and ethyl chloride. The alkali cellulose is prepared by mixing a 50% aqueous sodium hydroxide solution with cellulose. Since high sodium hydroxide concentration favors the main reaction, the concentration is kept as high as possible.

After several hours, the alkali cellulose is added to a nickellined pressure vessel along with ethyl chloride and a diluent such as benzene or toluene. The conversion to ethyl cellulose requires 6-12 hours at 90-150°C.

The exact substitution may be controlled by the sodium hydroxide concentration, the ethyl chloride input, or the reaction temperature.

A number of side reactions occur during this conversion, the principal ones being the hydrolysis of ethyl chloride to ethanol and the subsequent formation of ethyl ether.

 $C_2H_5C1 + NaOH \longrightarrow C_2H_5OH + NaC1$

 $C_2H_5OH + C_2H_5C1 + NaOH \longrightarrow C_2H_5OC_2H_5 + NaC1 + H_2O$

The extent of these side reactions if reduced by increasing the sodium hydroxide concentration, decreasing the water content of the reaction mixture, and the presence of benzene or toluene. However, the ethyl chloride efficiency is still rather low.

At the end of the etherification, the pressure is released slowly, allowing the volatile ethyl chloride, ether, alcohol, and any diluent to distill off. The spent sodium hydroxide is drained off for recovery, and the product is purified by washing in stainless steel equipment. The by-products, ethanol and ethyl ether may be reconverted to ethyl chloride by heating with HCl in the presence of ZnCl₂ catalyst.

- 2. <u>Input Materials</u> Basis 56 kg ethyl cellulose Cellulose - 45 kg (99.2 lbs) 50% NaOH solution - 628 kg (1384.5 lbs) Ethyl chloride - 220 kg (485.0 lbs) Benzene or toluene Hydrogen chloride
- 3. Operating Parameters

Temperature: Alkali cellulose 35-40°C (95-104°F)

Ethylation 90-150°C (194-302°F)

Pressure: 0.2-2.2 MPa (2-22 atm)

Catalyst: By-product conversion - ZnCl₂

4. Utilities

Not given

5. Waste Streams

Purification (air)

Ethyl chloride, ethanol, ethyl ether, and benzene or toluene may be present in air emissions from distillation operations.

Purification (water)

Waste water from washing operations may be expected to contain quantities of caustic soda, ethyl cellulose, and all of the pollutants previously mentioned. Degraded cellulose may also be present along with sodium chloride.

By-product conversion

Ethyl chloride, ether, alcohol, spent catalyst, and tars may be present in the waste streams from this process step.

Benzene/Toluene recovery

Benzene or toluene may be present in the extract water, and in air emissions along with purification solvents.

6. EPA Source Classification Code - None

7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 4 (1964), p. 640, 641.

INDUSTRIAL ORGANIC CHEMICALS

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PROCESS NO. 119
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Ethanol (hydration of ethylene) and Diethyl Ether

$$CH_2 = CH_2 + H_2O \xrightarrow{(H_3PO_4)} CH_3CH_2OH + CH_3CH_2OCH_2CH_3 + 44.2 \text{ MJ/kg-mole}$$
(19,000 Btu/lb-mole)

1. <u>Function</u> - Synthetic ethanol has been manufactured from ethylene by two processes, i.e., the direct hydration process and the absorption process. The last large absorption process plant shut down in late 1974, so that essentially all of the synthetic ethanol is now being manufactured by the direct hydration process.

The hydration process involves catalytic addition of water to ethylene. Phosphoric acid, impregnated on an inert support such as Celite diatomite is commonly used. High pressures and temperatures are required for this exothermic process.

Fresh ethylene feed (98+%) plus recycle ethylene are compressed and mixed with 0.5-1.0 mole water per mole of ethylene. The gaseous mixture is preheated and then fed to a reactor. The vapor leaving the reactor is slightly hotter than the feed because of the exothermic reaction. The reactor effluent is cooled and treated with a small amount of caustic soda. The condensed ethanol/water mixture is sent to a separator where the aqueous ethanol is separated from unreacted gases. The gases are scrubbed with water to remove traces of ethanol, and are returned to the reactor as recycle ethylene. A small purge stream is removed to prevent buildup of impurities in the recycle ethylene.

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The aqueous ethanol solution from the scrubbing step is combined with the liquid product from the separator. The mixture is concentrated to 190° proof ethanol (95 vol %) by conventional distillation techniques. For anhydrous ethanol (absolute ethanol; 200° proof ethanol), the 95 vol % ethanol is fed to a dehydrator where water is removed as an azeotrope. Benzene is commonly used.

Relatively small amounts of by-products are produced in this reaction. They are: ether, aldehydes, higher hydrocarbons, higher alcohols, and ketones. Ether is the principle by-product.

The conversion of ethylene to ethanol is limited to low values per pass by the thermodynamic equilibrium at practical operating conditions. Therefore, a large recycle volume of unconverted ethylene is required. The temperature, pressure, water to ethylene ratio, and ethylene purity are important variables, and must be closely controlled for maximum efficiency.

Ethanol is also produced by fermentation. It can be synthesized by an oxo-related process which involves the reaction of methanol with carbon monoxide and hydrogen at high temperature and pressure over a cobalt catalyst. Ethanol is also produced in minor quantities during the oxidation of n-butene.

2. Input Materials

Ethylene - 747 kg/metric ton (1495 lb/short ton) product Water - 4,682 kg/metric ton (9,365 lb/short ton) product Hydrogen - 0.035 kg/metric ton (0.07 lb/short ton) product Sodium hydroxide - 2.5 kg/metric ton (5 lb/short ton) product

- 3. Operating Parameters - The conditions recommended for highest efficiency are: Reactor temperature - 299°C (570°F) Reactor pressure - 6.7-7.0 MPa (661-69.1 atm) Reactor feed ethylene concentration, water free basis - 85% Ethylene makeup concentration -97+% Water to ethylene ratio in feed - 0.6 Space velocity - 26.5-30 (volume of gas at 15.6°C (60°F) and 101 kPa (1 atm)/min - vol. of catalyst) Ethylene conversion per pass - 4.2-5% Water conversion - 7.0% Overall yield, ethylene to ethanol - >97% Utilities - Basis - 84,900 metric tons (93,600 short tons)/yr 4. Water - $1.8 \text{ m}^3/\text{s}$ (28.900 gpm) Steam - 97,800 kg (216,000 1b)/hr Fuel gas - 11 MW (38 MM Btu)/hr (excluding 1.2 dam (45,000 scf)/hr gas bleed) Electricity - 1.747 kW Nitrogen - 6.2 m^3 (2,200 scf)/hr
- 5. Waste Streams

<u>Water</u> - The major source results from separation of product from process bottoms and may amount to 15-30 kg (33-66 1b) of COD/metric ton of product.

<u>Air</u> - 1.1 kg (2.5 lb) ethanol/metric ton of product plus traces of acetaldehyde, ether, ethylene, and ethylene impurities from the purification section. Leaks in compressor seals, as well as in

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the gas handling system, are also a possible source of air pollution. Also present are olefin polymers, acetaldehyde, and diethyl ether.

6. EPA Source Classification Code - None

7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 8 (1965), p. 434, 435, 436.

Considine, D. M., Ed., <u>Chemical and Process Technology Encyclopedia</u>, McGraw-Hill Book Co., New York, N.Y., 1974, p. 423-427.

Gloyna, E. F., and Ford, D. L., "The Characteristics and Pollutional Problems Associated with Petrochemical Wastes," Prepared for FWPCA, Contract 14-12-461, Robert S. Kerr Water Research Center, Ada, Oklahoma, February 1970.

U.S. Patent 2,773,910 (December 11, 1956).

Sittig, M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition, Noyes Development Corp., Park Ridge, N.J., 1969, p. 297. Mono-, di-, triethylamine (from ethanol and ammonia)

 $C_{2}H_{5}OH + 2NH_{3} \rightarrow C_{2}H_{5}NH_{2} + H_{2}O$ $C_{3}H_{5}NH_{2} + C_{2}H_{5}OH + NH_{3} \rightarrow (C_{2}H_{5})_{2}NH + H_{2}O$ $(C_{2}H_{5})_{2}NH + C_{2}H_{5}OH + NH_{3} \rightarrow (C_{2}H_{5})_{3}N + H_{2}O$

 <u>Function</u> - Ethylamine, diethylamine, and triethylamine are all produced by the reaction of ethyl alcohol and ammonia under heat and pressure. The reaction is run in the vapor phase.

Although mixtures of amines are always produced, the reaction products can be controlled to a certain extent. A large excess of ammonia favors ethylamine production. If this product is recycled, more di- and triethylamines will be produced. These amines used to be synthesized from ethyl chloride until they became large volume chemicals. Then the starting material was switched to the cheaper ethyl alcohol.

The alkylation of ammonia by alcohols has been accomplished in the presence of hydrogen and a hydrogenation catalyst consisting of a mixture of nickel and copper deposited on alumina activated with boric acid. Thus two moles of ethanol, one mole of ammonia, and three moles of hydrogen were passed over the catalyst at 220°C to yield a product consisting of ethyl-, diethyl-, and triethylamines in the ratio of 1:5:3. The conversion of ethanol amounted to 52 percent.

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2. Input Materials - per metric ton (2,205 lbs) product

	MEA	DEA	TEA
Ethyl alcohol, kg (lbs)	1122 (2474)	1384 (3051)	1500 (3307)
Ammonia - excess, kg (1bs)	402 (886)	248 (547)	179 (395)
Catalyst, kg (lbs)	12 (2.6)	1.2 (2.6)	1.2 (2.6)
Hydrogen, m ³ (ft ³)	14.2 (500)	14.2 (500)	14.2 (500)

3. Operating Parameters

Temperature - 400°C (752°F) Pressure - 10.13 MPa (100 atm) Reaction time - 2-3 hrs.

- 4. <u>Utilities</u> per 45.5 kg (100 lbs) product Steam @ 1.04 MPa (10.3 atm) - 680.4 kg Cooling water (10°C rise) - 26.5 m³ (7,000 gal.) Electricity, MJ-28.8 (8 kWh)
- 5. <u>Waste Streams</u> Excess ammonia, ethyl alcohol, and all three amines may be present in the off-gas from the ammonia stripper. Organic and inorganic ammonium salts, as well as the pollutants mentioned, should be expected in the wastewater stream. If the liquid phase process is used, the alcoholic solvent may be present in both cases. Volatiles may also be emitted from other processing steps.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition Interscience Publishers, New York, N.Y., Vol. 8 (1963), p. 455. 7. References

Astle, M. J., <u>Industrial Organic Nitrogen Compounds</u>, Rheinhold Publishing Corp., New York, N.Y., 1961, p. 7, 8.

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 511, 512.

"1973 Petrochemical Handbook","Hydrocarbon Processing,"November, 1973, p. 115.

Ethyl Oxalate (direct esterification)

 $(\text{COOH})_2 \cdot 2\text{H}_20 \longrightarrow (\text{COOH})_2 \xrightarrow{\text{EtOH}} (\text{COOEt})_2$

 Function - Ethyl oxalate is manufactured by the conventional esterification of oxalic acid. Oxalic acid is sufficiently acidic to serve as its own esterification catalyst, but mineral acids and ion exchange resins are sometimes used.

Since commercial oxalic acid is generally the dihydrate, the process may be more economical if the acid is dehydrated and esterified in a single operation. If the dihydrate is reacted, it is necessary to remove twice the usual proportion of water to complete the reaction.

Low-boiling solvents capable of forming azeotropes with water are preferred to remove the water of crystallization. After dehydration, esterification is carried out in the same reactor using the same solvent to remove water produced during the reaction. The last traces of water are most difficult to remove and this is accomplished by a special step in the rectification. Yields of 90 - 92% are achieved.

2. Input Materials

Oxalic acid dihydrate - 0.95 kg/kg ethyl oxalate Ethanol - 0.69 kg/kg ethyl oxalate Low-boiling solvent

3. Operating Parameters

Temperature: not given

Pressure: not given

Catalyst: Mineral acids

Ion exchange resins

4. Utilities

Not given

- 5. <u>Waste Streams</u> Although no information was available, wastewater streams from the separator may be expected to contain quantities of solvent, unreacted ethanol and oxalic acid, ethyl oxalate, and reaction intermediates and by-products. Some solvent and ethanol are probably released through air vents in the separator and other processing equipment.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 14 (1967), p. 370.

Ethyl Acrylate (direct esterification)

 $CH_2 = CHCOOH + C_2H_5OH \longrightarrow CH_2 = CHCOOC_2H_5 + H_2O$

1. <u>Function</u> - Ethyl acrylate is usually made in a modification of an acrylic acid process by adding ethanol to the reactant mix. The processes based on propylene for acrylic acid appear to be growing fastest because of propylene's low cost; acetylene and ethylene are being phased out as raw materials. The esterification of acrylic acid is accomplished in the presence of sulfuric acid, Dowex[®] 50 ion exchange resin, or silica gel catalyst.

Hydroquinone or other polymerization inhibitors are added during distillation.

2. Input Materials

Acrylic acid - 737.5 kg/Mg product

Ethanol - 476.5 kg/Mg product

3. Operating parameters

Temperature - not given Pressure - not given Catalyst - H₂SO₄, Dowex[®] 50 ion exchange resin or silica gel. 4. <u>Utilities</u>^{*} - basis: 0.430 kg/sec (0.95 lb/sec) capacity Steam - 364 kg/sec (8 lb/sec) Power - 169 kW capacity Cooling water - 151 dm³/sec (40 gal/sec) Makeup water - 5.11 dm³/sec (1.35 gal/sec)

Refrigeration - 15.4 Mg

* Data from plant using Dower 50 ion exchange resin.

5. <u>Waste Streams</u>*

Heavy ends from the ester purification column: Polymers - 11.9 kg/Mg (1b/1000 1b) product Hydroquinone - 13.75 kg/Mg (1b/1000 1b) product Overhead from the ester purification section (air): Ethanol - 2.65 kg/Mg (1b/1000 1b) product Ethyl acrylate - 1.6 kg/Mg (1b/1000 1b) product Ethyl acetate - 5.25 kg/Mg (1b/1000 1b) product Sodium carbonate - 0.26 kg/Mg (1b/1000 1b) product

- 6. EPA source classification code None
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 4," "Chemical Engineering," April 15, 1974, p. 90.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical Processes</u>, Technomic Publishing Co., 1975.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 297, 298.

* Data from plant using Dowex 50 ion exchange resin.

Acetal (from acetaldehyde and ethanol)

 $CH_3CHO + CH_3CH_2OH \xrightarrow{cat.} CH_3CH(OCH_2CH_3)_2$

- 1. <u>Function</u> Acetal (specifically, diethyl acetal) is formed by the condensation reaction of acetaldehyde and ethanol. Catalysts used in this process may be acids (hydrochloric, p-toluenesulfonic) or salts (calcium chloride, ammonium chloride). In some cases, azeo-tropic distillation is employed to remove the water of reaction and improve the yield.
- 2. Input Materaisl

Acetaldehyde Ethanol

3. Operating Parameters

Temperature: Not given Pressure: Not given Catalyst: acids or salts

- 4. Utilities Not given.
- 5. <u>Waste Streams</u> Wastewater streams from the purification section may contain acetaldehyde, ethanol, acetal, and either acid or salt catalyst. Volatile reactants and products may be emitted through air vents in the reactor, separator, and other process equipment.
- 6. EPA Source Classification Code None.
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 81, 108. Acetaldehyde (from ethanol)

 $CH_3CH_2OH + 1/2 O_2 \xrightarrow{Ag} CH_3CHO + H_2O$

 <u>Function</u> - As of 1974, only 15% of the United States acetaldehyde capacity was based on ethanol. There are two processes for conversion of ethanol to acetaldehyde, i.e., oxidative dehydrogenation and catalytic dehydrogenation.

Oxidative dehydrogenation

The vapor phase reaction is carried out over solid silver gauze catalyst at 538°C (1000°F). Aqueous ethanol, steam, and air are fed to the oxidizer (reactor). The reactor effluent is condensed and is passed to a phase separator which also serves as a scrubber (refrigerated water). The off gases are vented from the system and the wash is combined with the liquid stream. The combined liquid stream is sent to a flash column where it is separated into acetaldehyde product, alcohol for recycle, and waste water. The acetaldehyde product from the flash column is sent to an ethanol recovery still where acetaldehyde product is taken from the top and the bottoms (primarily ethanol) are recycled to the reactor.

Catalytic dehydrogenation

The primary reaction is:

 $CH_3CH_2OH \xrightarrow{Cu} CH_3CHO + H_2$

The vapor phase reaction is carried out over a solid copper catalyst promoted by cobalt or chromium on an asbestos support at 260°C (500°F). The recovery and isolation systems are almost identical to those in oxidative dehydrogenation. The yields in both processes range from 85 to 95%. 2. Input Materials

Oxidative dehydrogenation: air ethanol steam water Catalytic dehydrogenation: ethanol - 1150 kg/metric ton (2,535 lbs/ton) acetaldehyde 3. Operating Parameters Oxidative dehydrogenation: temperature - 538°C (1000°F) pressure - 410 kPa (4.05 atm) flow rate - not given equipment - multitubular reactor, phase separator, flash column, still catalyst - solid silver gauze temperature - 260°C (500°F) Catalytic dehydrogenation: pressure - not given flow rate - not given equipment - see oxidative dehydrogenation catalyst - solid copper catalyst promoted by cobalt or chromium on an asbestos support 4. Utilities - The water usages of two plants are: Cooling water Process water

Plant 1	5.9 kg/kg product	47.2 kg/kg product
Plant 2	0.45 kg/kg product	45.4 kg/kg product

5. Waste Streams

<u>Air</u> - Off gases from the phase separator; it has been estimated that 12.2 Mg (27 MM lb) of CO is emitted annually from this industry. <u>Water</u> - The only wastewater stream generated is either from the acetaldehyde flash column or ethanol recovery still. It contains liquid products such as acetaldehyde, ethanol, and ethyl acetate. Data on two plants (one using each of the two processes) was as follows:

	<u>Plant l</u>	<u>Plant 2</u>
Flow	6.0 m ³ / 454 kg product	529 dm ³ / 454 kg product
COD	0.186 kg/m ³ (186 mg/1) 1.1 kg/454 kg	
BOD	0.084 kg/m ³ (84 mg/ 1) 0.50 kg/454 kg	
TOC		14.4 kg/m ³ (14,400 mg/1) 7.6 kg/454

kg

6. EPA Source Classification Code - None

7. <u>References</u>

Austin, G. T., "Industrially Significant Organic Chemicals -Part 1," "Chemical Engineering," January 21, 1974, p. 128. Waddams, A. L., <u>Chemicals from Petroleum</u>, 3rd Ed., John Murray Ltd., London, Eng., 1973, p. 75, 76.

Sittig, M., Pollution Control in the Organic Chemical Industry,

Noyes Data Corporation, Park Ridge, N.J., 1974, p. 47-50.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N.Y., 1975, p. 3.

Diethyl Sulfate (from ethylene)

$$CH_2 = CH_2 \xrightarrow{H_2SO_4} (CH_3CH_2)_2SO_4$$

- 1. <u>Function</u> The most economical route to diethyl sulfate involves the action of 96% sulfuric acid on ethylene at 60°C. The resulting mixture of 43% diethyl sulfate, 45% ethyl hydrogen sulfate, and 12% sulfuric acid is heated with anhydrous sodium sulfate under vacuum and diethyl sulfate is obtained in 86% yield.
- 2. Input Materials

Ethylene

Sulfuric acid

Sodium sulfate

- <u>Operating Parameters</u>
 Temperature 60°C (140°F)
- 4. Utilities not given
- 5. <u>Waste Streams</u> No process information was available. If excess acid and the water of reaction are separated prior to distillation, wastewater streams may contain sulfuric acid, diethyl sulfate, and monoethyl sulfate, a reaction intermediate. Miscellaneous air emissions may contain the same pollutants.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 19 (1969), p. 492.

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7. <u>References</u> (continued)

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 278, 504.

Propanoic Acid (from ethylene)

 $H_2C=CH_2 + H_2O + CO \longrightarrow CH_3CH_2COOH$

1. <u>Function</u> - One competitive process for the production of propionic acid involves the reaction of ethylene, carbon monoxide, and water in the presence of a NiCO₃/H₃BO₃ catalyst. The liquid phase reaction is run in a stainless steel autoclave. The product (40% propionic acid in water) may be purified by rectification. The autoclave is charged with 300 g of 17.2 weight percent propionic acid, 0.823 g Ni as NiCO₃, 3.15 g H₃BO₃, 100 g C₂H₄, and 50 g CO. The temperature is raised to 153°C at 13.88 MPa (137 atm) at which time the temperature and pressure jump to 288°C and 23.3 MPa (230 atm). The reaction is cooled after 30 min and filtered to yield a 40% solution of propionic acid which also contains 0.70 g Ni. In a continuous process, the normal rate of 292 g acid/g Ni goes to 1320 g acid/g Ni by using a stoichiometric excess of H₃BO₃ with respect to the nickel ion concentration.

Propionic acid has also been prepared from ethanol and carbon monoxide.

2. Input Materials

Ethylene - 100 g (0.22 lbs) Carbon monoxide - 50 g (0.11 lbs) Propionic acid (17.2 wgt %) - 300 g (0.66 lbs) H₃BO₃ - 3.15 g (0.0069 lbs) Ni (as NiCO₃) - 0.823 g (0.0018 lbs)

3. Operating Parameters

Temperature:	lst stage	153°C (307° F)
	2nd stage	288°C (550° F)
Pressure:	lst stage	13.88 MPa (137 atm)
	2nd stage	23.3 MPa (230 atm)
Catalyst:	NICO3/H3BO3	

- 4. Utilities None given.
- 5. <u>Waste Streams</u> Propionic acid will be in the aqueous waste streams along with nickel salts and boric acid. Excess CO and ethylene may be present in air emissions.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 16 (1968), p. 555.

Sittig, M., Oxo Process and Products, Noyes Development Corp., Park Ridge, N.J., 1966, p. 105, 106.

U.S. Patent 3,151,155 (September 29, 1964).

PROCESS NO. 127

Diethyl Ether (from ethanol)

$$2 \text{ CH}_3 \text{CH}_2 \text{OH} \longrightarrow (\text{CH}_3 \text{CH}_2)_2 \text{O} + \text{H}_2 \text{O}$$

 Function - There have been several processes for the manufacture of ethyl ether, i.e., dehydration of ethanol with sulfuric acid;

$$cH_3cH_2OH + H_2SO_4 \longrightarrow CH_3CH_2HSO_4 + H_2O$$

 $cH_3cH_2OH + CH_3cH_2HSO_4 \longrightarrow (CH_3CH_2)_2O + H_2SO_4$

the addition of sulfuric acid to ethylene (indirect hydration or absorption process);

$$CH_2 = CH_2 + H_2 SO_4 \longrightarrow CH_3 CH_2 HSO_4$$

$$CH_3 CH_2 OS = O + CH_2 = CH_2 + H_2 O \longrightarrow (CH_3 CH_2)_2 O + H_2 SO_4$$

the direct hydration of ethylene.

$$2 \text{ CH}_2 = \text{CH}_2 + \text{H}_2 0 \longrightarrow (\text{CH}_3 \text{CH}_2)_2 0$$

The dehydration process was designed primarily for the production of ethyl ether, whereas ethyl ether is the principal by-product in the direct or indirect hydration process. At present, most of the ethyl ether produced is manufactured by the vapor phase catalytic dehydration of ethanol.

2. Input Materials

Et hanol

Catalyst (tungsten oxide/A1203)

3. Operating Parameters

Temperature: 120-375°C (248-707°F) Pressure: 0.103-10.3 MPa (1.02-102.1 atm) Contact Time: 30 min

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Unreacted ethanol and some catalyst should be present in the waste streams.
- 6. EPA Source Classification Code None

7. References

Faith, W. L., et al., Industrial Chemicals, 3rd Edition, John Wiley and Sons, New York, N. Y., 1965, p. 335-338.

U. S. Patent 2,805,260 (September 3, 1957).

Chemical Technology, Barnes and Noble Books, New York, N. Y., Vol. 4 (1972), p. 333.

Sittig, M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition, Noves Development Corp., Park Ridge, N. J., 1969, p. 326. Acetamide (ammonolysis of ethyl acetate)

 $\operatorname{CH}_3\operatorname{COOC}_2\operatorname{H}_5 + \operatorname{NH}_3 \longrightarrow \operatorname{CH}_3\operatorname{CONH}_2 + \operatorname{C}_2\operatorname{H}_5\operatorname{OH}$

 Function - Acetamide is currently produced by the interaction of ethyl acetate and aqueous ammonia. Ethanol is a by-product of this reaction. The crude product is purified by crystallization.

In the past, acetamide has been made from the acid chloride, acetic anhydride, ammonium acetate, acetic acid, and ketene, among other materials. Recently, the ethyl acetate route has proven most economical.

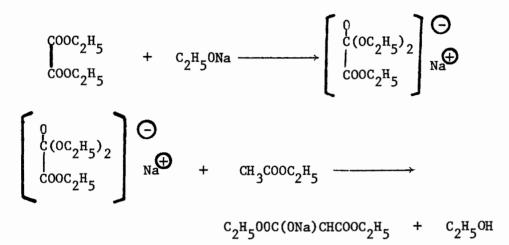
- <u>Input Materials</u>
 Ethyl acetate
 Aqueous ammonia
- 3. <u>Operating Parameters</u> Not given
- 4. <u>Utilities</u>

Not given

- 5. <u>Waste Streams</u> Waste water and air emissions from the ammonia stripper may contain any of the reactants or products. Some additional air emissions may result from recycling operations.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 144.

Ethyl Sodium Oxalacetate



- <u>Function</u> Ethyl sodium oxalacetate is made by the reaction of pure ethyl acetate with the adduct formed by the reaction of diethyl oxalate and sodium alcoholate.
- 2. Input Materials

Ethyl acetate Ethyl oxalate Sodium

Absolute alcohol ether

- Operating Parameters
 Addition of reagents Ice-water bath
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Wastewater streams may contain organic sodium salts and any of the reactants or products.

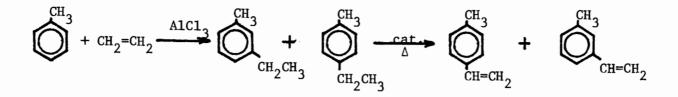
6. <u>EPA Source Classification Code</u> - None

7. <u>References</u>

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Houben-Weyl, <u>Methoden Der Organischen Chemie</u>, Vierte Auflage, Georg Thieme Verlag, Sttutgart, Bd. 8 (1952), p. 582.

Vinyltoluenes



 <u>Function</u> - Vinyltoluenes are produced commercially by alkylation of toluene with ethylene followed by dehydrogenation of the m-, and p-ethyltoluenes. Toluene is alkylated with ethylene in a reactor similar to that used for ethylbenzene manufacture. Reaction temperature is kept below 100°C.

The crude alkylation product consists of a mixture of o-, m-, and p-ethyltoluene, polyethyltoluenes, benzene, ethylbenzene, xylenes, "lights", and tars.

The crude product is cooled, washed with alkali, and purified by a series of fractional distillations. Toluene, polyethyltoluenes, and the unusable o-ethyl toluene are recycled to the alkylator while other by-products are reclaimed by other means. The m- and p-ethyltoluene mixture is then heated to 450-500°C, mixed with two to three times its weight of super-heated steam, and passed over a dehydrogenation catalyst.

The separation of the m- and p- vinyltoluenes from the crude hydrogenation mixture is accomplished by a series of vacuum distillations.

2. Input Materials

Ethylene

Toluene

A1C13

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- 3. Operating Parameters
 - **Ethylation**

Temperature: < 100°C (212°F)

Pressure: Not given

Dehydrogenation

Temperature: 450-500°C (842-932°F)

Pressure: Not given

Catalyst: various dehydrogenation catalysts

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Ethylation: Effluents likely contain solutions of aluminum salts, HCl, sodium hydroxide, sodium chloride, and traces of the various aromatic reactants and by-products.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 19 (1969), p. 77-80.

INDUSTRIAL ORGANIC CHEMICALS

PROCESS NO. 131

Ethylene Dichloride (1,2-dichloroethane) (direct chlorination)

 $\mathbf{H}_{2}\mathbf{C}=\mathbf{CH}_{2} + \mathbf{C1}_{2} \xrightarrow{\mathbf{FeC1}_{3}} \mathbf{C1CH}_{2}\mathbf{CH}_{2}\mathbf{C1}$

1. <u>Function</u> - There are two commercial processes for making ethylene dichloride (EC) from ethylene: the oxychlorination process and the direct addition process. Over 95% of the EC produced in the United States in 1974 was made by the "balanced process," which is a balanced combination of the two processes. Approximately 2.4% of the EC was made exclusively by oxychlorination, while 2.6% was made exclusively by the direct addition of chlorine to ethylene. The oxychlorination process is described in Process No. 131.

As of 1975 EC accounts for close to half of the chlorine used to make chlorinated organics. Most of the EC is produced captively in the synthesis of vinyl chloride monomer.

The direct chlorination of ethylene may be carried out in the liquid phase in the presence of ferric chloride catalyst.

Approximately equimolar proportions of acetylene-free ethylene and chlorine are fed to a tower-type reactor through distributors. The reaction is fast, complete, and exothermic. The tower-type reactor is unique in that the top is a fractionator, complete with vented reflux condenser.

The gas stream from the reactor is passed through a caustic scrubber, where the unreacted gases and traces of HCl are removed. The uncondensed gases (primarily unreacted ethylene and chlorine) are then totally recycled to the reactor.

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The liquid stream from the reactor is sent to a distillation column to remove heavy ends and then to a wash tower, where a caustic solution is used to remove some impurities. The crude product is sent to a distillation column for purification. Liquid EC, 99% pure (95% yields), is taken from the top of the fractionation column.

2. Input Materials

Acetylene-free ethylene - 297 kg/metric ton product Chlorine - 730 kg/metric ton product Ferric chloride - amount not given

3. Operating Parameters

Temperature of reactor - 90°C (194°F)

Pressure in reactor - 150 kPa (1.48 atm)

4. Utilities

Basis: 72.5 Gg/yr capacity (reactor section)

243 Gg/yr capacity (purification section)

Water: cooling - 21.3 m³/minute process and makeup - 450 dm³/minute Steam - 19.5 Mg/hr

Refrigeration - 21.9 MJ (8.09 kWh)

5. <u>Waste Streams</u>

Total hydrocarbon emissions (est.) from the direct process industry -

13.1 Gg (29 MM 1b)/yr (all volatile organics except methane)

Air: vent on reflux condenser

Ethane - 3.0 kg/metric ton EC

Ethylene - 7.5 kg/metric ton EC

- Methane 3.0 kg/metric ton EC
- Chlorine 500 g/metric ton EC
- HC1 500 g/metric ton EC

Water: HCl absorber (scrubber)

Chlorine - 874 g/metric ton EC

EC - 2.45 kg/metric ton EC

HC1 - 3.8 kg/metric ton EC

Vinyl chloride (VCM) - 600 g/metric ton EC

Methyl chloride - 50 g/metric ton EC

Ethyl chloride - 50 g/metric ton EC

Purification section - caustic storage

EC - 150 g/metric ton EC

Sodium hydroxide - 600 g/metric ton EC

Sodium chloride - 200 g/metric ton EC

Purification section - filter effluent

EC - 300 g/metric ton EC

Sodium hydroxide - trace

The waste water streams of one plant were surveyed (combined liquid effluents from the reactor offgases scrubber and from the wash tower) Flow - 3.63 dam³/454 kg EC COD - 6.050 kg/m³; 2.9 kg/454 kg EC BOD₅ - not given TOC - 1.106 kg/m³; 0.40 kg/454 kg EC Solid: purification section - filter effluent Mercuric hydroxide - 3.5 g/metric ton EC Tars - trace Solids (as carbon) - 50 g/metric ton EC Purification section - distillation column bottoms EC - 1.5 kg/metric ton EC

1,1,2-trichloroethane - 2.45 kg/metric ton EC Tetrachloroethane - 2.45 kg/metric ton EC Tars - trace

- 6. EPA Source Classification Code None
- 7. References

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corp., Park Ridge, N.J., 1974, p. 146.

Considine, E. M., Ed.-in-Chief, <u>Chemical and Process Technology</u> <u>Encyclopedia</u>, McGraw-Hill Book Company, New York, N.Y., 1974, p. 1135-1136.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Prepared for EPA, Final Report MRC-DA-406, Contract No. 68-02-0226, December 1973, p. 194-195.

"Chemical Week," March 12, 1975, p. 35, <u>High Polymers</u>, Leonard, E. C., Editor, Vol. 24, Part 3, p. 1220-1221.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 392. Ethylene Dichloride (oxychlorination) $CH_2=CH_2 + 1/2 \ O_2 + 2HC1 \xrightarrow{CuCl_2} C1CH_2CH_2C1 + H_2O$

1. <u>Function</u> - As of late 1974, one plant of the 12 plants producing EC, used oxychlorination exclusively. The other 11 plants used the oxychlorination of ethylene as part of the "balanced process." The balanced process is a combination of direct addition of chlorine to ethylene and oxychlorination of ethylene. The balanced process acquired its name from the fact that the overall process is balanced to yield only vinyl chloride, (VCM). There is no net production of HC1.

The manufacture of EC exclusively by the oxychlorination process accounted for only 2.4% of the total production in 1974 (108 Mg (240 MM 1b) out of 46 Gg (10.045 billion 1b)).

Either a fluid bed catalyst or fixed bed catalyst can be used. Approximately stoichiometric proportions of ethylene, anhydrous hydrogen chloride, and air are fed to the "oxy" (catalytic) reactor at low pressure and moderate temperatures. The reactor effluent is cooled generally either by direct water quench or indirect heat exchange. The partially condensed effluent is sent to a phase separator. The gases are contacted with water in a quench column (absorber) for removal of HC1. The resulting hydrochloric acid stream is treated offsite to recuperate the anhydrous hydrogen chloride. The gases are then sent to the EC stripper for recovery of entrained EC which is combined with the EC effluent from the phase separator. Noncondensible gases (mainly nitrogen) are vented to the atmosphere.

The aqueous phase from the decanter is collected in the effluent separator and discharged to waste. The organic phase is usually treated with aqueous caustic soda to remove traces of HCl. It is then sent to product distillation to remove water and chlorinated hydrocarbon impurities which are sent to offsite disposal. The crude EC (96 - 98% purity) is usually combined with the crude EC from the direct chlorination. The combined stream is purified by distillation in an EC finishing column prior to being sent to the cracking furnace for product of VCM (Process No. 133).

<u>Input Materials</u> - Basis: Production of 317.5 Mg/yr EC
 Ethylene (99.9% purity) - 12.3 Mg/hr;

0.288 metric tons/metric ton EC

Anhydrous hydrogen chloride - 30.5 Mg/hr;

0.711 metric tons/metric ton EC

Air - 42 Mg/hr; 0.961 metric tons/metric ton EC

Dilute caustic soda - 313 kg/hr; 0.007 metric tons/metric ton EC Catalyst - cupric chloride impregnated on a fluid or fixed bed support Waste disposal system (direct fired boiler plus scrubber emission control system):

Process vent gas - 36 Mg/hr; 493 m³;

(17,420 scf)/minute @38°C (100°F)

Caustic feed - 367 kg/hr

Waste disposal system (thermal incinerator and scrubber system):

Combustion air - 14 Mg/hr @27°C (80°F)

Process vent gas - 36 Mg/hr; 493 m³;

(17,420 scf)/minute @38°C (100°F)

Caustic feed - 367 kg/hr

3. Operating Parameters

Reactor outlet temperature - 302°C (575°F) Reactor temperature - 232 - 315°C (450 - 600°F) Preheated feed temperature - 149°C (300°F) Reactor pressure - 239 - 618 kPa (2.36-6.10 atm) Waste disposal system (direct fired boiler plus scrubber emission control system): Boiler temperature - 982°C (1800°F) Flue temperature - 288°C (550°F) Flue gas temperature from packed scrubbing tower - 60°C (140°F) Waste disposal system (thermal incinerator and scrubber system): Incinerator temperature - 982°C (1800°F) Combustion air and process gas preheat - 149°C (300°F) Incinerator flue temperature - 871°C (1600°F) Flue gas temperature from packed scrubbing tower - 77° (170°F) 4. Utilities - not given for overall oxychlorination process; data

available on some parts of process based on reactor outlet tempera-

Heat out

Steam generation - 2.82 MG/kg EC

Reactor heat loss - 13.9 kJ/kg EC

Quench plus effluent cooling (302°C to 38°C) - 1.4 MJ/kg EC

Heat in

Exothermic heat of reaction

EC formation - 3.21 MJ/kg EC

Effluent neutralization - 4.6 kJ/kg EC

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Feed vaporization and preheat (149°C) - 372 kJ/kg EC
    Waste disposal system (direct fired boiler plus scrubber emission
    control system):
    Feed water - 21.2 Mg/hr @116°C
    Steam generation @1.8 MPa (245 psig) - 20.2 Mg/hr (17.8 atm)
    Blowdown - 998 kg/hr @207°C
    Natural gas - 420 kg/hr
    Incinerator flue gas to packed scrubbing tower - 57.2 Mg/hr;
    794 \text{ m}^3/\text{min}
    Quench water - 1.64 Mg/hr
5. Waste Streams - basis: production of 317.5 Mg/yr EC
   Air emissions:
    Process vent gas - 0.9311 metric tons/metric ton EC
    Distillation vent gas - 0.0123 metric tons/metric ton EC
    Total hydrocarbon air emissions (est.) from oxychlorination industry
    (all volatile organics) - 43 Gg/yr
    Total carbon monoxide emissions (est.) from oxychlorination industry -
    9.9 Gg/yr
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Typical composition of process vent gas:

Component	Composition, 	Flow rate, kg/hr
Carbon dioxide	0.6-3.5	957
Carbon monoxide	0.6-1.3	264
Nitrogen	82–95	31.6
Oxygen	0.5-7.5	1.8
Methane	0 -5.0	78
Ethylene	0.2-0.8	191
Ethane	0 -3.8	260
EC	0.07-0.75	272
Ethyl chloride	0 -0.75	231
Aromatic solvent	0 -0.75	42.6

<u>Water</u>:

Combined waste water - 0.1908 metric tons/metric ton EC Waste disposal system - scrubber reject (from thermal incinerator and scrubber system) - 11.9 Mg/hr Scrubber effluent (from thermal incinerator and scrubber system) -80 Mg/hr; 1.29 dam³/min Waste disposal system - scrubber reject (from direct fired boiler plus scrubber emission control) - 11.9 Mg/hr Scrubber effluent (from direct fired boiler plus scrubber emission control) - 62.1 Mg/hr; 906 m³/min. Solids emissions (est.): Particulates - 181 Mg/yr

6. EPA Source Classification Code - None

7. References

Considine, D. M., Ed.-in-Chief, <u>Chemical and Process Technology</u> <u>Encyclopedia</u>, McGraw-Hill Book Comapny, New York, N.Y., 1974, p. 1137-1138.

Anon., "Engineering and Cost Study Industry, Vol. 3, Ethylene Dichloride Manufacture by Oxychlorination," PB 240, 492, prepared for EPA, Contract 68-02-0255, Air Products and Chemicals Inc., November 1974. Vinyl Chloride ("Balanced Process")

$$CH_2C1CH_2C1 \longrightarrow CH_2=CHC1 + HC1$$

 <u>Function</u> - The synthesis of vinyl chloride monomer (VCM) uses an ethylene and chlorine feedstock first to produce ethylene dichloride (EC) which is then pyrolyzed to yield VCM. In the "balanced process" the HCl formed in the cracking of EC, is made to react with more ethylene in the presence of oxygen (oxychlorination reaction) to form more EC.

As of 1975, approximately 94% of the commercial vinyl chloride monomer (VCM) was manufactured by the thermal dehydrochlorination of EC. The other 6% was produced by addition of HCl to acetylene.

If low pressure cracking is used, the VCM and EC are generally removed from the quench vapor stream by condensation or absorption before the remaining HCl is compressed and fed to an oxychlorinating unit. If high pressure cracking is used, the quench vapor stream is fed directly to the distillation unit which consists of two columns, i.e., the anhydrous HCl recovery column, and the VCM recovery column.

In the HCl recovery column, anhydrous HCl is recovered overhead by distillation with refrigerated reflux. The HCl is purified to remove acetylene and vinyl chloride which would yield higher chlorinated by-products in the oxychlorination unit. In the VCM recovery column, EC and other high boiling impurities are separated by fractionation to produce high purity VCM. The EC and higher boiling impurities, as well as the EC and heavy bottoms from the quench

column, are reprocessed in the EC purification unit. Purified EC is recycled to the cracking furnace, and the heavy bottoms (higher chlorinated organics) are sent to waste disposal.

2. Input Materials

Ethylene dichloride - 2700 kg/metric ton VCM

- 3. <u>Operating Parameters</u> Temperature of cracking furnace effluent: 500 - 515°C (932-959°F) Pressure: 2.53 MPa (24 atm)
- 4. <u>Utilities</u> Basis: 91 Mg/yr capacity Total process water usage - 1.27 kg/kg VCM Total cooling water usage - 1571 kg/kg VCM Steam: 317 kg/hr Power: 361 kW (484 hp) Natural gas: 1.34 dam (47,500 scf)/hr Refrigeration: 46 kW (130 tons)/hr
- 5. Waste Streams

Tail gas absorber (air)

Hydrogen chloride - 0.1 kg/metric ton product Vinyl chloride - 5.0 kg/metric ton product 1,2-Dichloroethylene - 0.15 kg/metric ton product 1,1-Dichloroethylene - 0.4 kg/metric ton product Acetylene - 1.5 kg/metric ton product <u>Water</u> - The major waste water sources are the effluents from scrubbing systems required for HCl removal, recycle purification of EC and effluent from associated by-product production units. Some typical data are:

 Flow
 1.27 m³/454 kg product

 COD
 2.733 kg/m³

 3.475 kg/454 kg product

 TOC
 0.120 kg/m³

 0.150 kg/454 kg product

Solids (filter solids)

EC - 0.8 kg/metric ton product Tars as (C_2HC1) - 0.05 kg/metric ton product Solids (as c) - 0.2 kg/metric ton product

- 6. EPA Source Classification Code None
- 7. References

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corporation, Park Ridge, N.J., 1974, p. 214-215. Considine, D. M., Ed.-in-Chief, <u>Chemical and Process Technology</u> <u>Encyclopedia</u>, McGraw-Hill Book Co., New York, N.Y., 1974, p. 1136-1137. Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical Processes</u>, Final Report MRC-DA-406, prepared for EPA, Contract 68-02-0226, Task No. 9, December 1973, p. 198-199.

Anon., <u>Engineering and Cost Study of Air Pollution Control for the</u> <u>Petrochemical Industry. Ethylene Dichloride Manufacture by Oxychlori-</u> <u>nation</u>, PB-240 492, prepared for EPA, Contract No. 68-02-0255, Air Products and Chemicals, Inc., November 1974.

Leonard, E. C., Editor, High Polymers, Vol. XXIV, Part 3, p. 1214-1245.

7. References (continued)

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition John Wiley & Sons, New York, N.Y., 1975, p. 868.

"1975 Petrochemical Handbook," Hydrocarbon Processing," November 1975, p. 213-217.

Ethylene Diamine

 $\texttt{C1CH}_2\texttt{CH}_2\texttt{C1} + \texttt{2NH}_3 \longrightarrow \texttt{NH}_2\texttt{CH}_2\texttt{CH}_2\texttt{NH}_2 \cdot \texttt{2HC1}$

 <u>Function</u> - Both aqueous and anhydrous ammonia react readily with ethylene dichloride, in both the liquid and vapor phases to form ethylene diamine.

In the vapor-phase reaction ethylene dichloride and an excess of anhydrous ammonia are reacted at 150°C and 9.0 MPa (88.8 atm). Anhydrous ethylene diamine hydrochloride is formed, which, on treatment with caustic soda at 100°C, yields the free amine. The diamine vapors, steam, and unreacted ammonia are led to a dehydrating column where the diamine is dried and condensed.

In the liquid phase process, ethylene dichloride is treated with excess aqueous ammonia at 100°C and 1.0 MPa (9.87 atm). The aqueous product solution containing ethylene diamine hydrochloride, ammonium chloride, and ammonia is heated with caustic soda and fractionated. The ethylene diamine is drawn off and the ammonium chloride is returned to the reaction vessel.

Both processes result in low yields, on the order of 70%. Byproducts of this reaction include diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, and higher polymers.

2. Input Materials

Ethylene dichloride - 2.4 kg/kg product Ammonia Water (liquid-phase process) Sodium hydroxide 6-353 3. Operating Parameters

Vapor-phase reaction Temperature: 150°C (302°F) Pressure: 9.0 MPa (88.8 atm) Dehydrochlorination temperature: 100°C Liquid-phase reaction Temperature: 100°C (212°F) Pressure: 1.0 MPa (9.87 atm)

4. Utilities

Not given

5. <u>Waste Streams</u> - Reactor pressure vents, dehydration columns, and distillation columns are probably sources of ammonia, diamine, higher amine, and unreacted ethylene dichloride emissions.

Waste water streams from dehydrochlorination and drying operations undoubtedly contain quantities of caustic soda, and possibly smaller amounts of ammonium chloride, as well as the pollutants previously mentioned.

6. EPA Source Classification Code - None

7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 5," "Chemical Engineering," April 29, 1974, p. 145, 146.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 7 (1965), p. 31. U.S. Patent 2,805,254 (September 3, 1957).

Sittig, M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition, Noyes Development Corp., Park Ridge, N.J., 1969, p. 313.

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 513.

Aminoethylethanolamine

- a) $\operatorname{NH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{NH}_2$ + $\operatorname{C1CH}_2\operatorname{CH}_2\operatorname{OH} \longrightarrow \operatorname{NH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{NHCH}_2\operatorname{CH}_2\operatorname{OH}$ + $\operatorname{HC1}$
- b) $\operatorname{NH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{NH}_2 + \operatorname{CH}_2\operatorname{CH}_2 \longrightarrow \operatorname{NH}_2\operatorname{CH}_2\operatorname{CH}_2\operatorname{NHCH}_2\operatorname{CH}_2\operatorname{OH}$
- <u>Function</u> Aminoethylethanolamine may be prepared by the reaction of ethylenediamine with ethylene chlorohydrin or ethylene oxide.
- 2. Input Materials
 - a) Ethylenediamine
 Ethylene chlorohydrin
 - b) Ethylenediamine
 Ethylene oxide
- 3. Operating Parameters Not given
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste water may contain traces of acids, products of decomposition, and polymeric products.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition,

Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 307.

Ibid., Vol. 1 (1963), p. 815.

Houben-Weyl, <u>Methoden Der Organischen Chemie</u>, Vierte Auflage, Georg Thieme Verlag Sttutgart, Bd. 11, T1 (1957), p. 312. Ethylene Chlorohydrin (from ethylene) CaO + Cl₂ \longrightarrow CaClOCl

 $CaClOCl + Cl_2 + H_2O \longrightarrow CaCl_2 + 2 HOCl$

 $CH_2 = CH_2 + HOC1 \longrightarrow HOCH_2CH_2C1$

1. <u>Function</u> - Ethylene chlorohydrin is most economically produced by the reaction of ethylene gas and dilute hypochlorous acid in aqueous media. In this process ethylene and chlorine are simultaneously introduced into an aqueous solution of hydrated lime at 20°C and 20.3 MPa so that the ethylene concentration is about 28 g/l alkali. The calcium oxychloride immediately decomposes to calcium chloride and hypochlorous acid which reacts with the ethylene. To avoid excess formation of ethylene dichloride and β,β' -dichloroethylene ether, the process is interrupted when a 6-8% solution of ethylene chlorohydrin has been formed, which is quite satisfactory for industrial applications.

Anhydrous ethylene chlorohydrin can be obtained by concentrating the reaction product to 25-30% chlorohydrin, causing an oily layer to separate. This layer is fractionated and the water removed azeotropically with benzene.

2. Input Materials

Ethylene Chlorine Water Lime

3. Operating Parameters

Temperature	20°C (68°F)
Pressure	20.3 MPa (200 atm)

4. Utilities

Not given

5. <u>Waste Streams</u> - Spent catalysts, solvents, various salts, or HCl itself may be present in the waste streams from this operation. The resulting waste water may contain hypochlorous acid, chlorine, spent caustic, HCl, some ethylene chlorohydrin, ethylene dichloride, and β,β'-dichloroethyl ether.

Waste products from purification, principally hypochlorous acid and its degradation products (HCl and oxygen), are rejected, and should be present in other waste streams.

- 6. EPA Source Classification Code None
- 7. References

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1974), p. 281.

Faith, W. L. et al., <u>Industrial Chemicals</u> 3rd Ed., John Wiley & Sons, Inc., New York, N.Y., 1965, p. 373.

Astle, M. J., <u>The Chemistry of Petrochemicals</u>, Reinhold Publishing Corp., New York, N.Y., 1956, p. 75, 76.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 308.

INDUSTRIAL ORGANIC CHEMICALS

PROCESS NO. 137

<u>1,1,2-Trichloroethane (liquid-phase</u> chlorination of ethylene dichloride)

 $\texttt{C1CH}_{2}\texttt{CH}_{2}\texttt{C1} + \texttt{C1}_{2} \xrightarrow{} \texttt{C1}_{2}\texttt{CHCH}_{2}\texttt{C1} + \texttt{HC1}$

 <u>Function</u> - Most 1,1,2-trichloroethane is made by chlorinating ethylene dichloride in the liquid phase at 120°C and 345 kPa (3.40 atm).

Many variations of this process are in commercial use.

2. Input Materials

Ethylene dichloride - 0.62 kg/kg product Chlorine - 0.77 kg/kg product

3. Operating Parameters

Temperature: 120°C (248°F)

Pressure: 345 kPa (3.40 atm)

4. <u>Utilities</u>

Basis: 0.59 kg/sec capacity (41 \overline{M} lb/yr) Cooling water - 51.2 dm³/sec 948.700 gph) Makeup water - 2.9 dm³/sec (2,800 gph) Steam - 1.36 kg/sec (10,800 lb/hr) Power - 48 kW

5. <u>Waste Streams</u> - The primary sources of emissions from this process are probably the waste streams from the HCl scrubber. Waste water streams may contain chlorine, HCl, spent caustic, and various chlorohydrocarbons, including ethylenedichloride, trichloroethane and reaction by-products. Hydrogen chloride and a number of organic chlorides are probably present in the waste gas.

- 6. EPA Source Classification Code None
- 7. References

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> Processes, Technomic Publishing Co., 1975.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u> 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 158.

Elkin, L.M., "Chlorinated Solvents," Report No. 48, Stanford Research Institute, Menlo Park, Calif., 1969.

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INDUSTRIAL ORGANIC CHEMICALS

PROCESS NO. 138

<u>1,1,2-Trichloroethane (oxychlorination</u> of ethylene dichloride)

 $C1CH_2CH_2C1 + HC1 + 1/2 0_2 \longrightarrow C1_2CHCH_2C1 + H_20$

- <u>Function</u> Some 1,1,2-trichloroethane is produced by the oxychlorination of ethylene dichloride with HCl. Reaction conditions vary from one process to another.
- 2. Input Materials

Ethylene dichloride

Hydrogen chloride

Oxygen

- 3. Operating Parameters Not given
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste water and vent gases from the separator contain a number of chlorohydrocarbons, including ethylene dichloride, trichloroethane, and by-products.

The crude product is probably scrubbed to remove unreacted acid. Waste water from this operation would contain some HC1.

- 6. EPA Source Classification Code None
- 7. References

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> Processes, Technomic Publishing Co., 1975.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 159. Vinylidene Chloride (from 1,1,2-trichloroethane)

 $CH_2C1CHCl_2 + NaOH \longrightarrow CH_2=CCl_2 + NaCl + H_2O$

<u>Function</u> - Vinylidene chloride is made by dehydrochlorinating
 1,1,2-trichloroethane with lime or aqueous sodium hydroxide at
 ~70°C. A long cylindrical reaction vessel is used. Crude product
 is separated and purified by distillation under a nitrogen atmosphere
 and washing with ferrous sulfate and caustic soda solutions.

Purified vinylidene chloride is generally polymerized within 48 hours of its production. If it is to be stored, small amounts of polymerization inhibitors (hydroquinone, alkylamines or organic sulfur derivatives) are added. Peroxide formation has to be monitored. Vinylidene chloride may also be manufactured by continuous chlorination of ethane.

2. Input Materials

1,1,2-trichloroethane - 1.38 kg/kg product Sodium hydroxide - 0.46 kg/kg product

3. Operating Parameters

Temperature - 70°C (158°F) Pressure - 101 kPa (1 atm)

4. <u>Utilities</u> - Basis: 0.427 kg/sec capacity (2.97 M lb/yr) Cooling water - 5.15 dm³/sec (4900 gph) Process water - 1.60 dm³/sec (1520 gph) Power - 305 kW

5. Waste Streams

Vinylidene chloride separation columm (water)
Water stream (1.69 dm³/sec or 1604 gph) contains
Sodium hydroxide - 45.5 kg/Mg product
Sodium chloride - 605.5 kg/Mg product
Ferrous sulfate and sodium hydroxide may also be present in the wastewater
from washing operations.

6. EPA Source Classification Code - None

7. <u>References</u>

Hedley, W. H., et al., <u>Potential Pollutants From Petrochemical Processes</u>, Technomic Publishing Co., 1975.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 129.

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., (1975), p. 838-840.

Perchloroethylene, Trichloroethylene, and Carbon Tetrachloride (oxychlorination of ethylene dichloride)

 $HC1 + 1/2 \ 0_2 \longrightarrow C1_2 + H_20$ $2CH_2C1CH_2C1 + 1.5 \ C1_2 + 1.75 \ 0_2 \longrightarrow C_2C1_4 + C_2HC1_3 + CC1_4 + 3.5 \ H_20$

 <u>Function</u> - Perchloroethylene, trichloroethylene, and carbon tetrachloride are co-produced by the oxychlorination of ethylene dichloride. The chlorine is produced from hydrochloric acid by the Deacon process and combined with ethylene dichloride and additional air in the presence of fluid catalysts.

The actual reaction is highly complex with substitutive chlorination, cracking, Deacon reaction, and carbon burning all occurring simultaneously. Ethylene dichloride, chlorine, oxygen, and recycled chlorinated organics are fed to a fluid bed reactor. An inexpensive oxychlorination catalyst (PPG) is used in the main reaction and the Deacon process catalyst contains copper chloride. The catalysts are contained in a vertical, tubular reactor which operates at moderate pressure and around 425°C (or 600-900°F). Reaction heat generates a large portion of the process steam requirements.

After vent scrubbing, the condensed crude and weak acid are phase separated and the crude dried by azeotropic distillation. The crude is fed to a distillation train where it is split into a perchlorrich and trichlor-rich stream. The products are separated in stills, neutralized, washed, and dried.

Carbon tetrrchloride is recovered as a by-product of this vigorous chlorination.

2. <u>Input Materials</u> - Basis - 1 metric ton C₂Cl₄ (and 793 kg C₂HCl₃) Ethylene dichloride - 1195 kg (2,632 lbs) Chlorine - 692 kg (1,414 lbs) Oxygen - 388 kg (855 lbs) Catalysts - Small

3. Operating Parameters

Temperature - $\sim 425^{\circ}C$ (or $600-900^{\circ}F$)

Pressure - moderate

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Although no information was available, mixed chlorohydrocarbons, chlorine, and hydrogen chloride may be present in the waste gases of various production components. Heavy ends from the various stills are usually incinerated.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 604, 605, 845.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 162.

"1973 Petrochemical Handbook," "Hydrocarbon Processing," November, 1973, p. 157.

7. References (continued)

"1975 Petrochemical Handbook," "Hydrocarbon Processing," November, 1975, p. 169.

Belgian Patent 602,840 (April 20, 1961).

Austin, G. T., "The Industrially Significant Organic Chemicals-Part 7," "Chemical Engineering," June 24, 1974, p. 156.

Ibid., Part 8, July 22, 1974, p. 115.

INDUSTRIAL ORGANIC CHEMICALS

1,1,2-Trichloro-1,2,2-Trifluoroethane (from perchloroethylene)

 $\text{CC1}_2\text{CC1}_2 + 3\text{HF} + \text{C1}_2 \longrightarrow \text{CC1}_2\text{FCC1F}_2 + 3\text{HC1}$

1. <u>Function</u> - 1,1,2-Trichloro-1,2,2-trifluoroethane (fluorocarbon 113) is produced by reacting a mixture of hydrogen fluoride and chlorine with perchloroethylene at 225-400°C in the presence of partially-fluorinated antimony pentachloride or zirconium chloride catalyst. The by-product of this reaction is an extremely pure grade of anhydrous HCl which is important in several industrial operations.

The product is purified by distillation and by scrubbing through water and slightly alkaline solution. It is then dried by passage in the liquid phase through beds of silica gel, alumina gel, or synthetic zeolite.

2. Input Materials

Perchloroethylene Hydrogen fluoride

Chloride

3. Operating Parameters

Temperature: 225-400°C (437-752°F)

Pressure: Not given

4. Utilities

Not given

- 5. <u>Waste Streams</u> The main pollutant source in this process is probably the scrubber effluent. Waste water streams should contain quantities of caustic soda or other alkali, and perhaps some hydrochloric acid. Various chlorofluorocarbons may be present in low concentrations in both the waste water and vent gas.
- 6. EPA Source Classification Code None

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 198. Bis(2-Chloroethyl) Ether

$$2\text{ClcH}_2\text{CH}_2\text{OH} \xrightarrow{\text{H}_2\text{SO}_4} (\text{ClcH}_2\text{CH}_2)_2\text{O} + \text{H}_2\text{O}$$

Function - In the past, bis(2-chloroethyl) ether has been produced in 75% yield by heating ethylene chlorohydrin with sulfuric acid at 90-100°C.

It has also been prepared by saturating an aqueous solution of ethylene chlorohydrin with chlorine and ethylene. Bis(2-chloroethyl) ether has also been produced by chlorinating ethyl ether in the presence of a catalyst.

$$(CH_3CH_2)_20 + 2C1_2 \longrightarrow (C1CH_2CH_2)_20 + 2HC1$$

- <u>Input Materials</u>
 Ethylene chlorohydrin
 Ethyl ether chlorine
- Operating Parameters
 Not given
- 4. Utilities

Not given

- 5. <u>Waste Streams</u> Although no process description was available, the HCl scrubbers probably contribute to waste water and air emissions. Ethyl ether, chlorine, hydrogen chloride, and some dichloroethyl ether may be present in these emissions.
- 6. EPA Source Classification Code None
- References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 8 (1965), p. 487.

INDUSTRIAL ORGANIC CHEMICALS

PROCESS NO. 143

Ethylene Oxide (oxidation of ethylene)

$$H_2^{C=CH_2+1/2} O_2 \longrightarrow H_2^{C-CH_2} O_2$$

 <u>Function</u> - Presently, ethylene oxide is manufactured by direct vaporphase oxidation of ethylene over silver oxide catalyst. Approximately 75% of the processes use air as the oxidant, and the remainder use oxygen.

Silver is the only effective high selectivity catalyst. Selectivity is highly sensitive to temperature, dropping as the temperature rises. Therefore, careful temperature control within a narrow range is an absolute necessity. The selection of the carrier is also of considerable importance because of the critical problem of heat removal.

Methods have been sought for retarding the combustion of ethylene to carbon dioxide. Numerous compounds have been proposed, but only ethylene dichloride and polychloroaromatics have been effective on a commercial scale.

A mixture of ethylene, air, and recycle gas (3-5 vol. % ethylene) is pressured and sent to a tubular reactor with a fixed bed, silver catalyst. A heat transfer agent is used to hold the temperature within a narrow range which is adjusted to the temperature/activity relationship of the particular catalyst bed. The reactor effluent gas is cooled by a circulating gas in a heat exchanger. The cooled gas is sent to a scrubbing tower in which the ethylene oxide is scrubbed with water.

The gas that is not absorbed is primarily unreacted ethylene and oxygen. Part of this mixture is returned to the reactor as recycle gas (3-5 mol. % ethylene). The other part is sent forward, reheated in a heat exchanger and sent to a second reactor where oxidation is completed. The effluent is sent to a scrubbing tower where the ethylene oxide is absorbed. The noncondensable gases are purged.

The dilute aqueous ethylene oxide solutions from both scrubbing towers are combined and sent to a stripper (desorber) where ethylene oxide is removed by heating.

The crude ethylene oxide is fractionated on distillation columns. The water from the stripper (desorber) can be returned to the scrubbing towers, or in some cases it is sent to an ethylene glycol plant because this water contains ~2% ethylene glycol.

In the oxygen process, ethylene, oxygen, and recycle gas are fed to the reactor under pressure. The reactor effluent is sent through a carbon dioxide removal system, and is recycled to the reactor to reduce the partial pressure of ethylene. The gases are ultimately sent to a scrubber, thence to the stripper (desorber).

2. Input Materials Per kg ethylene oxide

Ag	$4.37 \times 10^{-4} g$
Air	13,100 g
Ethylene	1,100 g
Steam	100 g
Water	0.208 m ³

3. Operating Parameters

Reactor temperature - 104-149°C (219-300°F) Reactor pressure - 0.929-2.2 MPa (9.2-21.7 atm) Catalyst - silver oxide supported on inert carriers 6-371

4. Utilities

Electricity 6.74 x 10^6 J (1.87 kWh)/kg prod.

5. Waste Streams

Air: Purge gases from air oxidation may contain small amounts of ethylene oxide and ethylene. Ethylene oxide escape from oxide compressor seals. Reactor gas leaks from cycle compressor seals. Water: The main waste stream is the draw-off from the ethylene oxide separator (stripper; desorber) bottoms. The flow from two plants is given:

	Plant 1	<u>Plant 2</u>
Flow	67.3 dm	496 dm
	454 kg	454 kg
COD	52 kg/m (52,000 mg/1)	4.8 kg/m (4,800 mg/1)
	3.49 kg	2.4 kg
	454 kg	454 kg
BOD	4.8 kg/m (4,800 mg/1)	0.65 kg/m (650 mg/l)
	0.32 kg	0.32 kg
	454 kg	454 kg
TOC	19 kg/m (19,650 mg/1)	2.699 kg/m (2,699 mg/l)
	1.32 kg	1.34 kg
	454 kg	454 kg

Process water usage (including steam) - 0.113 kg/0.45 kg of product Cooling water - 0.043 kg/0.45 kg of product

6. EPA Source Classification Code - None

7. References

Considine, D. W., Ed.-in-Chief, <u>Chemical and Process Technology</u> <u>Encyclopedia</u>, McGraw-Hill Book Company, New York, N.Y., 1974, pp. 443-446.

References (continued)

Kent, J. A., Ed., <u>Riegel's Handbook of Industrial Chemistry</u>, Seventh Ed., Van Nostrand Reinhold Company, New York, N.Y., 1974, pp. 779-780.

Sittig, M., "Ethylene Oxide from Ethylene," <u>Pollution Control in the</u> <u>Organic Chemical Industry</u>, Noyes Data Corp., Park Ridge, N.J., 1974, pp. 150-152.

Faith, W. L., et al., <u>Industrial Chemicals</u>, 3rd Ed., John Wiley & Sons, New York, N.Y., 1965, p. 382.

Mono-, Di-, and Triethylene Glycols (from hydration of ethylene oxide)

$$(CH_2)_2 0 + H_2 0 \longrightarrow HOC_2 H_4 OH$$
$$HOC_2 H_4 OH + (CH_2)_2 0 \longrightarrow HOC_2 H_4 OC_2 H_4 OH$$
$$HOC_2 H_4 OC_2 H_4 OH + (CH_2)_2 0 \longrightarrow HOC_2 H_4 OC_2 H_4 OC_2 H_4 OH$$

1. <u>Function</u> - Ninety percent of the ethylene glycols produced in the U.S. are made by the direct catalytic oxidation of ethylene to ethylene oxide followed by hydration. Process No. 143 discusses the ethylene to ethylene oxide conversion, so only the hydration step will be considered here.

Ethylene oxide can be converted to glycol by catalytic or noncatalytic hydration. The catalytic process employs a large excess of dilute aqueous acid, usually sulfuric acid and the noncatalytic process employs a large excess of water. The reaction is carried out at 180°C and 2.17 MPa in the liquid phase.

Di- and triethylene glycols are reaction by-products which normally account for 9% and 1%, respectively, of the total product.

However, yields of these ether glycols may be increased by modest alternations (higher temperature and slightly lower pressure) in the reaction conditions. Polyethylene glycols are also formed (in minute quantities only under normal reaction conditions) but their yields may be increased by using a NaOH catalyst (see Process No. 155).

Following reaction, the respective glycols are separated and purified by dehydration of the reaction effluent and vacuum distillation.

2. Input Materials

Ethylene oxide For ethylene glycol - 0.75 kg/kg For diethylene glycol - 0.84 kg/kg For triethylene glycol - 0.90 kg/kg Water - 2.0 kg/kg product

3. Operating Parameters

	Catalytic	Noncatalytic	
Temperature	165–180°C (329–356°F	95°C	(203°F)
Pressure	2.17 MPa (21.4 atm)	1.5-2.0 MPa	(14.8-19.7 atm)
Catalyst	0.15–1.0% H ₂ SO ₄		
Reaction time	30 min		

4. Utilities

Not given

- 5. <u>Waste Streams</u> Dehydration (water) Water flow - 4.873 m³/Mg (2575 gal/ton) product COD - 8.66 kg/Mg (lb/1000 lb) product BOD - 0.34 kg/Mg (lb/1000 lb) product TOC - 4.53 kg/Mg (lb/1000 lb) product The chief organic pollutants are ethylene glycol ethylene oxide, acetaldehyde, crotonaldehyde, and some sulfuric acid.
- 6. EPA Source Classification Code None

7. References

Austin, G. T., "The Industrially Significant Organic Chemicals, -Part 4,""Chemical Engineering," April 15, 1974, p. 88.

ibid., Part 5, April 29, 1974, p. 146, 147, 148

ibid., Part 9, August 5, 1974, p. 96, 97.

"1973 Petrochemical Handbook Issue,""Hydrocarbon Processing," November 1973, p. 130.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Technomic Publishing Co., 1975.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 10 (1966), p. 642, 646, 648.

Faith, W.L. et al., <u>Industrial Chemicals</u>, 3rd Ed., John Wiley and Sons, New York, N.Y., 1965, p. 375.

Sittig, M., Organic Chemical Processes, Noyes Press, Inc., Pearl River, New York, N.Y., 1962, p. 59.

Chemical Technology, Barnes & Noble Books, New York, N.Y., Vol. 4 (1972), p. 293, 337, 339.

Ethylene Glycol Mono- And Diacetates

 $HOCH_2CH_2OH + CH_3COOH \iff CH_3COOCH_2CH_2OH + H_2O$ $HOCH_2CH_2OH + 2CH_3COOH \iff CH_3COOCH_2CH_2OOCCH_3 + 2H_2O$

 Function - Ethylene glycol mono- and diacetates are coproduced by any of the standard methods of esterificatiion of hydroxyl groups such as esterification with acid halides, acid anhydride, and acids.

The ester and diester are separated by distillation.

- <u>Input Materials</u>
 Ethylene glycol
 Acetic acid (glacial)
- 3. Operating Parameters Not given
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Air and wastewater emissions may contain ethylene glycol, acetic acid, and ethylene glycol mono- or diacetate.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 10 (1966), p. 645. Curme, George O., Johnston, F., <u>Glycols</u>, ACS Monograph 114, Reinhold Publishing Corp., 1952, p. 128. Dioxane (from ethylene glycol)

$$^{2\text{HOCH}_2\text{CH}_2\text{OH}} \xrightarrow{\text{H}_2\text{SO}_4} \left(\int_{0}^{0} + 2\text{H}_2^{0} \right)$$

- Function 1,4-Dioxane is produced on a commercial scale by heating ethylene glycol in the presence of a dehydration catalyst such as sulfuric acid.
- 2. Input Material

Ethylene glycol

3. Operating Parameters

Temperature: 160°C (320°F)

Pressure: Not given

Catalyst: H_2SO_4 (4% by weight of ethylene glycol)

4. Utilities

Not given

- 5. <u>Waste Streams</u> The separator water effluent may contain quantities of sulfuric acid, ethylene glycol, and dioxane.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 10 (1966), p. 643.

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4, (1972), p. 352.

1,3-Dioxolane

$$\underset{OH OH}{\overset{CH_2CH_2}{\leftarrow}} + \underset{CH_20}{\overset{CH_2-CH_2}{\leftarrow}} + \underset{CH_2}{\overset{CH_2-CH_2}{\leftarrow}} + \underset{CH_20}{\overset{CH_2-CH_2}{\leftarrow}} + \underset{CH_20}{\overset{CH_20-CH_2}{\leftarrow}} + \underset{CH_20-CH_2}{\overset{CH_20-CH_2}{\leftarrow}} + \underset{CH_20-CH_20}{\overset{CH_20-CH_2}{\leftarrow}} + \underset{CH_20-CH_20-CH_2}{\overset{CH_20-CH_2}{\leftarrow}} + \underset{CH_20-CH_20-CH_20-CH_2}{\overset{CH_20-CH_20-CH_2}{\leftarrow}} + \underset{CH_20-CH_2$$

- Function Ethylene glycol derivatives react with aliphatic and aromatic aldehydes or ketones to give 1,3 dioxolanes.
- 2. Input Materials

Ethylene glycol

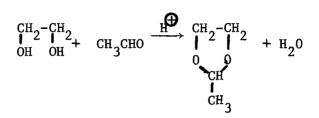
Formaldehyde

- 3. Operating Parameters Not given
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Wastewater from the separator may contain unreacted formaldehyde and ethylene glycol, and possibly, dioxolane. Some air emissions may also result from this operation.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 10 (1966), p. 639. Van der Plas, H. C., <u>Ring Transformations of Heterocycles</u>, Academic Press, 1973 p. 17.

UaS. Patent 3,324,145 (June 6, 1967).

2-Methy1-1,3-Dioxolane



- Function 2-Methyl-1, 3-dioxolane is derived from the reaction of ethylene glycol and acetaldehyde.
- 2. <u>Input Materials</u>

Ethyl glycol

Acetaldehyde

- 3. Operating Parameters Not given
- 4. Utilities Not given
- 5. <u>Waste Streams</u> The separator may release a waste stream containing acetaldehyde, ethylene glycol, and some methyldioxolane.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 10 (1966), p. 639-646. Van der Plas, H. C., <u>Ring Transformations of Heterocycles</u>, Academic Press, Vol. 1 (1973), p. 17. Ethylene Glycol and Diethylene Glycol Monothers

$$(CH_2CH_2)$$
 + ROH \longrightarrow H \rightarrow OCH_2CH_2) $(CH_2CH_2)_{1,2}$ R

1. <u>Function</u> - Ethylene glycol monoethers are made by reacting ethylene oxide and anhydrous alcohol under a variety of reaction conditions. The reaction proceeds spontaneously at 180°C - 200°C and 3.0 - 4.0 MPa (435-580 psig), but can be carried out at 100 - 150°C in the presence of an acid or base catalyst (caustic soda or boron trifluoride). Alcohols commonly used to produce glycol monoethers include methanol, ethanol, propanol, butanol, hexanol, octanol, and phenol.

Diethylene glycol monoethers are by-products of ethylene glycol monoether production, normally accounting for 10 - 15% of the total product. Higher polyglycol monoethers (2-3%) are also formed. The yield of di- and polyglycol monoethers may be increased by lowering the ratio of alcohol to ethylene oxide.

Of the 230 million lbs. of glycol ethers produced in 1965, 78% were ethylene glycol monomethyl ethers, 19% were diethylene glycol ethers, and 3% were triethylene glycol ethers.

2. Input Materials - Ethylene oxide

For ethylene glycol monomethyl ether-0.58 kg/kgFor ethylene glycol monoethyl ether-0.54 kg/kgFor ethylene glycol monobutyl ether-0.41 kg/kgFor diethylene glycol monomethyl ether-0.74 kg/kgFor diethylene glycol monoethyl ether-0.69 kg/kgFor diethylene glycol monobutyl ether-0.59 kg/kgFor diethylene glycol monoethyl ether-0.39 kg/kg

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Alcoho1

For ethylene glycol monoethers Methanol, ethanol, propanol, hexanol, octanol, phenol
For diethylene glycol monomers Methanol, ethanol, butanol, hexanol
Operating Parameters - Noncatalytic Process
Temperature - 180-200°C (356-392°F)
Pressure - 3-4 MPa (29.6-39.5 atm)
Catalytic process
Temperature - 100-150°C (212-302°F)
Pressure - not given
Catalyst - acid or base

- 4. Utilities not given
- 5. <u>Waste Streams</u> No information was available, but waste streams may contain ethylene oxide, ethylene and higher polyglycols, alcohols, glycol monoethers, reaction by-products, and traces of acid or base catalyst.

6. EPA Source Classification Code - None

7. References

Austin, G. T., "The Industrially Significant Organic Chemicals - Part 5," "Chemical Engineering," April 29, 1974, p. 150.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 10 (1966), p. 643.

7. References (continued)

Chemical Technology, Barnes and Noble, New York, N.Y., Vol. 4, (1972). p. 336.

Hahn, A. V., <u>The Petrochemical Industry: Markets and Economics</u>, McGraw-Hill Book Co., New York, N.Y., 1970, p. 282.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 403, 404.

Mono-, Di-, and Triethylene Glycol Diethers

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 $RO(CH_2CH_2O)_nNa + RC1 \longrightarrow RO(CH_2CH_2O)_nR + NaC1$

n = 1, 2, 3
R = methyl, ethyl, butyl

- Function Glycol diethers may be prepared by the general methods of ether preparation, but the preferred method is by reacting an alkyl chloride with the sodium salt of the corresponding glycol monoether.
- 2. Input Materials

Mono, di- or triethylene monoether sodium glycolate Alkyl chloride

- 3. Operating Parameters Not given
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Wastewaters contain sodium chloride, alkyl chloride, and possibly other reactants and products.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 10 (1966), p. 643. Curme, George O., Johnston, F., <u>Glycols</u> in ACS Monograph 114, Reinhold Publishing Corp., 1952, p. 118.

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Mono- and Diethylene Glycol Monoether Acetates

 $R(OCH_{2}CH_{2})_{n}OH + CH_{3}COOH \longrightarrow R(OCH_{2}CH_{2})_{n}OOCCH_{3} + H_{2}O$ R = methyl, ethyl, butyl n = 1, 2

- <u>Function</u> Glycol monoether acetates are made by esterifying the glycol monoethers with acetic acid. The reaction is similar to that used to produce ethylene glycol acetate and diacetate. See Process No. 145.
- 2. Input Materials

Mono- or diethylene glycol monoether Acetic acid

- 3. Operating Parameters Not given
- 4. Utilities Not given
- <u>Waste Streams</u> The waste water stream from the separator may contain any of the reactants or products.
- 6. EPA Source Classification Code None
- 7. References

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Technomic Publishing Co., 1975.

Curme, G. O. and Johnston, F., <u>Glycols</u>, ACS Monograph Series 114, Reinhold Publishing Corp., New York, N.Y., 1952, p. 163.

Ethanolamines (from ethylene oxide)

$$\overset{\text{CH}}{\xrightarrow{}} \overset{\text{-CH}}{\xrightarrow{}} \overset{\text{H}}{\xrightarrow{}} \overset{\text{H}}{\xrightarrow{}} \overset{\text{NCH}}{\xrightarrow{}} \overset{\text{CH}}{\xrightarrow{}} \overset{\text{OH}}{\xrightarrow{}} \overset{\text{H}}{\xrightarrow{}} \overset{\text{CH}}{\xrightarrow{}} \overset$$

 Function - Monoethanolamine is produced together with di- and triethanolamines by a reaction between ethylene oxide and an excess of aqueous ammonia at 50-100°C. The yield is about 95% based on ethylene oxide.

Excess ammonia is stripped from the reaction effluent. The overhead from the ammonia stripper, together with fresh ammonia makeup, enters an ammonia absorber where the aqueous ammonia solution is prepared for reaction. The bottoms from the ammonia stripper are first evaporated to produce a recycle water stream and are then dried in a separate column. A product distillation train of three columns produces the three products, recycle amine streams, and rejected heavies.

The product mixture can be partially controlled by temperature, the ratio of ammonia to ethylene oxide, and recirculation of products. A large excess of ammonia favors monoethanolamine production. Recirculation of this product shifts the reaction equilibrium in favor of diand triethanolamines.

2. Input Materials

Ethylene oxide

For monoethanolamine - -.75 kg/kg For diethanolamine - 0.88 kg/kg For triethanolamine - 0.93 kg/kg Aqueous NH3

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3. Operating Parameters

Temperature: 50-100°C (122-212°F) Pressure: Not given 1.03-2.07 MPa (10.2-20.4 atm)

4. Utilities

Not given

- 5. <u>Waste Streams</u> Some atmospheric emissions probably result from stripping, evaporating, drying, and fractionating operations. Ammonia and traces of the various ethanolamines may be present in these waste gases. Rejected heavies from still bottoms are primarily higher amine ethers.
- 6. EPA Source Classification Code None
- References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 4," "Chemical Engineering," April 15, 1974, p. 87,88.

"1973 Petrochemical Handbook," "Hydrocarbon Processing," November 1973, p. 120.

"1975 Petrochemical Handbook," "Hydrocarbon Processing," November, 1973, p. 136, 137.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 814.

INDUSTRIAL ORGANIC CHEMICALS

PROCESS NO. 153

Morpholine (from diethanolamine)

$$\operatorname{HOCH}_{2}\operatorname{CH}_{2}\operatorname{NHCH}_{2}\operatorname{CH}_{2}\operatorname{OH} \longrightarrow \operatorname{OCH}_{2}\operatorname{CH}_{2}\operatorname{NHCH}_{2}\operatorname{CH}_{2} + \operatorname{H}_{2}\operatorname{OH}_{2}$$

 <u>Function</u> - Morpholine is almost exclusively made by dehydration of diethanolamine with sulfuric acid.

The reaction mixture is neutralized to give an aqueous solution of morpholine. Morpholine is extracted with organic solvents and purified by distillation.

2. Input Materials

Diethanolamine

95% H₂SO4

3. <u>Operating Parameters</u> Temperature - 150-180°C (302-356°F)

Pressure - not given

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste water may contain alkali sulfate from neutralization as well as traces of diethanolamine, morpholine, and the organic solvent used in distillation.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 13 (1967), p. 662.

Weissberger, A., Editor, <u>The Chemistry of Heterocyclic Compounds</u>, Interscience Publishers, New York, N.Y., Vol. 17 (1962), p. 378.

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7. <u>References (continued)</u>

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Waddams, A. L., <u>Industrial Organic Chemicals</u>, 3rd Edition, John Wiley and Sons, New York, N.Y., 1973, p. 89.

$$\begin{array}{c} \underline{\text{Piperazine (from ethanolamines)}} \\ 2\text{H}_2\text{NCH}_2\text{CH}_2\text{OH} + \text{NH}_3 \longrightarrow \begin{pmatrix} N \\ N \\ M \\ H \end{pmatrix} + 2\text{H}_2\text{O} \\ H \\ H \end{pmatrix} + 2\text{H}_2\text{O} \\ H \\ H \end{pmatrix} + \text{H}_2\text{O} \\ H \\ N (\text{CH}_2\text{CH}_2\text{OH})_3 + \text{NH}_3 \longrightarrow \begin{pmatrix} N \\ M \\ H \\ H \end{pmatrix} + \text{H}_2\text{O} + \text{H}_2\text{NCH}_2\text{CH}_2\text{OH} \end{array}$$

- Function Piperazine is produced by treating mono-, di- or triethanolamines with excess ammonia over a Ni/Cu/Cr catalyst.
- 2. Input Material

Ethanolamines Ammonia (excess)

Catalyst (Ni/Cu/Cr)

3. Operating Parameters

Temperature: 200-260°C (392-500°F)

Pressure: 10.3-41.4 MPa (102.1-408.3 atm)

- 4. Utilities Not given
- <u>Waste Streams</u> The only wastes should be some unreacted ethanolamines, ammonia, and catalysts.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 15 (1968), p. 640, 641.

U. S. Patent 3,151,115 (September 29, 1964).

Sittig, M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition, Noyes Development Corp., Park Ridge, N. J., 1961, p. 531. Polyethylene Glycol (hydration of ethylene oxide)

 $H_{2}O + (CH_{2})_{2}O \longrightarrow HOC_{2}H_{4}OH$ $HOC_{2}H_{4}OH + (CH_{2})_{2}O \longrightarrow HOC_{2}H_{4}OC_{2}H_{4}OH$ $HOC_{2}H_{4}OC_{2}H_{4}OH + (CH_{2})_{2}O \longrightarrow HOC_{2}H_{4}OC_{2}H_{4}OC_{2}H_{4}OH$ $HOC_{2}H_{4}OC_{2}H_{4}OC_{2}H_{4}OH + n(CH_{2})_{2}O \longrightarrow HO(C_{2}H_{4}O)_{n+3}H$

- <u>Function</u> Like di- and triethylene glycols, polyethylene glycol is a by-product of ethylene glycol production. For significant conversion to the polyglycol, however, ethylene oxide and water must be combined in the presence of sodium hydroxide catalyst.
- 2. Input Materials

Ethylene oxide - 1.10 kg/kg

Water

3. Operating Parameters

Temperature: 120-150°C (248-302°F)

Pressure: 294 kPa (2.9 atm)

Catalyst: NaOH

4. Utilities

Not given

 <u>Waste Streams</u> - Process slops may carry ethylene glycol and sodium hydroxide.

6. EPA Source Classification Code - None

7. <u>Reference</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 10 (1966), p. 655. Ethylene Carbonate (from ethylene oxide)

$$CH_2CH_2 + CO_2 \xrightarrow{CH_2O}_{Cat.} CH_2O$$

 <u>Function</u> - Ethylene oxide reacts with carbon dioxide under pressure and in the presence of a catalyst to give ethylene carbonate.

The product is centrifuged to remove the catalyst and the crude product distilled in vacuum to give pure ethylene carbonate.

2. Input Materials

Ethylene oxide

Carbon dioxide

3. Operating Parameters

Temperature - 190-220°C

Pressure - 13.2 MPa (130 atm)

Catalyst - LiI

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste water may contain traces of ethylene carbonate, ethylene glycol, ethylene oxide, and carbon monoxide.
- 6. EPA Source Classification Code None
- 7. References

U.S. Patent 3,025,305 (1962).

German Patent 1,135,490.

SECTION V METHANE METHANE

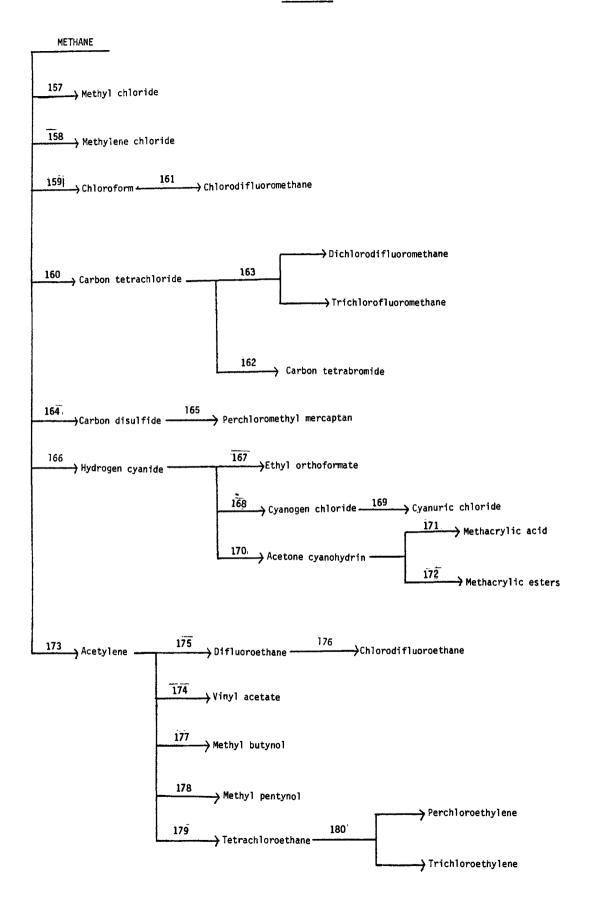


Figure 9. Methane Section Chemical Tree

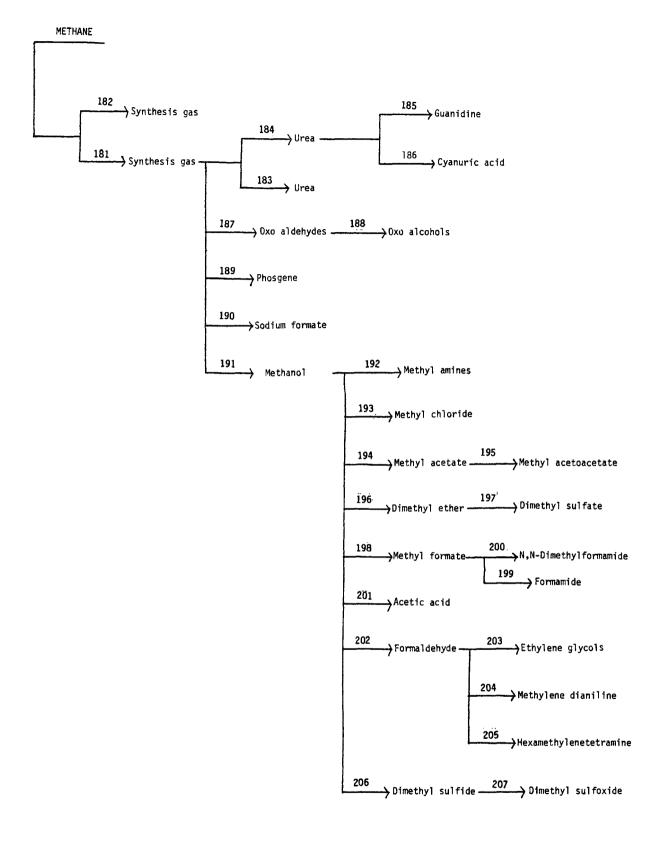
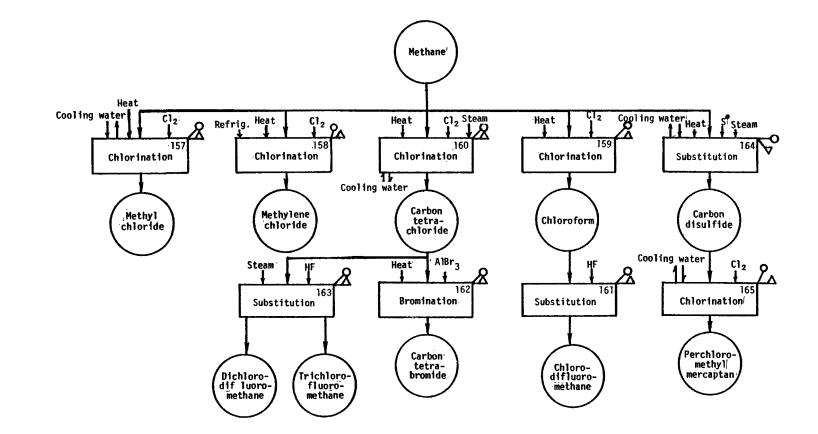


Figure 9. Methane Section Chemical Tree (Cont.)



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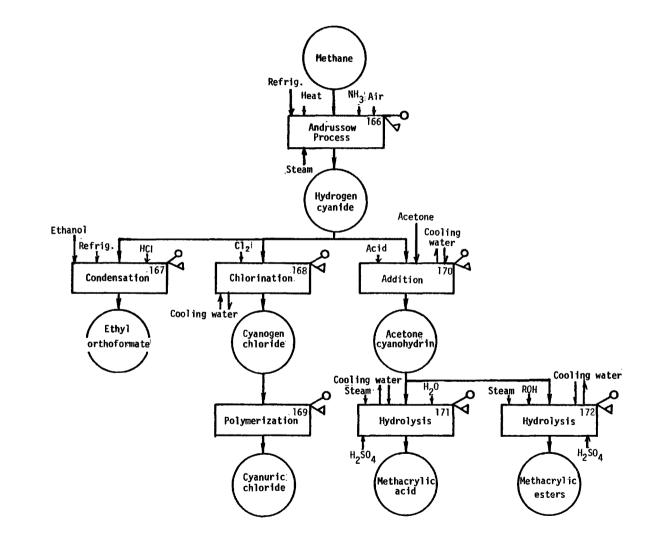


Figure 10. Methane Section Process Flow Sheet (Cont.)

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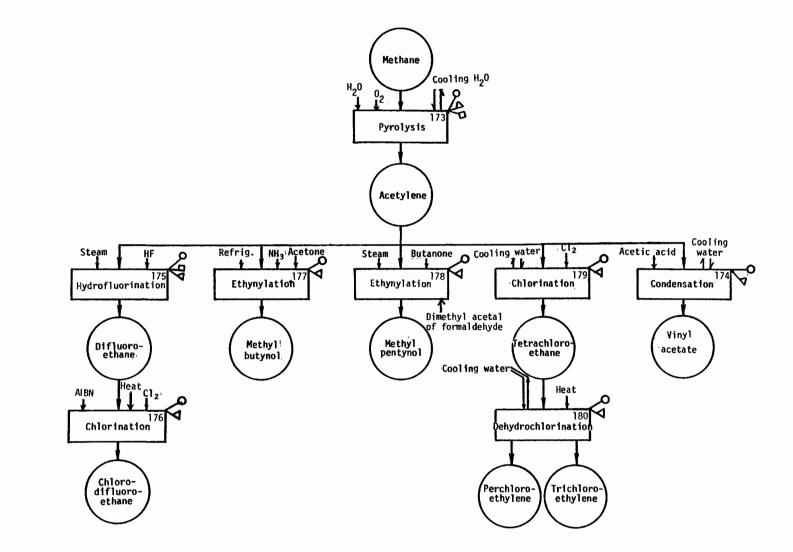


Figure 10. Methane Section Process Flow Sheet (Cont.)

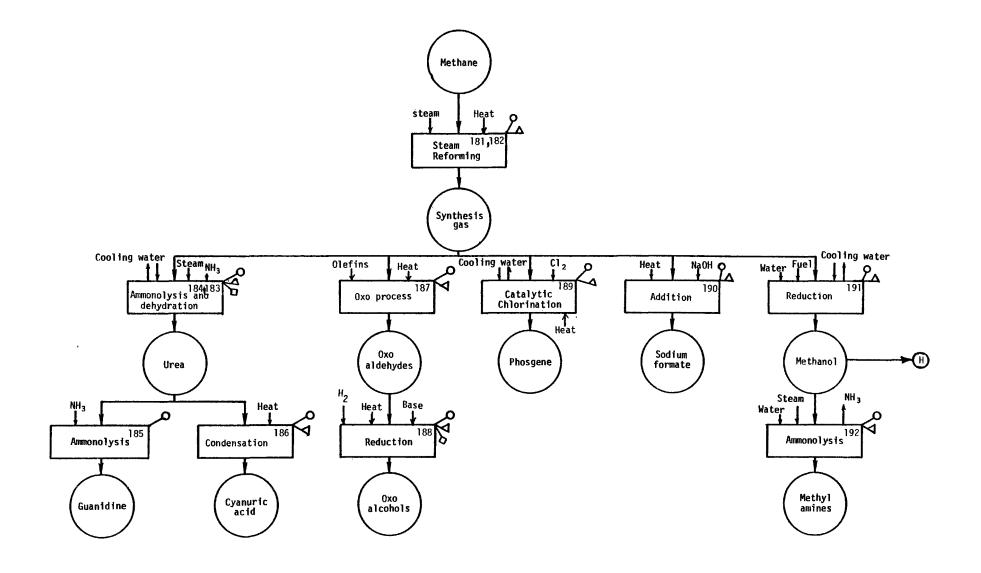


Figure 10. Methane Section Process Flow Sheet (Cont.)

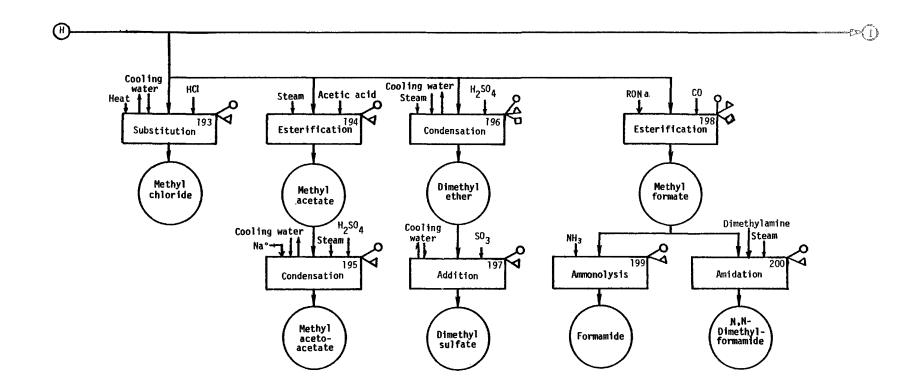


Figure 10. Methane Section Process Flow Sheet (Cont.)

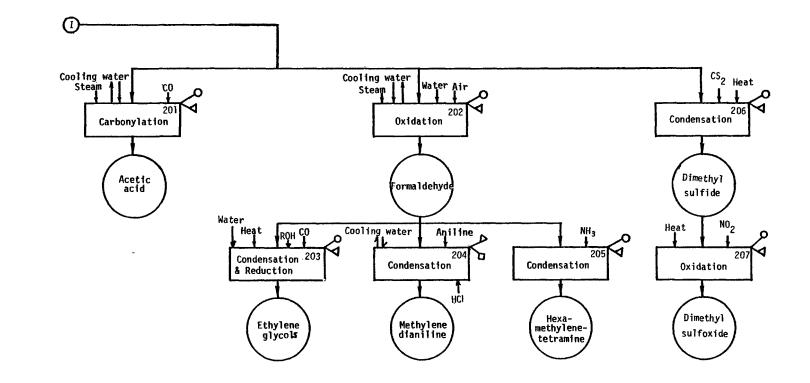


Figure 10. Methane Section Process Flow Sheet (Cont.)

Methyl Chloride

 $CH_4 + C1_2 \longrightarrow CH_3C1 + HC1$

 Function - As of 1970, chloromethane was made either by the chlorination of methane (70%) or the hydrochlorination of methanol (22%).

The chlorination of methane process sequence requires four main steps; reaction, HCl recovery, chlorides recovery and chlorides refining. High purity methane, chlorine and recycle methane are premixed and fed to the reactor. The reactor effluent, containing organic chlorides, HCl, excess methane, and only traces of chlorine, is cooled and fed to the HCl recovery system.

The first column in this system is an absorber designed for efficient HCl removal. The bulk of the absorbing liquor is HCl azeotrope (about 20 percent by weight HCl). The rich acid is thus above the azeotrope and allows stripping of anhydrous HCl. The second column distills off anhydrous HCl and produces the required azeotrope in the bottoms. For high yields of methyl chloride, the amount of recirculating methane is increased.

The HCl-free gases from the absorber are washed with caustic soda to remove final traces of HCl and are then ready for chlorides recovery by compression, cooling, and drying with sulfuric acid.

2. <u>Input Materials</u> - Basis - 1 metric ton methyl chloride Methane - 179 kg/Mg (358 lb/ton) product 1445 m³ (15,713 ft³/ton) Chlorine - 1587 kg/Mg (3,174 lb/ton) product 1405 kg (3,097 lbs/ton) Sulfuric Acid Caustic Soda

3. Operating Parameters

Temperature - 400 - 500°C (752-932°F) Pressure - 200 kPa (2 atm) Flow Rate - not given Catalyst - None

4. Utilities

Electric Power - not given

Cooling Water - not given

5. <u>Waste Streams</u>

Dehydrator (air)

Purge on recycled methane to remove inerts $CH_4 - 1 \text{ kg/Mg} (2 \text{ lb/ton}) \text{ product}$ $CH_3C1 - 13 \text{ kg/Mg} (26 \text{ lb/ton}) \text{ product}$ $CH_2C1_2 - 2 \text{ kg/Mg} (4 \text{ lb/ton}) \text{ product}$ $CHC1_3 - 1 \text{ kg/Mg} (2 \text{ lb/ton}) \text{ product}$ $CC1_4 - 1 \text{ kg/Mg} (2 \text{ lb/ton}) \text{ product}$

Waste acid solution is discharged from the dehydrator.

Waste caustic solution is discharged from the washer.where traces of HCl are removed from the product gases.

- 6. EPA Source Classification None
- 7. References

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corporation, Park Ridge, N.J., 1974, p. 105.

Austin, G. T., "Industrially Significant Organic Chemicals - Part 3," "Chemical Engineering," March 18, 1974, p. 89,90.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N.Y., 1975, p. 531,532. 6-405 Methylene Chloride (chlorination of methane)

 $CH_4 + 2C1_2 \longrightarrow CH_2C1_2 + 2HC1 + co-products$

 <u>Function</u> - Processes for CH₂Cl₂ manufacture are based on chlorination of methane, although the other chloromethanes are probable co-products of this route, their relative proportions are determined by process operating conditions.

A typical methane chlorination synthesis of methylene chloride and co-products is as follows. A preheated mixture of methane and chlorine passes into a vessel where reaction is promoted by a control of feed-gas flow rate and the reactor temperature. In addition to chloromethanes, the exit gas contains unreacted methane and hydrogen chloride. Initial separation of the product group from CH_4 and HCl is generally affected by scrubbing the effluent gas with a refrigerated mixture of higher chloromethanes, in which the methane and hydrogen chloride are only slightly soluble. The methane, freed from acid by water scrubbing, is recycled to the chlorinator and the chloromethanes, containing the desired CH_2Cl_2 , after washing, alkali scrubbing, and drying, pass to a sequence of fractionating columns.

2. Input Materials

Methane - 0.179 kg/kg product Chlorine - 1.587 kg/kg product

3. Operating Parameters

Temperature: 360 - 500°C (680 - 932°F)

Pressure: 205 kPa (2 atm) Catalyst: UV light from mercury vapor lamps

4. Utilities

Not given

5. <u>Waste Streams</u> - Scrubbing water effluent with chloromethanes to remove methane and hydrogen chloride from the desired products results in the following emissions.

CH₄ - 1 g/kg product

 $CH_{3}C1 - 13$ g/kg product

CH₂Cl₂ - 2 g/kg product

CHC1₃ - 1 g/kg product

CC1₄ - 1 g/kg product

Water scrubbing to free HCl from methane stream should lead to emissions of Cl_2 and a waste acid solution. Alkali used in neutralizing the latter and in scrubbing the CH_2Cl_2 - containing stream yield spent caustic as a further pollutant.

Note that methylene chloride forms toxic products, such as phosgene, when exposed to hot surfaces or open flames.

- 6. EPA Source Classification Code None
- 7. References

Hedley, W. H., et. al., <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Technomic Publishing Co., 1975.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 115. Austin, G. T., "The Industrially Significant Organic Chemicals -Part 7," Chemical Engineering, June 29, 1974, p. 154.

"Air Pollution from Chlorination Processes," prepared for Office of Air Program, Environmental Protection Agency, Contract No. CPA 70-1, Task Order No. 23, March, 1972.

Chloroform (chlorination of methane)

 $CH_{4} + Cl_{2} \longrightarrow mixed products including CHCl_{3}$

1. <u>Function</u> - Chloroform was formerly made by reaction of chlorinated lime (bleaching powder) and acetone, acetaldehyde, or ethanol, but this appears to be uneconomical in most cases. Currently, chlorination of methane is the principal route to chloroform, with other chloromethanes usually co-produced. Control of the chlorine/methane feed ratio and other operating conditions influence the yield of CHCl₃. A two-stage chlorination provides the maximum yield. Purification of chloroform is accomplished by extraction with concentrated sulfuric acid followed by repeated distillation.

Chloroform may also be made by substituting methanol for methane.

- 2. <u>Input Materials</u> Basis 1 metric ton chloroform Methane - 187 m³ (6,604 ft³) Chlorine - 1780 kg (3924 lbs)
- 3. Operating Parameters

Temperature: elevated (250 ~ 800°C ?) (482-1472°F)

Pressure: not given

Catalyst: ultraviolet light (optional)

4. Utilities

Not given

5. <u>Waste Streams</u> - Various chloromethanes might be emitted from the methane chlorinator. Neutralization of sulfuric acid used in purification and by-product hydrochloric acid may lead to spent caustic and traces of acid in the waste water flow. Note that chloroform slowly oxidizes to phosgene on exposure to sunlight.

6. EPA Source Classification Code - None

7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 3," "Chemical Engineering," March 18, 1974, p. 89.

"1975 Petrochemical Handbook," "Hydrocarbon Processing," November 1975, p. 127.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N.Y., 1975, p. 266.

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PROCESS NO. 160
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Carbon Tetrachloride (chlorination of methane)

 $CH_4 + C1_2 \longrightarrow CC1_4 + CHC1_3 + CH_2C1_2 + CH_3C1_3$

Function - Since the 1950's chlorination of hydrocarbons, particularly 1. methane, has been a more important production route to carbon tetrachloride in the United States than chlorination of carbon disulfide. The chemical process is referred to as chlorinalysis, which involves the simultaneous breakdown of hydrocarbons and chlorination of molecular fragments. As methane and chlorine react in this manner, some carbon tetrachloride is produced, along with varying amounts of other chloro-The relative quantities depend on the composition of the methanes. hydrocarbon starting material and the conditions of chlorination. With a Cl_2/CH_4 molar ratio of 0.6, and a reaction temperature of 340-370°C, the following yields are obtained: CC14-2%, CHC13-10%, CH2C12-29%, CH₂C1-58%. Recycling partially chlorinated materials and using light as a catalyst permits essentially complete conversion to carbon tetra-The gas flow must be rapid to keep the likelihood of an chloride. explosion to a minimum. This process requires corrosion resistant metals (Ni) and exacting controls since the reaction is quite exothermic.

In Hüls process, a 5:1 ratio of Cl_2 to CH_4 by volume is reacted at 650°C, the temperature being controlled by regulating the gas flow rate. A heat exchanger cools the exit gas to 450°C before it is passed to a second reactor for the addition of more methane. Perchloroethylene is the principal co-product in this case.

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Crude carbon tetrachloride is generally purified by neutralization and drying, followed by distillation. Additional purification can be obtained at the distillation stage by maintaining the carbon tetrachloride for a prolonged period under total reflux before actually starting the distillation itself. Decomposition of carbon tetrachloride upon contact with water or on heating in air make it practical to add a small quantity of stabilizer to the commercial product.

Carbon tetrachloride may also be prepared from carbon disulfide:

 $CS_{2} + 3Cl_{2} \xrightarrow{Fe} CCl_{4} + S_{2}Cl_{2}$ $CS_{2} + 2S_{2}Cl_{2} \longrightarrow CCl_{4} + 6S$ $4S + 2Cl_{2} \longrightarrow 2S_{2}Cl_{2}$

Carbon tetrachloride is also a by-product of the vigorous chlorination and dehydrochlorination of ethylene dichloride and the Deacon process.

- 2. <u>Input Materials</u> Basis 1 metric ton product Methane - 110 kg (242.5 lbs) Chlorine - 2.210 kg (4872 lbs)
- 3. Operating Parameters

Temperature - 250-650°C (482-1202°F)

Pressure - atmospheric

Catalyst - light (optional)

Reaction time - very short

- 4. <u>Utilities</u> Basis 1,000 kg CCl₄ Electricity, GJ - 0.486 (135 kWh) Steam (1.2 MPa, 12 bar), kg-135 (298 lbs) Steam (0.95 MPa, 4.5 bar), kg-135 (298 lbs) Cooling water, m³ - 85 (22,457 gal) Fuel, GJ-0.837 (2 x 10⁵ kcal)
- 5. <u>Waste Streams</u> Various chloromethanes emitted from the process during the early repeated-chlorination stage (8 lbs./100 lbs. product). An alkali of some sort is used to neutralize hydrochloric acid (118 lbs./ 100 lbs. product) which is formed by the chlorination reaction and traces of the spent liquid might appear in wastewater flow.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 2," "Chemical Engineering," February 18, 1974, p. 127.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 132,133.

Faith, W. L., et. al., <u>Industrial Chemicals</u>, 3rd Ed., John Wiley & Sons, Inc., New York, N.Y., 1965, p. 229-231.

Sittig, M., Organic Chemical Processes, Noyes Press, Inc., Pearl River, N.Y., 1972, p. 39,40.

7. References (continued)

"1973 Petrochemical Handbook," "Hydrocarbon Processing," November 1973, p. 156-157.

"1975 Petrochemical Handbook," "Hydrocarbon Processing," November 1975, p. 126.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N.Y., 1975, p. 232. Chlorodifluoromethane (chloroform and hydrogen fluoride)

$$CHC1_3 + 2HF \xrightarrow{(SbC1_3)} CHC1F_2 + 2HC1$$

- <u>Function</u> Chlorodifluoromethane is derived by reaction of chloroform with anhydrous hydrogen fluoride, catalyzed by antimony trichloride.
- 2. Input Materials

Chloroform

Anhydrous hydrogen fluoride

3. Operating Parameters

Temperature: not given

Pressure: not given

Catalyst: SbCl,

- 4. <u>Utilities</u> not given
- 5. <u>Waste Streams</u> Various chlorofluoromethanes are potential gaseous emittants. By-product hydrochloric acid and caustic solution used in neutralization may appear in waste water streams.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 9 (1966), p. 743, 746. Carbon Tetrabromide (from carbon tetrachloride)

$$CC1_4 \xrightarrow{A1Br_3} CBr_4$$

- <u>Function</u> Carbon tetrachloride reacts with aluminum tribromide at high temperature to yield carbon tetrabromide.
- 2. Input Materials

Carbon tetrachloride Aluminum tribromide

3. Operating Parameters

Temperature - 100°C (212°F)

Pressure - Not given

- 4. Utilities Not given
- 5. <u>Waste Streams</u> The various bromethanes are possible emissions from this process. Carbon tetrachloride, aluminum hydroxide, and possibly some HBr or Br₂ may be present in the waste streams.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 131. INDUSTRIAL ORGANIC CHEMICALS

Dichlorodifluoromethane and Trichlorofluoromethane (catalytic fluorination of carbon tetrachloride)

 $3CC1_4 + 2SbF_3 \xrightarrow{SbC1_5 \text{ catalyst}} 3CC1_2F_2 + 2SbC1_3$

 $6HF + 2SbC1_3 \longrightarrow 2SbF_3 + 6HC1$

$$2CC1_4 + 3HF \xrightarrow{SbC1_5} CC1_3F + CC1_2F_2 + 3HC1_3F$$

1. <u>Function</u> - Preparation of these two chlorofluoromethanes is not by direct fluorination but rather by the replacement of chlorine atom of carbon tetrachloride with fluorine due to the action of SbF_3 containing antimony pentahalide, either SbCl_5 or SbF_5 , as catalyst. The industrial process uses liquid hydrogen fluoride as an inexpensive source of fluorine and involves continuous regeneration of a small initial batch of SbF_3 .

The process is usually conducted at about 100° C and from 0 to 3.45 MPa (0-34.0 atm) with gaseous HF. Dichlorodifluoromethane and hydrochloric acid, which is insoluble in liquid HF, are taken off to a column which readily separates the partially fluorinated substance CCl₃F.

2. <u>Input Materials</u> - Basis - 1 metric ton dichlorodifluoromethane Carbon tetrachloride CCl₄ - 1600 kg (3527 lbs) Antimony (III) fluoride SbF₃ - small Hydrogen fluoride - 413 kg (911 lbs) 3. Operating Parameters

Temperature: 0-100°C (0-212°F) Pressure: 0-3.45 MPa (0-34.0 atm) Catalyst: SbCl₅ (or SbF₅)

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Hydrogen chloride produced, which is insoluble in liquid HF, must be removed and neutralized before ultimate disposal, leading to possible pollution of waste liquid flow by HCl, spent caustic, and perhaps traces of dissolved HF. Any gas-phase reaction is a potential source of chlorofluorohydrocarbons to be emitted to the air.
- 6. EPA Source Classification Code None
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 4," "Chemical Engineering," April 15, 1974, p. 86, 87.

U.S. Patent 3,381,044 (April 30, 1968).

Sittig, M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition, Noyes Development Corp., Park Ridge, N.J., 1969, p. 232.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 325, 326.

INDUSTRIAL ORGANIC CHEMICALS

PROCESS NO.164

Carbon Disulfide (catalytic methane-sulfur reaction)

 $CH_4 + 4S \longrightarrow CS_2 + 2H_2S$

1. <u>Function</u> - The basic production of CS₂ in the United States is currently limited to the catalytic reaction of methane (or natural gas) and sulfur vapor; this Thacker process having almost completely (70%) replaced the older charcoal-sulfur retort method. This system provides yields of over 90 mole percent carbon disulfide per pass with the use of active catalysts such as silica gel. The process usually operates in the temperature range 500-700°C, and the pressure may be about 170 kPa (25 psi). Space velocities, based on hydrocarbon gas charge, in this case methane, are on the order of 100-400 volumes of gas per hour per unit volume of catalyst. Sulfur is usually charged in slightly higher than stoichiometric amounts.

The hydrogen sulfide formed may be used as an end product or it may be reconverted to elemental sulfur, for recycle to the reaction system, in a separate partial oxidation unit using the Claus process. This involves burning H_2S with air to form sulfur dioxide, which then reacts with the remaining H_2S , at about 300°C in the presence of catalyst, to form sulfur. The Claus process permits about 95% conversion to sulfur based on the hydrogen sulfide charge.

The process flow for the carbon disulfide formation reaction is as follows. Molten sulfur, maintained at about 130°C, is transferred to a sulfur boiler where it is vaporized and further heated to 575-650°C to convert the sulfur vapor to the diatomic form. Methane, or natural

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gas from which higher molecular weight paraffins are substantially removed, is preheated to $550-650^{\circ}$ C and mixed with the sulfur vapor. The mixed stream, with or without additional heating, is passed downward through a fixed-bed catalytic reactor for the formation of CS₂. The reason for avoiding higher molecular weight hydrocarbons in the feed is that under specified conditions, these are more reactive than CH₄ and will combine with sulfur to produce polymerization and condensation products, leading to catalyst contamination.

The reactor effluent is cooled to about 130° C and the unreacted sulfur is separated in a gas-sulfur separator and recycled to the process. Simultaneously, small amounts of sulfur dust in the product stream are removed by scrubbing with liquid sulfur. The carbon disulfide is separated from H₂S by preferential absorption in a suitable mineral oil solvent from which it is subsequently stripped and sent to a distillation section.

The stripped carbon disulfide is separated from small amounts of impurities in two successive distillations with low-boiling impurities removed overhead in the first column. The bottoms material from this section is distilled in a second column where the final high-purity CS_2 is recovered as the distillate. The off-gas from the carbon disulfide absorber contains 90-95% H_2S and passes to the sulfur recovery unit.

Due to the corrosive nature of sulfur and hydrogen sulfide at high temperatures, stainless-steel alloys are employed in the preheaters and reactor units. High-chromium (25% Cr) and stabilized nickelchromium alloys are satisfactory.

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2. <u>Input Materials</u> - Basis - 1 metric ton CS₂

Methane: (or natural gas stripped of higher molecular weight paraffins) 345 m^3 (12,184 ft³)

Sulfur:(vapor) 925.kg (2,039 lbs)

3. Operating Parameters

Temperature: 500-700 °C (932-1292°F) Pressure: 130-300 kPa (1.28-2.96 atm) Catalyst: activated $Al_20_3 + Cr_20_3$ (others - alumina, silica-alumina, bauxite, silica-zirconia) Hourly space velocity: 600 per hr.

4. <u>Utilities</u>

Not given

- 5. <u>Waste Streams</u> Carbon disulfide manufacture contains a large number of potential emission sources and hence pollutants. The sulfur boiler and the introduction of recycle sulfur at the start of the process flow may lead to sulfur vapor escaping. Heating the methane or natural gas feed stream could be a source of gaseous hydrocarbons. Light mercaptans and heavy di-acid polysulfides are formed. The Claus sulfur recovery unit and the purification of carbon disulfide by staged distillation should give off undetermined amounts of sulfur compounds, including H_2S and SO_2 .
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 2," "Chemical Engineering," February 18, 1974, p. 127. 7. <u>References</u> (continued)

Kirk-Othmer, Encyclopedia of Chemical Technology, Interscience Publishers, New York, N.Y., Vol. 4 (1964), p. 376-378.

Hahn, A. V., <u>The Petrochemical Industry: Markets and Economics</u>, McGraw-Hill Book Co., New York, N.Y., 1970, p. 168,169.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 224,225.

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PROCESS NO. 165
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Perchloromethyl Mercaptan (chlorination of carbon disulfide)

 $CS_2 + 6C1_2 \longrightarrow SC1_2 + C1_3CSC1_4$

1. <u>Function</u> - Perchloromethyl mercaptan is prepared by the chlorination of carbon disulfide at 20°C in the presence of iodine as a catalyst. The reaction is carried out in glass-lined jacketed vessels. Chlorination is continued until 3-5% excess chlorine is present. (The excess chlorine converts any S_2Cl_2 to SCl_2).

The reaction mixture is then fractionally distilled under a 20 in. vacuum to remove the SCl_2 , excess chlorine, unreacted CS_2 and CCl_4 . An 85% yield of 97-98% purity product is obtained. Perchloromethyl mercaptan is an intermediate for the fungicide Captan.

2. Input Materials

Carbon disulfide

Chlorine

3. Operating Parameters

Temperature - 20°C (68°F) Pressure (for distillation) - 2.66 kPa (0.026 atm) Catalyst - Iodine

- 4. Utilities Not given
- <u>Waste Streams</u> Emission probably contains traces of reactants, hydrolysis products of chlorinated compounds, and sulfur from decomposition of S₂Cl₂.

6. EPA Source Classification Code - None

7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 19 (1969), p. 374.

Senning, A., Editor, <u>Sulfur in Organic and Inorganic Chemistry</u>, Marcel Dekker, Inc., New York, N. Y., Vol. 1, 1971, p. 244. Kharasch, N. and Meyers, C.Y., <u>The Chemistry of Organic Sulfur Compounds</u>,

Vol. 1, 1961, p. 362-364.

INDUSTRIAL ORGANIC CHEMICALS

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PROCESS NO. 166
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Hydrogen Cyanide (reaction of methane, ammonia, and air)

 $2CH_4 + 2NH_3 + 30_2 \longrightarrow 2HCN + 6H_20$

- 1. <u>Function</u> As of January 1971, 70% of the hydrogen cyanide produced in the United States was manufactured via the Andrussow process. In the process a mixture of air, CH_4 , and NH_3 in a volume ratio of 6:1:0.9 is passed over the catalytic surface at a pressure of about 250 kPa (22 psig) and gas velocity of .53 m/sec. A typical catalyst consists of a number of layers of woven, 80-mesh 90% platinum - 10% rhodium gauze made of 3-mil wire. The hot gases from the reactor are quenched (to prevent polymerization of HCN), and unreacted ammonia is removed (as $(NH_4)_2SO_4$) or recycled. The off-gas, with ammonia removed goes to a cold water acidic absorber to remove HCN which is then stripped and fractionated by conventional means. Assuming recycle of unreacted NH_3 , the ultimate yield of HCN can be 87% of the theoretical value. The DEGUSSA and Fluohmic processes are variations of the Andrussow process.
- 2. <u>Input Material</u> Basis 1 metric ton HCN (99.5%) Methane - 115m³ Air - 7500 m³ Ammonia - 830 kg (assuming 75% yield) Phosphoric acid, 85% (stabilizer) Sulfuric acid, sp.gn.1.7 - 725 kg

3. Operating Parameters

Temperature - 1000-1200°C (1832-2192°F) Pressure - ~250 kPa (2.47 atm) Gas feed velocity - .53 m/sec. Catalyst: Pt/Rh mesh

- 4. Utilities Not given
- <u>Waste Streams</u> Possible air emissions NH₃, CH₄, H₂, HCN, CO. Waste water solutions of sulfuric acid, and ammonium sulfate.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 6 (1965), p. 576-580.

Lowenheim, F. A. and Moran, M. M., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N. Y., 1975, p. 482-486.

Ethyl Orthoformate(from HCN/HC1/EtOH)

HCN + EtOH $\xrightarrow{\text{HC1}}$ H-C-OEt · HC1 $\xrightarrow{\text{EtOH}}$ HC(OEt)₃

- Function Ethyl orthoformate is prepared in a two-step process by reacting hydrogen cyanide, ethanol, and hydrochloric acid at room temperature followed by reaction with ethanol in the cold.
- 2. Input Material

Hydrogen cyanide

Ethanol

Hydrochloric acid

3. Operating Parameters

Temperature: 1st Step - room temperature

2nd Step - reduced temperature

- 4. Utilities Not given
- <u>Waste Streams</u> Unreacted HCN, EtOH, and HC1 should be present along with ammonia and/or ammonium salts.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 6 (1965), p. 574. Cyanogen Chloride (chlorination of hydrogen cyanide)

NaCN (aq) + $C1_2 \longrightarrow NCC1 + NaC1$ HCN + $C1_2 \longrightarrow NCC1 + HC1$

- <u>Function</u> Cyanogen chloride is readily formed by the reaction of hydrogen cyanide and chlorine in the liquid phase. A possible preliminary stage in cyanogen chloride manufacture is the reaction of hydrogen cyanide with sodium hydroxide in aqueous solution to form NaCN. Sodium cyanide may then be chlorinated in aqueous solution (pH <8.5) to give NCC1.
- 2. <u>Input Materials</u>

Hydrogen cyanide

Chlorine

- 3. <u>Operating Parameters</u> Not given
- 4. Utilities

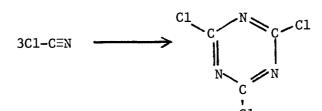
Not given

- 5. <u>Waste Streams</u> Chlorine gas, HCN, and NCC1 are all possible airborne emissions. Wastewater will probably contain trace of hydrogen cyanide as well as spent caustic and sodium chloride from scrubbing operations used to nuetralize the hydrochloric acid by-product.
- 6. EPA Source Classification Code None

7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 3.

Hahn, A. V., <u>The Petrochemical Industry: Markets and Economics</u>, McGraw-Hill Book Co., New York, N.Y., 1970, p. 160. Cyanuric Chloride (polymerization of cyanogen chloride)



- Function Cyanuric chloride is prepared by the vapor phase polymerization of cyanogen chloride.
- 2. Input Materials

Cyanogen chloride Charcoal carrier impregnated with 3.75% CaCl₂, BaCl₂, or S_2^{Cl}

3. Operating Parameters

Temperature: 250-480°C (482-896°F).

- 4. Utilities Not given.
- <u>Waste Streams</u> Spent polymerization catalysts may be present in process wastes. Possible atmospheric emissions include cyanogen chloride and by-products.
- 6. EPA Source Classification Code None.
- 7. <u>References</u>

British Patent 602,816 (June 3, 1948).

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 20 (1969), p. 667.

Acetone Cyanohydrin

 $(CH_3)_2CO + HCN \rightarrow (CH_3)_2COHCN$

- <u>Function</u> Acetone cyanohydrin is manufactured on an industrial scale by the base-catalyzed condensation of acetone and hydrogen cyanide. The reaction temperature is normally kept under 40°C. The product must be acidified to prevent decomposition.
- 2. Input Materials

Acetone - 0.6 kg/kg product Hydrogen cyanide Unspecified acid

3. Operating Parameters

Temperature: < 40°C (104°F) Pressure: atmospheric pressure Catalyst: caustic soda

4. Utilities

Not given

- 5. <u>Waste Streams</u> Information available on this process was too limited to identify specific pollutant sources. However, reactants are probably present in air emissions from reactor vents and purification procedures.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 6 (1965), p. 672.

7. <u>References</u> (continued)

Waddams, A. L., Chemicals from Petroleum, 3rd Ed., John Murray Ltd., London, Eng., 1973, p. 127.

INDUSTRIAL ORGANIC CHEMICALS

Methacrylic Acid (from acetone cyanohydrin)

$$(CH_3)_2 COHCN + H_2SO_4 \xrightarrow{130-160°C} CH_2 = C(CH_3)CONH_2 \cdot H_2SO_4$$

 $CH_2 = C(CH_3)CONH_2 \cdot H_2SO_4 + H_2O \xrightarrow{90°C} CH_2 = C(CH_3)COOH + NH_4HSO_4$

 <u>Function</u> - In the preparation of methacrylic acid, acetone cyanohydrin and concentrated sulfuric acid are pumped to a hydrolysis kettle where they react to form methacrylamide sulfate. This conversion is usually carried out at 130 - 150° C.

After cooling, the crude intermediate is taken to a second reactor where is combines with water to form methacrylic acid and ammonium bisulfate.

The product stream is then pumped to the acid-stripping column where methacrylic acid and some water distill. The residue, made up of sulfuric acid, ammonium bisulfate, and water, is sent to the ammonium sulfate plant.

The overhead from the acid-stripping column enters a rectifier column where methacrylic acid comes over the top, is condensed, and is sent to the wash column. Crude methacrylic acid comes off on the top of the wash column, and is shipped to other plants for further distillation. The water solution from the bottom of the column is recycled to the rectified column to complete methacrylic acid recovery.

Polymerization inhibitors are added at the acid-stripping column and the rectified columns.

2. Input Materials

Acetone cyanohydrin - 1.18 kg/kg product

Sulfuric acid

Water

Polymerization inhibitors

3. Operating Parameters

Temperature: first reactor - 130-160° C (266-320°F) second reactor - 90° C (194°F)

Pressure: Not given

- 4. Utilities Not given
- 5. <u>Waste streams</u> The waste water stream from the rectifier column probably contains small quantities of methacrylic acid and polymerization inhibitors. Traces of methacrylic acid and other organics may be discharged to the air by various processing equipment.
- 6. <u>EPA Source Classification Code</u> None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 13 (1967), p. 333.

Methacrylic Esters (from acetone cyanohydrin)

 $(CH_3)_2 COHCN + H_2SO_4 \xrightarrow{130-160^{\circ}C} CH_2 = C(CH_3) CONH_2 \cdot H_2SO_4$ $CH_2 = C(CH_3) CONH_2 \cdot H_2SO_4 + ROH \xrightarrow{90^{\circ}C} CH_2 = C(CH_3) COOR + NH_4HSO_4$

 Function - Methacrylic esters are prepared from acetone cyanohydrin in the same manner as methacrylic acid (see Process No. 171). In this process variation, the methacrylamide sulfate intermediate is reacted with ethyl, n-butyl, isobutyl, n-hexyl, or n-lauryl alcohol rather than water to yield the corresponding ester.^{*}

Ester recovery operations are essentially the same as those used in methacrylic acid purification. An alcohol recovery section is necessary, however, to strip excess alcohol from the rectifier bottoms for recycle.

2. Input Materials

Acetone cyanohydrin Sulfuric acid Water

Alcoho1

Polymerization inhibitors

- 3. Operating Parameters see Process No. 171
- 4. Utilities

Cooling water - 166 kg/kg product

Steam -0.25 kg/kg product

^{*}Many other alcohols are also used.

5. <u>Waste Streams</u> - Waste water from the alcohol-recovery column probably contains some methacrylic acid, alcohol, and polymerization inhibitors. Traces of alcohol and methacrylic acid may also be discharged through reactor and various distillation column vents. Sulfuric acid is discharged in waste water streams.

COD -
$$1.78 \times 10^5 \text{ mg/l}$$

BOD₅ - $2.07 \times 10^4 \text{ mg/l}$
TOC - $6.99 \times 10^4 \text{ mg/l}$

- 6. EPA Source Classification Code None
- 7. <u>References</u>

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corporation, Park Ridge, N.J., 1974, p. 164-166.

Acetylene (BASF process)

 $2CH_4 \longrightarrow CHECH + 3H_2$

 <u>Function</u> - In the United States, the initial commercial production of acetylene from hydrocarbon sources began in 1951. Today, most of the manufacture of acetylene for chemical synthesis is based on the process researched by Badische Anilin-und Soda-Fabrik (BASF) in the 1920's.

In this so-called partial oxidation, or one-stage combustion method, the necessary energy for cracking the feedstock is derived by partial combustion of the hydrocarbon feed. Natural gas or other methane-rich feedstock is mixed with a limited amount of oxygen sufficient for complete combustion, and fed through a specially designed distributor or burner to a single reaction zone in which ignition occurs. Improved results are claimed for variations which involve preheating of the separate gas streams (Societe Belge de l'Azote, SBA) or preheating the premixed composite feed (Hydrocarbon Research, Inc.). The Montecatini process, in addition employs pressure operations of up to six atmospheres and effects partial cooling of the burner gas by injecting higher hydrocarbons after the flame, resulting in production of ethylene and additional acetylene.

Design of the burner is of considerable importance and is a common point of process variation. Preignition, stability, and blowoff of the flame, the possibility of backfiring through the burner head ports, and deposition of carbon on the burner walls all depend

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on the burner design and the gas and flame velocities. The combustion of the gas mixture must be as uniform as possible across the reaction chamber so that the residence time of the reactant hydrocarbon is as short as possible, usually on the order of 1 to 10 milliseconds.

Yields of acetylene based on carbon in the natural gas feed vary from 30 - 36% by weight for the various processes. The composition of the cracked gas produced from a natural gas feedstock by the BASF one-stage combustion process is given in the following table:

Component	<u>% by Volume</u>
acetylene	8.5
hydrogen	57.0
carbon monoxide	25.3
carbon dioxide	3.0
methane	4.0
higher acetylenes	1.0
inert material	1.0

Composition of BASF Process Gas

The actual operation of the BASF convertor begins with separate preheating of methane and oxygen (95 - 98% pure) to about 650°C. The feed streams are then mixed in a venturi-type chamber in a molar ratio of about 0.6:1.0, oxygen to methane. The mixed gas is passed to the flame space through a number of tubular channels in a burner block. About one third of the methane entering the burner is cracked to acetylene, the remainder is burned with 0₂. The pyrolysis products are immediately quenched to about 280°C by one or more water sprays located in the lower part of the reactor, and the effluent gases pass through scrubbers for the removal of water and soot. Higher acetylenes present in the pyrolysis gas must be removed because of this tendency to polymerize. Electrostatic units, combined with water scrubbers, moving coke beds, and bag filters, are being used for soot removal.

The unstable, explosive nature of acetylene imposes certain limitations on the use of customary separation techniques. Studies indicate that operating conditions where acetylene partial pressure exceeds 100 to 200 kPa or where temperatures exceed 95 - 105°C should be avoided. All commercial processes for the recovery of hydrocarbon-derived acetylene are based on absorption/desorption techniques using one or more selective solvents (i.e., dimethyformamide).

2. Input Materials

Methane - 4.11 kg/kg acetylene produced Oxygen - 4.75 kg/kg acetylene produced

3. Operating Parameters

Temperature: 1480 - 1540°C (2,696-2,804°F) Pressure: reduced

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Hydrocarbons from the feedstock may be emitted to the air. Water spray used to quench the reaction mixture may pick up traces of dissolved gases, such as carbon oxides, hydrogen,

5. Waste Streams (continued)

or hydrocarbons, which would eventually find their way to waste water streams. Carbon black may give rise to particulates suspended in air or water.

Flow - 0.0047 m³/kg (561 gal/10³ lbs) COD - 1,274 mg/1 5.95 g/kg BOD₅ - 410 mg/1 1.92 g/kg TOC - 393 mg/1 1.80 g/kg

- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 178-180.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N.Y., 1975, p. 30-33.

Vinyl Acetate (from acetylene)

$$HC=CH + CH_3COOH \xrightarrow{cat.} CH_2=CHOCCH_3$$

 <u>Function</u> - Until 1967 vinyl acetate was produced in the United States predominantly from acetylene. By 1973 about 75% of the vinyl acetate was manufactured by the vapor-phase oxyacetylation of ethylene.

In the acetylene process, the acetylene is specially purified to remove H₂S and phosphorus compounds. It is then mixed with gaseous acetic acid and fed into a fixed-bed reactor with zinc acetate on carbon as catalyst. Reactor temperature is maintained at 175-200°C. The reactor effluent is condensed, light ends removed, and vinyl acetate distilled.

2. Input Materials

Acetylene - 325 kg/metric ton vinyl acetate Acetic acid - 710 kg/metric ton vinyl acetate

3. Operating Parameters

Temperature - 175-200°C (347-392°F) Pressure - not given Catalyst - Zinc acetate on carbon

- 4. Utilities not given
- 5. <u>Waste Streams</u> Waste gases may contain traces of light ends (methyl acetylene, allene, acetylene). Waste waters may contain traces of acetic acid.
- 6. EPA Source Classification Code None

7. References

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, '4th Edition, John Wiley & Sons, New York, N.Y., 1975, p. 862-867.

Waddam, A. L., <u>Chemicals from Petroleum</u>, 3rd Edition, John Wiley & Sons, New York, N. Y., 1973, p. 42.

INDUSTRIAL ORGANIC CHEMICALS

PROCESS NO. 175

1,1-Difluoroethane (hydrofluoric acid and acetylene)

H-C=C-H + $2HF \longrightarrow CH_3CHF_2$

- Function 1,1-Difluoroethane is derived by passing acetylene and a selected catalyst into the bottom of a stainless steel column of liquid hydrogen fluoride. The gaseous reaction products are washed with soda lime, distilled and condensed.
- 2. Input Materials Basis 0.93 part.

Acetylene: 1 part Hydrogen fluoride: 1.6 parts BF₃ (10%): 0.52 parts

3. Operating Parameters

Temperature: 0-20°C (0.68°F) Pressure: 68.9-517 kPa (0.58-5.10 atm) Catalyst: Anhydrous stannic-chloride Contact Time: 20 sec.

- 4. Utilities Not given.
- 5. <u>Waste Streams</u> Acetylene, difluorethane, and HF may be emitted to the atmosphere. Soda lime sludge should be present.
- 6. EPA Source Classification Code None.
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 9 (1966), p. 835.

U. S. Patent 2,830,099 (April 8, 1958).

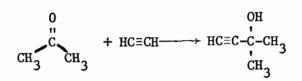
U. S. Patent 2,425,991 (1947).

Sittig, M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition, Noyes Development Corp., Park Ridge, N. J., 1969, p. 246. INDUSTRIAL ORGANIC CHEMICALS

PROCESS NO. 176

1,1,1-Chlorodifluoroethane (chlorination of difluoroethane) AIBN $CH_3CHF_2 + Cl_2$ ____ CH₃CC1F₂ + HC1 Function - 1,1,1-Chlorodifluoroethane is prepared by chlorinating 1. 1,1-difluoroethane in the presence of azobis-isobutyronitrile (AIBN). 2. Input Materials Difluoroethane Chlorine 3. **Operating Parameters** Temperature: 70-100°C (158-212°F) Pressure: 2.59 - 3.79 MPa (25.5-37.9 atm) Catalyst: AIBN Reaction Time: 2-8 seconds. 4. Utilities - Not given. 5. Waste Streams - Spent caustic and salt are pollutants from the scrubber used to remove hydrochloric acid by-product. Some chlorine may be emitted to the air as well as chlorinated compounds, acetylene and vinyl chloride. 6. EPA Source Classification Code - None. 7. References Sittig, M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition, Noyes Development Corp., Park Ridge, N. J., 1969, p. 169.

Methyl Butynol (ethynylation of acetone)



 <u>Function</u> - 2-Methyl-3-butyn-2-ol is produced by ethynylation of acetone with excess acetylene in liquid ammonia in the presence of sodamide (NaNH₂) or some other basic catalyst. The reaction is carried out at a temperature of 10-40°C and high pressure (1.97 MPa).

The process is terminated by adding a material to decompose the catalyst. The pressure is then dropped to atmospheric in a suitable flash tank. Ammonia and excess acetylene are recycled to the reactor, and unreacted acetone is removed from the product in a distillation column. A second distillation step takes the methyl butynol overhead as an azeotrope containing 28.4% water, leaving behind deactivated catalyst salts and heavy by-products.

2. Input Materials

Acetylene

Acetone

Ammonia

3. Operating Parameters

Temperature: 10-40°C (50-104°F) Pressure: 1.97 MPa (19.4 atm) Catalyst: NaNH₂ (alkali or alkaline earth oxides also acceptable)

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Recycling of ammonia and excess acetylene to the reactor is a potential source of leaks to the atmosphere. Distillation to remove remaining reactants may cause atmospheric emission of solvents. The second distillation bottoms include deactivated catalyst salts and heavy by-products, which will eventually appear in waste water flow.
- 6. EPA Source Classification Code None

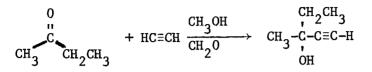
7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 208.

Ibid., Vol. 12 (1967), p. 120.

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 291.

Methyl Pentynol (acetylation of 2-butanone)



 <u>Function</u> - 3-Methyl-1-pentyn-3-ol is manufactured by the reaction of acetylene and 2-butanone in dimethylacetal of formaldehyde as the solvent. Sodamide, sodium or potassium hydroxide, potassium t-butoxide, or other alkali or alkaline earth oxides are used as condensing agents.

A typical yield for this process is 50% based on 2-butanone.

2. Input Materials

2-Butanone - 1.47 kg/kg product

Acetylene

Dimethylacetal of formaldehyde (solvent purposes only)

3. Operating Parameters

Temperature: not given

Pressure: not given

Catalyst: NaNH₂, NaOH or KOH, KOC(CH₃)₃, or other alkali or alkaline earth oxides.

- 4. Utilities Not given
- 5. <u>Waste Streams</u> See description under Process No. 177.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 208.

<u>References</u> (continued)
 <u>Ibid.</u>, Vol. 12 (1967), p. 120.

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1,1,2,2-Tetrachloroethane (chlorination of acetylene)

 $\text{HC=CH} + 2\text{Cl}_2 \xrightarrow{\text{cat.}} \text{HCCl}_2\text{CHCl}_2$

- 1. <u>Function</u> Chlorine and acetylene are mixed independently with portions of a mixture of tetrachloroethane and antimony trichloride. These two mixtures, one containing chlorine (60-80°C) and the other acetylene (80-100°C) are then brought in contact under controlled conditions. The product 1,1,2,2-tetrachloroethane is distilled from the reaction mixture and mostly used for production of trichloroethylene. Less than 10% of trichloroethylene is derived directly from acetylene.
- 2. Input Materials

Acety1ene

Chlorine

3. Operating Parameters

Temperature - 70-80°C (158-176°F)

Pressure - Not given

- 4. Utilities Not given
- 5. <u>Waste Streams</u> The following air emissions arise from the reflux condenser vent of the chlorination reactor.

Ethane - 1.25 g/kg product

Methane - 1.25 g/kg product

Tetrachloroethane - 0.50 g/kg product

Waste water flow may contain traces of tetrachloroethane and alkali metal compounds from washing operations as well as suspended particles of iron or other inorganic catalyst species used.

6. EPA Source Classification Code - None

7. References

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 607, 608, 845-848.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 161-163.

Hedley, W. H., et al., "Potential Pollutants from Petrochemical Processes," Technomic Publishing Co., Westport, Conn., 1975. Trichloroethylene (from tetrachloroethane)

 $CHC1_2CHC1_2 \xrightarrow{\wedge} CHC1=CC1_2 + HC1$

1. <u>Function</u> - The cracking of tetrachloroethane in the presence of a catalyst of BaCl₂ on carbon is the currently preferred method of production. The reaction takes place at 250-300°C and produces a mixture of trichloroethylene and 10 percent perchloroethylene, which may be separated by distillation. After distillation from heavy ends, a small amount (20 ppm by weight) of trimethylamine or pyrrole-based compounds may be added to stabilize the product.

A small amount of trichloroethylene can be made by pyrolyzing 1,1,2-trichloroethane in the presence of air or 0_2 :

 $2CH_2CICHCl_2 + O_2 \xrightarrow{\Delta} 2 CCl_2 = CHCl + H_2O$

2. Input Materials

Tetrachloroethane

3. Operating Parameters

Temperature.250-300°C (482-572°F)Catalyst30 percent BaCl₂/C

4. Utilities

Not given

- 5. <u>Waste Streams</u> No specific information was available, but one would expect some HCl and various chlorohydrocarbons to be present in the gaseous and aqueous waste streams.
- 6. EPA Source Classification Code None

7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 8," "Chemical Engineering," July 22, 1974, p. 115.

Faith, W. L. et al., <u>Industrial Chemicals</u>, 3rd Ed., John Wiley & Sons, Inc., New York, N. Y., 1965, p. 784.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Ed., Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 190. Synthesis Gas (catalytic steam-hydrocarbon reforming)

$CH_4 + H_2 0 \longrightarrow 0$	co +	3F	¹ 2
$CH_4 + 2H_20 \longrightarrow$	co ₂	+	^{4H} 2
co + H ₂ 0 →	co ₂	+	^н 2

1. <u>Function</u> - Synthesis gas is any mixture of carbon monoxide and hydrogen, in variable proportions, usually intended for conversion to ammonia, purified hydrogen, hydrocarbons, alcohols, or other organic compounds. By 1965, catalytic steam-hydrocarbon reforming used to recover hydrogen from hydrocarbon feedstocks up to and including light gasoline fractions, and producing more hydrogen, and synthesis gas mixture than any other method. In this process, gaseous hydrocarbons, such as methane are reacted with steam at 650°C to 1050°C in the presence of a suitable nickel catalyst to produce carbon oxides and hydrogen at about the same temperatures.

Important factors to be considered in the design of a steamhydrocarbon reforming plant are:

- Process Hydrocarbon. Basic requirements for a satisfactory hydrocarbon feed to a steam-reforming operation are:
 - a) <u>Freedom from sulfur compounds</u>. The total sulfur content should be less than 1-5 parts per million, since sulfur acts as a catalyst poison.
 - b) <u>Absence of unsaturated hydrocarbons</u>. These compounds tend to deposit carbon on the reforming catalyst, causing both loss of activity and physical deterioration.

- c) The hydrocarbon feed should be in the vapor phase when it contacts the catalyst.
- 2) Operating Pressure. Ammonia and methanol synthesis, petroleum hydrogenation, hydrogen liquefaction, and the pressure storage of hydrogen gas all require hydrogen at elevated pressures ranging up to 100 MPa (1000 atm). Since natural gas is often available at pipeline pressures of 4 MPa (40 atm) or more, and steam may be generated efficiently at this pressure, carrying out the steam hydrocarbon reforming process at higher pressures, 1.8-3.2 MPa (18-32 atm), may result in substantial economics. Increased pressure operation also permits heat recovery from the reaction product stream at higher temperature levels, due to the higher partial pressure of the excess steam in the gas mixture.
- 3) <u>Catalyst selection</u>. Several commercial catalyst are available. These catalysts contain 20-35% nickel oxide mixed with refractory cement. Coimpregnation of a small amount of magnesium oxide with the nickel oxide has been found to improve the activity and stability of alumina-supported catalyst.
- 4) <u>Tube surface temperature</u>. The low strength of 25-20 chromenickel steel tubes imposes an external surface temperature limit of 930-980°C for operation at pressure greater than 1 MPa (10 atm).
- 5) <u>Steam-hydrocarbon ratio</u>. At atmospheric pressure, hydrocarbons may be reacted to produce hydrogen with less than 0.1% residual CH, by using two molecules of steam per atom of

carbon in the hydrocarbon, and carrying out the reaction at temperatures above 870°C. As the operating pressure is increased, the ratio is generally increased to between 3 and 4 molecules of steam per carbon atom in the feed material.

- 6) <u>Product gas temperature at furnace outlet</u>. This parameter is important in determining the amount of unreacted methane remaining in the product stream and is influenced by the maximum allowable tube surface temperature, the tube diameter, and the type of furnace.
- 7) <u>Flue gas temperature</u>. The flue gas temperature will probably be between 900°C and 1050°C, and the flue gas will be raised to preheat the furnace feed streams and to generate steam.
- 8) <u>Carbon monoxide removal</u>. Substantially complete removal of CO from the product stream is required when synthesis gas is used as a source of hydrogen in the synthesis of ammonia. This processing step is accomplished by causing the raw gas mixture to react with steam via the water gas shift. The carbon dioxide formed is scrubbed with appropriate solvents.
- 2. Input Materials

Natural gas (methane) or other hydrocarbon feed Steam - 2 to 6 kg/kg synthesis gas produced

3. Operating Parameters

Temperature: 650-1050°C (1202-1922°F)

3. Operating Parameters (continued)

Pressure: 1.8-3.2 MPa (17.8-31.6 atm) Catalyst: 20-35% nickel oxide on alumina support Residence time: 0.2-10 seconds

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Condensates from catalytic reforming generally contain spent catalyst particles, hydrogen sulfide formed from residual sulfur in the feed, and ammonia formed by reaction of air with the hydrocarbons at elevated temperatures.

Regeneration of the activated carbon used for sulfur removal may lead to gaseous emissions of hydrogen sulfide and/or sulfur dioxide, if this operation is performed on site.

It is unlikely that hydrocarbons from the feed stream or carbon monoxide from the product stream would be emitted to the air.

- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 275,276. Ibid., Vol. 10 (1966), p. 415-419.

U.S. Patent 3,367,882 (February 6, 1968).

Sittig, M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition Noves Development Corp., Park Ridge, N.J., 1969, p. 623. Synthesis Gas (continuous, non-catalytic partial oxidation)

 $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ $CH_4 + CO_2 \longrightarrow 2CO + 2H_2$ $CH_4 + H_2O \longrightarrow CO + 3H_2$ $CO + H_2O \longrightarrow CO_2 + H_2$

 <u>Function</u> - Synthesis gas is a mixture of carbon monoxide and hydrogen with minor amounts of carbon dioxide and nitrogen. There are two general processes used - the steam reforming process (using a nickel catalyst) and the process described here, the non-catalytic partial oxidation process.

The partial oxidation process involves the burning of hydrocarbons in air or oxygen to produce a gas containing hydrogen and carbon monoxide with small quantities of methane, CO₂ and water vapor. The use of oxygen yields a product gas of lower nitrogen content often necessary for subsequent uses of synthesis gas.

The mixture of hydrocarbon and oxygen is pre-heated to 235-650°C (455-1202°F) depending on the composition of the gas stream. It then passes to a reactor which operates at 1100-1600°C (2012-2912°F) and pressures up to 4 MPa (40 atm). The hot effluent gases are cooled in a heat exchanger, compressed and CO₂ removed by absorption in water or ethanolamine solution.

The non-catalytic partial oxidation process can operate on any hydrocarbon feedstock that can be compressed or pumped. No desulfurization process is necessary since there is no catalyst involved that can be poisoned.

2. Input Materials

Natural gas (methane) - 0.27 kg/Nm³ of crude dry gas produced (Nm³ = normal cubic meters, 0°C, 760 mm Hg. Steam - 13.40 kg/1000 Nm³ of crude dry gas or 0.05 kg/kg natural gas feed (steam saturated at 246°C (470°)). Oxygen - 0.26 Nm³/Nm³ of crude dry gas

3. Operating Parameters

Temperature: 1100-1600°C (2012-2912°F)

Pressure: 1.48-4.24 MPa (14.6-41.8 atm)

Residence time: <10 seconds

4. <u>Utilities</u>

Boiler feed water - 0.83 kg/Nm³ crude dry gas Cooling water - 0.32 kg/Nm³ crude dry gas Fresh water - 67.0 kg/1000 Nm³ crude dry gas Electricity - 16.2 kJ/Nm³ crude dry gas

- 5. <u>Waste Streams</u> The partial oxidation process produces 0.12 kg of condensate per Nm³ of crude dry product gas. Again as in catalytic reforming, it is doubtful that reactants, natural gas or oxygen, are emitted to the atmosphere during feed to the reactor. For natural gas, no soot will appear in the waste water flow. Carbon dioxide from stripping of the gas absorption system may be vented to the air.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 10 (1966), p. 419-422. Urea (once-through process)

 $2NH_3 + CO_2 \xrightarrow{H_2NCOONH_4}$

 H_2 NCOONH₄ \longrightarrow H_2 NCONH₂ + H_2 O

 Function - All commercial production of urea is based on the reaction of ammonia and carbon dioxide to form ammonium carbamate which in turn decomposes to urea and water.

The reaction is run at 175-190°C and a pressure of 16-25 MPa (160-250 atm). Under these conditions, the equilibrium urea conversions of only 40-70% can be expected. The effluent contains ammonium carbamate, urea and excess ammonia. The unreacted carbamate is decomposed to ammonia and carbon dioxide gas by heating the effluent at low pressure. The gaseous mixture is separated from the urea solution and used to produce ammonium salts by absorbing NH₃, either in sulfuric or nitric acid. CO_2 is vented to the air.

Urea is recovered from the stripped effluent solution either by evaporation or crystallization. Biuret, a condensation product of urea forms under conditions of high temperature and reduced pressure, and must be minimized for certain industrial uses of urea. Urea, produced by crystallization, contains only 0.2-0.3% of biuret. Product produced by evaporation contains a much higher biuret content.

Urea is marketed in the form of small spherical particles called prills. These are formed by spraying molten urea, at the top of a 50M cylinderical column into a counter current stream of air.

The molten urea freezes into spheres which are collected at the column bottom. The biuret content in this material is 0.6-1.5%.

2. Input Material

Ammonia - 1.87-1.77 kg/kg urea produced Carbon dioxide (from synthesis gas) - 0.91-1.47 kg/kg urea produced

- 3. <u>Operating Parameters</u> Temperature: 175-190°C (347-374°F) Pressure: 16-25 Mpa (160-250 atm)
- 4. Utilities Not given
- 5. <u>Waste Streams</u> The high vapor pressure of ammonium carbamate at elevated temperatures, may result in atmospheric emissions of that species from the urea synthesis reactor. Some ammonia may be emitted during solidification of urea by evaporation as a by-product of biuret formation. The prilling tower may be a source of particulates as well.
- 6. EPA Source Classification Code None
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 9," "Chemical Engineering," August 5, 1974, p. 97.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 21 (1970), p. 43-45.

U.S. Patent 3,072,721 (January 8, 1963).

Sittig, M., <u>Organic Chemical Process Encyclopedia - 1969</u>, 2nd Edition, Noyes Development Corp., Park Ridge, N.J., 1969, p. 690. Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 857. Urea (recycle processes)

 $2NH_3 + CO_2 \longrightarrow H_2HCOONH_4 \longrightarrow H_2NCONH_2 + H_2O$

1. <u>Function</u> - The urea synthetic processes can be divided into two general classes, the "once through process," described as a separate process, and the "recycle process." The recycle process is one in which unreacted carbon dioxide and ammonia either in the free form or combined as ammonium carbamate, are returned to the system for further conversion to urea.

There are many versions of the recycle process which differ basically in the manner in which the CO_2 and NH_3 are recovered and returned to the reactor. There may be two or three stages of carbamate decomposition each succeeding stage operated at a lower pressure and temperature.

Ammonia and carbon dioxide gases are liquified (compressed) and charged to a steam-heated, silver lined autoclave which is maintained at 175 - 200°C and 170 - 408 atm. The ammonia and carbon dioxide are converted to ammonium carbamate which decomposes to urea. The product mix consists of 35% urea, 15% ammonia, 21% ammonium carbamate and 14% water. The product is fed to a carbamate decomposer at a pressure reduced from that of the

reactor. Here carbamate decomposes into NH₃ and CO₂, the gas is recovered, cooled, and recycled to be again converted to ammonium carbamate. The effluent solution is passed to a second carbamate decomposer which is operated at a lower temperature and pressure. Additional carbamate decomposition occurs here, the gases being collected, cooled and recycled as before and the effluent passing to a third carbamate decomposer which again operates at a lower temperature and pressure. Effluent from the third stage passes to a crystallizer where urea crystals are recovered.

- 2. <u>Input Materials</u> Basis 1 metric ton urea Ammonia - 2000 kg Carbon dioxide - 900 kg
- 3. Operating Parameters

Temperature: Reactor - 175-200°C (347-392°F)

1st Decomposition stage - 150°C (302°F)

2nd Decomposition stage - 130°C (266°F)

- 3rd Decomposition stage 120°C (248°C)
- Pressure: Reactor 17.2-41.4 MPa (170-408 atm)

lst Decomposition stage - 1.8 MPa (18 atm)
2nd Decomposition stage - 0.4 MPa (4 atm)
3rd Decomposition stage - 100 kPa (1 atm)

4. <u>Utilities</u> - Data for Stamicarbon recycle urea plant producing fertilizer grade plus, biuret content = 0.2-0.25% Basis - 1000 kg urea Steam - (2.6 MPa) - 1100 kg Cooling water - 65 m³ Power - 504 MJ (140 kw)

- 5. <u>Waste Streams</u> Loss of NH₃ to the atmosphere during staged decomposition and absorption are possible emissions. CO₂ may also be emitted in the various stripping operations.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 21, (1970), p. 45-51.

"1975 Petrochemical Handbook," "Hydrocarbon Processing," November, 1975, p. 210-11.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., (1975), p. 854-857. Guanidine (from urea)

 $H_2N-C-NH_2$ + $NH_3 \xrightarrow{SO_2} H_2N-C-NH_2$ + H_2O

- 1. <u>Function</u> Guanidine may be manufactured by the reaction of urea with ammonia and sulfur dioxide. Urea, liquid sulfur dioxide, and ammonia (in molar ratio 1:3:7) are heated to 275°C under pressure for approximately 30 minutes. Guanidine (as the sulfate) is obtained in 80% yield. The reaction product is dissolved in water and filtered to remove sulfur. The solution is concentrated and treated with nitric acid to form guanidine nitrate. Guanidine is usually marketed as the nitrate or the chloride.
- 2. Input Materials

Urea

s02

NH 3

3. Operating Parameters

Temperature: 245-275°C

Pressure: 20.2 MPa (200 atm)

Time: 30 minutes

- 4. Utilities Not given
- 5. Waste Streams

Air - NH_3 and SO_2

Water - Traces of reactants and products

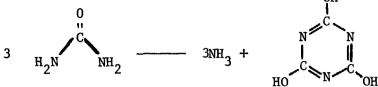
Solid waste - Sulfur

- 6. EPA Source Classification Code None
- 7. <u>References</u>

Astle, M. J., Industrial Organic Nitrogen Compounds, Reinhold Publishing Corp., New York, N.Y., 1961, p. 301.

Boivin, J. L., "Canadian J. Chem," 34, 827 (1966).

Cyanuric Acid (thermal decomposition of urea)



 Function - Heating urea for several hours at 200-300°C results in deamination and the formation of cyanuric acid.

For temperatures much above 300°C, the yield of product decreases due to depolymerization.

Conversion to cyanuric acid occurs in stages. Initially, urea melts at 133°C to form a free-flowing liquid. As heating continues, the reaction mass thickens and finally solidifies, although at this point significant amounts of urea, biuret, $H_2NCONHCONH_2$, and triuret, $H_2NCONHCONHCONH_2$, are present. Additional heating converts these to cyanuric acid. The product of pyrolysis strongly adheres to the walls of the reactor and is removed with great difficulty. Several methods have been patented to overcome such problems.

- (1) conducting pyrolysis on a molten tin or lead bath
- (2) conducting pyrolysis in a fluidized bed
- (3) recycling 60-90% of crude cyanuric acid into a rotating kiln to mix with urea prior to pyrolysis
- (4) running the reaction in certain high-boiling organic solvents
- (5) heating urea at 165°C for about two hours to get a liquid mixture consisting of urea, biuret, triuret, and cyanuric acid, followed by further pyrolysis for ten minutes at 240-270°C on a rotating heated drum.

Crude cyanuric acid produced by pyrolysis may be contaminated with as much as 20-30% impurities consisting mostly of ammelide and ammeline with minor amounts of melamine, biuret, urea, and triuret. Two general purification techniques will be described.

Cyanuric acid may be dissolved in ammonium hydroxide solution or hot dimethylformamide solution. Filtering the mixture will remove most of the impurities. The product may be precipitated from the ammonium solution by acidification with mineral acid or from the DMF solution by cooling and adding carbon tetrachloride.

Crude cyanuric acid may also be purified by heating it in 10-20% sulfuric, nitric, or hydrochloric acid for several hours. This process hydrolyzes most of the ammelide, ammeline, and melamine to cyanuric acid. The slurry is then filtered or centrifuged and the solids collected are washed with water to remove residual traces of the acid used earlier. Cyanuric acid can be dried in any conventional dryer, up to a maximum temperature of 200°C, to give a product of at least 98% purity.

- 2. Input Materials urea
- 3. Operating Parameters

Temperature: 200-300°C (392-572°F) Pressure: 101 kPa (1 atm)

4. Utilities

Not given

5. <u>Waste Streams</u> - Ammonia produced during decomposition of urea is probably emitted to the atmosphere. All other compounds (cyanuric acid, biuret, triuret, ammeline, ammelide, melamine) are solids at ordinary temperatures, and although they occur in the liquid phase

during reaction, the vapor pressures are probably too low to lead to any pollution problems.

Purification is a source of additional emissions. The precipitation method will lead to the presence of the various solvents or acid in wastewater. The acid-digestion process waste is probably neutralized, leading to spent caustic in wastewater. Drying operations should not pose any significant pollution problems.

6. EPA Source Classification Code - None

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 20 (1969), p. 667, 668. Oxo Aldehydes (oxo process)

 $\begin{array}{ccc} \text{RCH=CH}_2 + \text{CO} + \text{H}_2 & \xrightarrow{\text{cobalt}} & \text{RCH}_2\text{CH}_2\text{CH} + \text{R-CHCHO} \\ & \text{I} \\ & \text{CH}_3 \end{array}$

 Function - The oxo process consists of the hydroformylation of olefins to give aldehydes (and ultimately alcohols) of the next higher homologue. The olefin feed is usually mixed with a slurry of the cobalt catalyst (usually in the form of cobalt naphthenate) and introduced to the converter together with the synthesis gas. The reaction takes place in the liquid phase at 130-175°C and 200-300 atm.

The liquid reaction products go to a phase separator then to a cobalt removal system (decobalter). The cobalt catalyst is regenerated and recycled. The crude aldehydes are refined by distillation.

2. Input Materials

Olefin - (90%) Synthesis gas - [CO (98-99%) + H₂ (98-99%)] Co catalyst Steam CO₂

3. Operating Parameters

Temperature - 130-175°C

Pressure - 200-300 atm. (20.2-30.4 MPa)

4. Utilities - Not given

5. Waste Streams -

Air - Emissions stemming from the formation of by-products such as paraffins from hydrogenation of starting olefin; olefin feed and synthesis gas leaks.

Water or solid wastes - Wastes resulting from the high-boiling oxygenated compounds formed from condensation of aldehydes and alcohols.

6. EPA Source Classification Code - None

7. References

Sittig, M., "Oxo Products From Olefins," in <u>Pollution Control in the</u> <u>Organic Chemical Industry</u>, Noyes Data Corporation, Park Ridge, New Jersey, 1974, p. 175.

US Petrochemicals, Technologies, Markets, and Economics, Brownstein, A. M., Ed., The Petroleum Publishing Company, Tulsa, Oklahoma, 1972, pp. 92-93.

Hahn, A.V., <u>The Petrochemical Industry: Markets and Economics</u>, McGraw-Hill Book Company, New York, 1970, pp. 104-105.

"Oxo Process" in <u>Chemical and Process Technology Encyclopedia</u>, Considine, D. M., Ed-in-Chief, McGraw-Hill Book Company, New York, 1974, pp. 793-794.

Haberstroh, W. H. and Collins, E.M., "Oxo Chemicals," in <u>Riegels'</u> <u>Handbook of Industrial Chemistry</u>, 7th edition, Kent, J. A., Ed., Van Nostrand Reinhold Company, New York, 1974, pp. 774-775.

Oxo Alcohols

$$\operatorname{RCH}_{2}\operatorname{CHO}$$
 + H_{2} \longrightarrow $\operatorname{RCH}_{2}\operatorname{CH}_{2}\operatorname{OH}$

$$\begin{array}{ccccccc} 2\text{RCH}_2\text{CHO} & \xrightarrow{\text{OH}} & \text{R-C-CHO} & \xrightarrow{\text{H}}_2 & \text{R-CHCH}_2\text{OH} \\ & & & & & \\ \text{HCCH}_2\text{R} & & & \text{CH}_2\text{CH}_2\text{R} \end{array}$$

1. <u>Function</u> - Alcohols are usually the ultimate product of the oxo-process (Process No. 187). The alcohols are obtained by: (a) direct reduction of the aldehyde; (b) dimerization of the aldehyde by aldol condensation followed by reduction to the alcohol; or (c) single stage low pressure oxo process. In (a), the aldehyde from the decobalter is hydrogenated at elevated temperature and pressure to give the alcohol. In (b) the aldehyde from the decobalter is fed into a condensation reactor where the aldolization is carried out in the presence of caustic. Water is continually removed from the consendation reaction to drive it to completion. The resulting aldehyde is then hydrogenated to the alcohol.

An alternate route was recently introduced. Olefin feed and recycled catalyst are charged to the first of a series of packed reactors at controlled rates. Synthesis gas ($H_2:CO = 2.5:1$) is fed separately to each reactor. The overhead stream from the final reactor is sent directly to the recovery column. The bottoms from the recovery column contain catalyst complex in a mixture of alcohols and heavy ends. This stream is recycled to the first reactor with periodical purging to remove built-up heavy ends.

This reaction is carried out in alkaline medium with a specially promoted cobalt carbonyl catalyst. The dimer and monomer alcohols are obtained directly from the reaction mixture.

2. Input Materials

Aldehyde

Hydrogen

Phosphine-promoted cobalt carbonyl

Nickel catalyst

Zinc compound

01efin

Synthesis gas

Caustic

- 3. Operating Parameters
 - a. Temperature 150-200°C (302-392°F)
 Pressure (1500-3000 psi) 10.3-20.6 MPa (102-204 atm)
 - b. Temperature 90-230°C (194-446°F)

Pressure - <than (a)

c. Temperature - Not given

Pressure - < 30 atm. 3.04 KPa (30 atm)

- 4. Utilities Not given
- 5. <u>Waste Stream</u> Air hydrocarbons from leaks. Water High boiling oxygenated intermediates, byproducts, and heavy ends. A typical plant survey showed: Flow 1.59 m³/454 kg, COD 1.21 kg/m³ and 1.93 kg/454 kg, BOD₅ 0.9 kg/m³, 1.43 kg/454 kg, and TOC 0.549 kg/m³, .87 kg/454 kg.
- 6. EPA Source Classification Code None

7. References

Sittig, M., "Oxo Products from Olefins," in "Pollution Control in the Organic Chemical Industry," Noyes Data Corporation, Park Ridge, New Jersey, 1974, pp. 175-177.

Long, F.W., "Technology and Markets of Petrochemicals Derived from Synthesis Gas," in "US Petrochemicals: Technologies, Markets, and Economics," Brownstein, A. M., Ed., The Petroleum Publishing Company, Tulsa, Oklahoma, 1972, pp. 92-94.

Waddams, A.L., Chemicals From Petroleum, 3rd Edition, John Murray Ltd., London (1973), p. 204-206.

Phosgene (catalytic reaction of carbon monoxide and chlorine)

$$CO + C1_2 \xrightarrow{\text{catalyst}} COC1_2$$

 <u>Function</u> - Phosgene is manufactured by reacting chlorine gas and carbon monoxide in the presence of activated carbon. Dry carbon monoxide of the highest possible purity is metered and mixed in a reactor with dry and pure chlorine at a temperature of 200°C and 2 to 4 psig over gasmask grade activated charcoal.

The hot effluent gases leaving the reactor are led to a condenser, where liquid phosgene is removed. The non-condensable gases are scrubbed with a hydrocarbon solvent to remove entrained phosgene. Nearly all phosgene is used at the point of manufacture, mostly in the manufacture of isocyanates for polyurethane resins.

2. Input Materials

Carbon monoxide - 230 m^3 /metric ton product Chlorine - 720 kg/metric ton product

3. Operating Parameters

Temperature - 200°C (392°F) Pressure - 13.8-27.6 kPa (0.14-0.27 atm) Catalyst - activated charcoal 15 kg/metric ton product

4. Utilities - Not given

- 5. <u>Waste Streams</u> Any phosgene waste (not feasible to recycle) is scrubbed with sodium hydroxide.
- 6. EPA Source Classification Code None
- 7. References

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N. Y., 1975, p. 624-627.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Supplemental Volume (1971) p. 677-681. Austin, G. T., "The Industrially Significant Organic Chemicals - Part 8," "Chemical Engineering," July 22, 1974, p. 108-109. Sodium Formate (carbon monoxide and sodium hydroxide)

NaOH + CO
$$\xrightarrow{H_2^0}$$
 HCOONa

- Function Clean and compressed synthesis gas (source of carbon monoxide) is introduced countercurrently into a 25-30% sodium hydroxide solution at 160-200°C to give sodium formate. Sodium formate crystals are obtained by drying the reaction product.
- 2. Input Materials

Synthesis gas (source of carbon monoxide) Sodium hydroxide

3. Operating Parameters

Temperature - 160-200°C (320-392°F) Pressure - 140-170 kPa (1.38-1.68 atm)

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste water is likely to contain sodium hydroxide. Atmospheric emissions of carbon monoxide and hydrogen are possible.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 10 (1966), p. 101.

Gmelins Handbuck der Anorganische Chemie, System-Nummer 21, 8 Auflage Erganzungsband, Lieferung 4, Verlag Chemie, 1967, p. 1398.

INDUSTRIAL ORGANIC CHEMICALS

Methanol (high-pressure catalytic synthesis)

 $CO + 2H_2 \stackrel{?}{\leftarrow} CH_3OH \quad \Delta H_{298}^\circ = -90.79 \text{ kJ}$

Function - Methanol synthesis from CO and H₂ is favored by high pressures and low temperatures. The temperature and pressure applied in commercial processes is dependent on: composition of synthesis gas utilized, and rate of reaction at a given temperature and pressure in the presence of a given catalyst.

The main source of synthesis gas at present is the steam reforming of natural gas. Very exact process control is needed to maintain a desired carbon monoxide - hydrogen ratio.

The reforming of natural gas by steam may be represented by the following equation

 $3CH_{\Delta} + CO_{2} + 2H_{2}O \rightarrow 4CO + 8H_{2}$

The synthesis gas is compressed to remove water and entrained oil. The compressed mixture of gases is passed through a catalytic converter. Commercial processes usually operate at temperatures ranging from 350°C to 400°C and at pressures in the 19.6-29.4 MPa range. Catalyst used in the high-pressure synthesis consists mainly of mixtures of chromium oxide and zinc oxide. Close control of operating parameters to suppress side reactions is of utmost importance. The mixture of gases from the converter pass through a condenser and then through a separator. The crude methanol condensate is subsequently purified in a two-step distillation. By-products are mixed alcohols (19.3 g/kg methanol) and dimethyl ether (20.4 g/kg methanol).

Methanol plant equipment must be resistant to carbon monoxide at high temperatures and pressures.

Copper-based catalyst have been known to increase the rate of the reaction for the formation of methanol from synthesis gas, but were readily inactivated by sulfur impurities present in synthesis gas. Improved methods of removing sulfur from synthesis gas and newly-perfected copper-zinc catalyst has led to a new low-pressure process for the manufacture of methanol from synthesis gas. The new low-pressure process developed by Imperial Chemical Industries Limited of United Kingdom operates at pressures nearly half of those utilized in usual processes. Some methanol was also produced in the liquid phase oxidation of butane--rich hydrocarbon gas (Process No. 227). However, this process has not been in commercial use since 1973.

2. Input Materials

- Synthesis gas produced by steam reforming of 0.829 kg natural gas per kg CH₃OH.
 - a) 5.8-7.3 kg CO/kg CH₃OH (based on 12-15% conversion of CO)
 - b) .87-1.31 kg H_2/kg CH₃OH (based on H_2 :CO molar ratio of 2.1-2.5)
- 2) Carbon dioxide recovered from reformer flue gases.

3. Operating Parameters

Temperature: 350-400°C (662-752°F) Pressure: 20-30 MPa (200-300 atm.) Catalyst: Cr₂0₃ + Zn0

- 4. <u>Utilities</u> Basis 10.5 kg/sec (1000 tons/day) capacity Cooling water - 2.089 m³/sec (33,110 gal/min) Makeup water - 70.0 dm³/sec (1,100 gal/min) Power - 11.0 GJ (3.06 Mw) Natural gas - 13.49 Nm³/sec (1.715 M scfh)
- 5. <u>Waste Streams</u> Major waste water streams are from slab and vessel washdowns together with bottoms from the methanol purification process. This amounts to 0.4-2.1 m³/kg of product (100-500 gal/ton) and contains some oils, methanol, and higher-boiling organic compounds to the extent of about 0.2-0.5 kg/1000 m³.

	<u>Plant 1</u>	Plant 2
Flow	0.492 m ³ /kg	0.352 m ³ /kg
COD	320 mg/1 0.16 g/kg	4,930 mg/1 1.74 g/kg
BOD ₅	119 mg/1 0.059 g/kg	2,620 mg/1 0.92 g/kg
TOC	107 mg/1 0.053 g/kg	583 mg/1 0.21 g/kg

6. EPA Source Classification Code - None

7. References

<u>Chemistry In The Economy</u> - American Chemical Society Study, p. 31, 1973. Hedley, William H., et al., <u>Potential Pollutants From Petrochemical</u> <u>Processes</u>, Technomic Publishing Co., Westport, Conn., 1975. Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 13 (1967), p. 375-378.

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corp., Park Ridge, N.J., 1974, p. 158-159.

PROCESS NO. 192

 $\frac{\text{Methylamines}}{(\text{vapor-phase ammonolysis of methanol})}$ $CH_{3}OH + NH_{3} \longrightarrow CH_{3}NH_{2} + H_{2}O$ $CH_{3}NH_{2} + CH_{3}OH \longrightarrow (CH_{3})_{2}NH + (CH_{3})_{3}N + H_{2}O$

1. <u>Function</u> - The manufacture of methylamines is a classic example of vapor phase ammonolysis of alcohols. Methylamine, with smaller quanties of both dimethylamine and trimethylamine, is produced by passing methanol and ammonia, in a 1:5 volume ratio and preheated to 350° C, over a dehydrating catalyst at space velocities of 0.75 - 1.5 and a catalyst temperature of 450°C. The process is usually carried out under atmospheric pressure, but it can be performed under pressures in excess of 690 kPa (6.8 atm) with direct fractionation of the products at these conditions. Catalysts commonly used are alumina (Al₂O₃), aluminum silicate, aluminum phosphate, and diammonium phosphate. Conversion of the ammonia is 13.5% to primary, 7.5% to secondary, and 10.5% to tertiary amine.

Part of the exothermic heat of reaction may be used in the feed preheater.

Since exclusive production of one of the amines is difficult and frequently uneconomical, much of the process development concerning methanol ammonolysis has dealt with the problem of satisfactory separation of the three co-products. Recycling of the less desirable amines to increase the yield of the desired product is generally effective even if the secondary or tertiary

amine is preferred. If dimethylamine is desired, the other two amines may be recycled without separation from each other. Separation or fractionation of the product stream is rather difficult because the boiling points of the methylamines all lie in a temperature range of only about 10°C.

The crude product can be separated by a series of four column distillations. The first column is maintained at a suitable temperature and pressure so that the trimethylamine-ammonia azeotrope to be recycled is recovered overhead, the recyclable ammonia from the upper middle of the column, and a mixture of mono-, di-, and some tri-methylamine as bottoms. The mixture goes to the trimethylamine (TMA) column where water is added for extractive distillation and pure TMA is collected overhead and sent to storage or recycle. The bottoms from this operation are sent to the mono-methylamine (MMA) column where pure MMA is removed overhead. Finally, the MMA column bottoms are sent to a fourth column where pure dimethylamine goes overhead with water drained from the bottom to waste.

Procedures have also been devised for separating the methylamines from mixtures by extractive distillation. Mono-methylamine is separated from the other two by absorbing the vapors in a liquid in which it has the lowest solubility of the three, such as dimethylaniline, 1,2,3,4-tetrahydronaphthalene, or dimethylcyclohexylamine. Fractional distillation of this solution yields MMA overhead. Dimethylamine is separated from MMA and TMA by subjecting the mixture to extractive distillation using aniline, morpholine,

dimethylformamide, or diethanolamine, in which DMA is the most soluble. The diemthylamine is recovered by flashing from the solvent. By using solvents in which TMA is the least soluble, the member of the series may be distilled from mixture.

- Input Materials kg/kg of desired methylamine produced Methanol (industry average factor/highest value)
 - a) MMA; 1.05/1.2
 - b) DMA: 1.45/1.6
 - c) TMA: 1.65/1.8
 - Ammonia (assuming 97% yield)
 - a) MMA; 0.565
 - b) OMA: 0.389
 - c) TMA: 0.297
- 3. Operating Parameters

Temperature: 450°C (842°F) Pressure: 690 kPa (6.8 atm) Catalyst: Al₂O₃

- 4. <u>Utilities</u> basis: 45.4 kg (100 lb) of anhydrous product Steam - 590 kg (1300 lbs) Water - 13.2 m³ (3500 gallons) Electricity - 32.4 MJ (9 kWh)
- 5. <u>Waste Streams</u> The staged distillation process is the source of most of the pollutants in methylamine manufacture. The bottoms from the DMA column, the last in the series of four, are drained to wastewater and will contain some of all three methylamines in solution.

Two examples of the wastewater are:

	#1	#2
Flow	3.58 1/kg	3.57/1/kg
COD	22.56 g/kg	4.21 g/kg
	6.303 g/1	1.178 g/1
BOD ₅	0.35 g/kg	0.62 g/kg
	99 mg/1	1.74 mg/1
TOC	41.65 g/kg	13.63 g/kg
•••••	11.634 g/1	3.808 g/1

Atmospheric emissions of hydrogen and cqrbon monoxide and of methylamines will arrise from crude product storage and final storage, respectively.

6. EPA Source Classification Code - None

7. References

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"1973 Petrochemical Handbook," "Hydrocarbon Processing," November, 1973, p. 150.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 122.

$\frac{\text{Methyl Chloride}}{\text{CH}_{3}\text{OH} + \text{HCl} \xrightarrow{\Delta} \text{CH}_{3}\text{Cl} + \text{H}_{2}\text{O}}$

1. Function

Methyl chloride is produced by the action of hydrogen chloride on methanol, with the aid of a catalyst, in the vapor phase. Vapors of methanol and hydrogen chloride are continuously mixed in approximately equimolecular ratios and passed through a preheater maintained at about 180°C.

The gas mixture is then passed at substantially atmospheric pressure through a converter at a temperature of 340° C to 350° C. The converter is packed with previously ignited alumina gel of 8 to 12 mesh size or a similar catalyst, such as zinc chloride on pumice, cuprous chloride, or activated carbon. Space velocities of about 7.79 m³ (275 cubic feet) per hour per 28 dm³ (cubic foot) of gross catalyst volume are generally used (based on gas volumes at STP).

The effluent gases from the reactor are scrubbed with water to remove excess HCl, followed by an alkali wash, and a sulfuric acid wash (to dry the product). Crude methyl chloride is distilled under pressure at -24°C to yield pure methyl chloride.

2. <u>Input Materials</u> - Basis - 1 metric ton methyl chloride Methanol - 360 kg/Mg (720 lb/ton) of product 700 kg (1,543 lbs) HCl - 1587 kg/Mg (3,174 lb/ton) of product 800 kg (1,769 lbs) Sulfuric Acid

Caustic Soda

3. Operating Parameters

Preheater temperatures: 180 - 200°C (356 - 392°F) Converter temperatures: 350°C (662°F) Pressure: atmospheric Space velocity: 275 m³/hr Catalyst: Alumina gel. Cuprous chloride on activated carbon or pumice. Zinc chloride on activated carbon or pumice. Phosphoric acid on activated carbon.

4. Utilities

Not given

- 5. <u>Waste Streams</u> Waste water from scrubbers contains traces of HC1, some alkali and sulfuric acid.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1967), p. 106,107. Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 533. Methyl Acetate (by esterification)

 $ch_3 cooh + ch_3 oh \longrightarrow ch_3 cooch_3 + h_2 o$

- 1. <u>Function</u> In a general procedure for manufacturing methyl esters the aliphatic carboxylic acid (in this case acetic acid) is reacted with an excess of methanol in ethylene dichloride as solvent. Sulfuric acid is used as catalyst for the reaction. The mixture is heated to reflux from 6 to 15 hours. After cooling the reaction product is washed with water, sodium bicarbonate, water and dried by conventional methods. The ethylene dichloride is removed by distillation. The crude ester is then distilled.
- 2. Input Materials

Methano1

Acetic acid

H₂SO₄

Ethylene dichloride

3. Operating Parameters

Temperature: Reflux Pressure: 101 kPa (1 atm) Catalyst: H₂SO₄ Time: 6-15 hrs

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste water may contain dilute solutions of salts of acids, traces of methanol, methyl acetate, and other organic byproducts.

- 6. <u>EPA Source Classification Code</u> None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 8 (1965), p. 350.

U.S. Patent 2,787,636 (April 2, 1957).

Methyl Acetoacetate (action of metallic sodium on methyl acetate)

$$2CH_{3}C-OCH_{3} + 2Na \longrightarrow CH_{3}C = CH-COOCH_{3}$$
$$+ NaOCH_{3} + H_{2}$$
$$[CH_{3}COCHCOOCH_{3} \frown Na \oplus + H_{2}SO_{4} \longrightarrow CH_{3}CCH_{2}COCH_{3}$$

 Function - Methyl acetoacetate is prepared by the reaction of high-purity methyl acetate with metallic sodium in absolute methanol. The sodium derivative is then neutralized with sulfuric acid to give the product.

The crude ester is separated and purified by vacuum distillation.

2. Input Materials

Methyl Acetate Metallic sodium Absolute Methanol Sulfuric acid

- 3. Operating Parameters Not given
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Hydrogen, a by-product; may be released into the atmosphere. Wastewaters may contain sodium hydroxide and sodium bisulfate as well as traces of methanol and sulfuric acid.
- 6. EPA Source Classification Code None

7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 154-155.

Dimethyl Ether

 $CH_3OH + H_2SO_4 \longrightarrow CH_3OSO_2OH + H_2O$ $CH_3OSO_2OH + CH_3OH \longrightarrow CH_3OCH_3 + H_2SO_4$

 Function - Dimethyl ether is produced from methanol using sulfuric acid as the dehydration catalyst or by passage over catalyst such as alumina.

A mixture of methyl alcohol and concentrated sulfuric acid is slowly heated to 110-140°C. In this temperature range the reaction is initiated. An azeotrope of ether-water-alcohol distills from the reactor at 110°C and passes to a scrubber. The vapors pass countercurrently to a slow moving stream of dilute sodium hydroxide. The vapors from the top of the scrubber run to a continuous fractionation column where separation takes place. Alcohol and sulfuric acid are recycled.

2. Input Material

Methano1

Sulfuric Acid

3. Operating Parameters

Temperature: 140°C (284°F) Pressure: 101 kPa (1 atm) Catalyst: H₂SO₄

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste water may contain traces of ether, aldehydes, and peroxides as well as sodium sulfate from neutralization.

Some reduction of sulfuric acid occurs with evolution of sulfur dioxide. Tarry materials are disposed as solid waste.

6. EPA Source Classification Code - None

7. References

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Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 8 (1965), p. 474-476.

Houben-Weyl, <u>Methoden der Organischen Chemie</u>, Vierte Auflage, George Thieme Verlag, Stuttgart, Bd. 6, T. 3, (1965), p. 13.

Faith, W. L., <u>et al.</u>, <u>Industrial Chemicals</u>, 3rd Edition, John Wiley and Sons, New York, N. Y., 1965, p. 335-336.

Dimethyl Sulfate

$$(CH_3)_2 0 + so_3 \xrightarrow{45-47^{\circ}C} (CH_3)_2 so_4 + H_2 so_4 + CH_3 Hso_4$$

- 1. <u>Function</u> Dimethyl sulfate is obtained in a continuous process utilizing dimethyl ether and liquid sulfur trioxide as the input materials. Gaseous dimethyl ether is bubbled into the bottom of an aluminum tower filled with dimethyl sulfate. Liquid sulfur trioxide is introduced at the top of the tower. The mildly exothermic reaction is controlled at 45-47°C. The reaction product (96-97% dimethyl sulfate) is continuously withdrawn and purified by vacuum distillation over sodium sulfate.
- 2. Input Materials

Dimethyl ether (74.3 kg/hr) Sulfur trioxide (129.1 kg/hr)

3. Operating Parameters

Temperature 45-47°C (113-117°F)

4. Utilities

Not given

- 5. <u>Waste Streams</u> Possible gaseous emissions of SO_x. The bottoms from distillation contain sulfuric acid and methyl hydrogen sulfate.
- 6. EPA Source Classification Code None
- 7. Reference

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 19 (1969), p. 492.

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Methyl Formate

$$CH_3OH + CO \xrightarrow{} HCOOCH_3$$

 CH_3ONa

- 1. <u>Function</u> Methyl formate may be prepared industrially by the reaction of methanol with carbon monoxide (from synthesis gas) in the presence of metal alkoxides. Hydrogen reacts with excess carbon monoxide to form methanol which is re-cycled.
- 2. Input Materials

Methanol

Synthesis gas $(CO + H_2)$

 CH_3ONa (CH_3OH + Na)

- 3. <u>Operating Parameters</u> Temperature - 80°C (176°F) Pressure - 2.96 kPa (300 atm) Residence time - 350 sec.
- 4. Utilities Not given
- 5. <u>Waste Streams</u> By product of the reaction, e.g., dimethyl ether. Also some high-boiling tars are formed.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 4 (1965), p. 434-435. Waddams, A. L., <u>Chemicals from Petroleum</u>, 3rd Edition, John Wiley and Sons, New York, N.Y., 1973, p. 204.

Formamide

 $H_{COCH_3}^{\rho}$ + $NH_3 \longrightarrow H_{CNH_2}^{\rho}$ + CH_3OH

- Function Formamide can be manufactured by the reaction of ammonia with methyl formate. Formamide was used as a source of HCN. This HCN process is considered obsolete now.
- 2. Input Materials

Methyl formate

Ammonia

3. Operating Parameters

Temperature - 40°C (104°F)

Pressure - 140 kPa (200 psi) (1.38 atm)

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Gaseous emission of methanol, ammonia and methyl formate are possible.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 6 (1965), p. 576.

Ibid., Vol. 10 (1966) p. 105.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 484.

N,N-Dimethylformamide

$$H \sim C \sim OCH_3$$
 + $(CH_3)_2 NH \rightarrow CH_3 OH + H \sim C \sim N \sim (CH_3)_2$

- <u>Function</u> N,N-Dimethylformamide (DMF) is derived from the reaction of methyl formate with dimethylamine. The reaction product is separated from methanol and unconverted reactants by distillation.
- 2. Input Materials

Methyl formate

Dimethylamine

3. Operating Parameters

Not given

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Possible atmospheric emissions are methanol, methyl formate and dimethylamine.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 10 (1966), p. 109.

Astle, M.J., <u>Industrial Organic Nitrogen Compounds - ACS Monograph No. 150</u>, Reinhold Publishing Corp., 1961 p. 74. Acetic Acid (from methanol by carbonylation)

$$CH_3OH + CO \xrightarrow{catalyst} CH_3COOH$$

- <u>Function</u> Methanol is carbonylated with carbon monoxide to produce acetic acid. Various types of catalysts have been proposed for the carbonylation of methanol. The catalyst most widely employed consists of two main components: 1) a carbonyl-forming metal from the iron sub-group (iron, cobalt, or nickel), and 2) either BF₃ or H₃PO₄.
- 2. <u>Input Materials</u> Basis 1 metric ton acetic acid Methanol - 610 kg/Mg acetic acid 553 kg (1,175 lbs/ton) Carbon monoxide - 787 kg/Mg acetic acid 467 kg (1,030 lbs/ton)
- 3. Operating Parameters

Temperature: 200 - 300°C (392-572°F) Pressure: 20 to 70 MPa (197-691 atm) Flow rates: not given \longrightarrow reaction time 1 - 3 minutes; vapor or liquid phase Size of Equipment: not given - tubular reactor type Types of catalysts: Fe, Co, or Ni acetate + BF₃ or H₃PO₄. Monsanto has a new catalyst (a soluble rhodium-metal-carbonyl complex activated with an iodide promoter) which permits this reaction to proceed at pressures as low as 210 kPa (~ 2 atm) and allows use of synthesis gas as a CO source.

4. Utilities - Basis: 45.5 Gg/yr (100 M 1b/yr) capacity:

Water

Cooling - 287 dm³/s (4,560 gpm)

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Makeup - 6.1 dm³/s (97 gpm) Power - 6.98 GJ (1940 kWh) Steam - 15.8 Mg/hr (34,800 1b/hr)

- 5. Waste Streams Reaction section off-gas scrubber vent (air) Hydrogen - 5.5 kg/Mg acetic acid Carbon monoxide - 204 kg/Mg acetic acid Methane - 12.7 kg/Mg acetic acid Methanol - 14.9 kg/Mg acetic acid Light ends - 2.2 kg/Mg acetic acid About 40 kg (~88 pounds) of organics (50% propionic acid and 50% higher organics) are produced in the liquid waste stream per Mg (tonne) of acetic acid produced. The waste stream amounts to about 200 dm³/Mg (50 gallons per ton) of product including drains.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Yakaoka, S., "Acetic Acid," Report No. 37, Stanford Research Institute, Menlo Park, California, March, 1968.

Gloyna, E. F., and Ford, D. L., "The Characteristics and Pollutional Problems Associated with Petrochemical Wastes," for FWPCA, Contract No. 14-12-461, February, 1970.

Austin, G. T., "Industrially Significant Organic Chemicals - Part 1," "Chemical Engineering," January 21, 1974, p. 128,129.

Sittig, M., <u>Acetic Acid and Anhydride</u>, Noyes Development Corporation, Pearl River, N. Y., 1965, p. 24-29.

7. <u>References</u> (continued)

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 10,11.

Formaldehyde

(catalytic air oxidation of methanol)

$$CH_3OH + air \xrightarrow{cat} CH_2O$$

 Function - All formaldehyde in the United States is produced from methanol by either vapor-phase catalytic oxidation or by a combination oxidation-dehydrogenation process. The product is usually marketed as formalin -- a 37% solution stabilized with 9% methanol.

The catalytic conversion of methanol to formaldehyde involves the reaction of a mixture of methanol vapors and air over a stationary catalyst at approximately atmospheric pressure. Because methanol and air form explosive mixtures in the range 6-37% by volume of methanol in air at 60°C, the commercial processes operate either at methanol concentrations of nearly 50% or 5-10% by volume of methanol in air. In the catalytic conversion of methanol to formaldehyde, using silver catalyst, dehydrogenation and oxidation of methanol may occur simultaneously.

$$CH_3OH \longrightarrow HCHO + H_2 -20 \text{ Kcal.}$$

$$CH_3OH + 1/2 0_2 \longrightarrow HCHO + H_2O + 38 Kcal.$$

Clean air is heated and mixed with methanol vapors in a controlled ratio (1:1). Temperature may vary between 450°-700°C with the optimum around 635°C. Gases from reactors are quenched and the excess methanol in the resulting methanol-formaldehyde solution is removed by fractionation. In the direct oxidation of methanol to formaldehyde in the presence of iron-molybdenum oxide catalyst, a low (5-10%) methanol concentration stream in air is used. The product is essentially free of methanol.

Formaldehyde may also be produced in a vapor-phase oxidation of propane-rich LPG. However, this process has not been used since February 1973 when Celanese Corporation closed its Bay City, Texas plant.

2. <u>Input Materials</u> - (data for silver-catalyzed, oxidation-dehydrogenation process)

Methanol - 438 g/kg of 37% formaldehyde

Air - 888 g/kg of 37% formaldehyde

3. Operating Parameters

1) Oxidation - dehydrogenation

Temperature:	635°C (600-700°C) (1175°F)
Pressure:	146 kPa (1.44 atm)
Catalyst:	crystalline silver
Reaction time:	0.5 second

2) Direct oxidation

Temperature:	300-400°C (572-752°F)
Pressure:	~100 kPa (atmospheric)
Catalyst:	iron-molybdenum oxide

4. <u>Utilities</u> - Basis: 45.4Gg/yr (100 M lb/yr) capacity for production of 37% HCHo by silver-catalyzed dehydrogenationoxidation

Water, cooling - 88.3 dm³/sec (1400 gpm) Water, process - 2.4 dm³/sec (38 gpm) (includes water for steam generation) Steam - 0.794 kg/sec (6300 lb/hr) Power - 107 kW (143 hp) 5. <u>Waste Streams</u> - Off-gases from the absorber of the absorption and purification section will lead to the following atmospheric emissions: CO - 63.5 g/kg 37% formaldehyde H₂ - 7.6 g/kg 37% formaldehyde CH₄ - 1.25 g/kg 37% formaldehyde HCHO - trace CH₃OH - trace

formic acid - in water

The major wastewater sources are the scrubber waters and the dimethyl ether by-product. The total aqueous stream should not exceed 0.42 dm^3/kg (100 gal/ton) containing 1-5000 mg/dm³ COD unless on-site truck washing is practiced.

- 6. EPA Source Classification Code None
- 7. References

"1973 Petrochemical Handbook," "Hydrocarbon Processing," November 1973, p. 135,136.

"1975 Petrochemical Handbook," "Hydrocarbon Processing," November 1975, p. 149,150.

Hedley, W. H., et al., <u>Potential Pollutants From Petrochemical Processes</u>, Technomic Publishing Co., Eastport, Conn., 1975.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 10 (1966), p. 86-88.

7. <u>References</u> (continued)

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 6," "Chemical Engineering," May 27, 1974, p. 101.

Chemistry in The Economy - American Chemical Society Publication, 1973, p. 32.

Walker, J. F., <u>Formaldehyde</u>, 3rd Edition, ACS Monograph 159, 1964, p. 16-24.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N.Y., 1975, p. 422. Ethylene Glycol (from formaldehyde & CO via glycolic acid)

$$CH_2O + CO + H_2O \xrightarrow{BF_3} HOCH_2CO_2H \xrightarrow{H_2} HOCH_2CH_2OH$$

1. <u>Function</u> - Although more than 90% of ethylene glycol produced is made by catalytic oxidation of ethylene to ethylene oxide, followed by hydration, a reaction of formaldehyde, water, and carbon monoxide is also being used. These three chemicals combine at 200°C and about 70 MPa to form glycolic acid.

This is followed by hydrogen reduction of the product glycolic acid in the presence of a copper oxide-magnesium oxide catalyst (at 200°C and 10 MPa).

2. Input Materials Per kg ethylene glycol

Formaldehyde	650 g
Carbon monoxide	625 g
Hydrogen	75 g
Sulfuric Acid	45 g
Water	

3. Operating Parameters

Temperature: 200°C (392°F)

Pressure: 70 MPa; 10 MPa for hydrogenation

Catalyst: BF_3 for acid formation CuO - MgO (for hydrogenation) Space Velocity: 2×10^4 hrs⁻¹

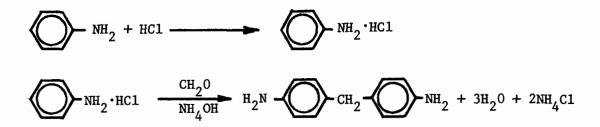
4. <u>Utilities</u>

Not given

- 5. <u>Waste Streams</u> Carbon monoxide fed to the primary reaction vessel is a possible, atmospheric emission. Process slops may carry formaldehyde, methanol, higher alcohols, and organic acids to waste water flow.
- 6. EPA Source Classification Code None
- 7. References

Faith, W. L. et al., <u>Industrial Chemicals</u>, 3rd Ed., John Wiley & Sons, New York, N.Y., 1965, p. 375, 376, 377.

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 294. Methylenedianiline (condensation of aniline and formaldehyde)



- 1. <u>Function</u> The production of methylenedianiline is a two-stage process. Aniline is neutralized with concentrated hydrochloric acid in aqueous solution at 100°C to form aniline hydrochloride. The solution is cooled to 15°C and 40% formaldehyde solution added, followed by heating at 55 60°C for four hours. The reaction mixture is then chilled again, and the product pre-cipitated out with dilute ammonium hydroxide. The product may be further purified by recrystallization from alcohol or water.
- 2. Input Materials

Basis - 1 kg (1b) product Aniline - 1.66 kg (3.66 lbs) Formaldehyde (40%) - 0.68 kg (1.50 lbs) Concentrated hydrochloric acid - 1.68 & Ammonium hydroxide Water - 3.57 &

3. Operating Parameters

Temperature: 55 - 60°C (131 - 140°F)

Pressure: not given

Catalyst: not given

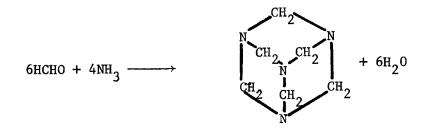
4. <u>Utilities</u> - Not given

- 5. <u>Waste streams</u> Waste water streams may contain ammonium hydroxide, ammonium chloride, and aniline compounds in solution. There will be no gaseous emissions. Resinous materials formed on contact of aniline and formaldehyde will be disposed of in process wastes.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Scalon, J.T., <u>J. Amer. Chem. Soc.</u>, <u>57</u>, May, 1935, p. 890, 891. Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 414.

INDUSTRIAL ORGANIC CHEMICALS

Hexamethylenetetramine (condensation of formaldehyde with ammonia)



 Function - Hexamethylenetetramine is a heterocyclic fused ring structure made by the condensation reaction of aqueous formaldehyde with liquid or gaseous ammonia.

A slight excess of ammonia may be introduced to prevent side reactions which occur at pH values below 8. The process is performed at 62-66°C and about 280 kPa (2.76 atm) in an aqueous solution within a steel, tower-type reactor.

After addition of activated charcoal for the removal of impurities, the liquid is filtered and then evaporated at reduced pressure (2-4 kPa, 0.02-0.04 atm) to collect the crystalline product. The crystalline solid mass is then centrifuged, washed, and dried to yield hexamethylenetetramine, usually of a purity better than 99%. According to industry sources, the yield is 97% from formaldehyde or 93.5% from ammonia.

2. Input Materials

Formaldehyde - 3.58 kg of 37% solution per kg of product (based on

97% yield)

Ammonia - 0.519 kg/kg product (93.5% yield)

3. Operating Parameters

Temperature: 62-66°C (144-151°F)

Pressure: 280 kPa (2.76 atm)

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- 4. <u>Utilities</u> Not given
- 5. <u>Waste Streams</u> Reactor off-gases contain formaldehyde, ammonia, and methanol (from formaldehyde production). If this stream is incinerated, NO_x will be emitted to the atmosphere. The bleed line from the centrifuge wash, a waste water stream, will contain dissolved formaldehyde, ammonia, methanol, and hexamethylenetetramine. The drier used in final preparation of hexamethylenetetramine will emit formaldehyde, methanol, and ammonia vapors to the air.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> Processes, Technomic Publishing Company, Westport, Conn., 1975.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 10 (1966), p. 98.

Austin, G. T., "The Industrially Significant Organic Chemicals - Part 6," "Chemical Engineering," May 27, 1974, p. 104.

U.S. Patent 3,288,790 (November 29, 1966).

Sittig M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition, Noyes Development Corp., Park Ridge, N.J., 1969, p. 364.

<u>Chemical Technology</u>, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 563. Dimethyl Sulfide (from methanol/carbon disulfide)

 $4CH_3OH + CS_2 \longrightarrow 2(CH_3)_2S + 2H_2O + CO_2$

- Function Dimethyl sulfide may be produced by the reaction of methanol with carbon disulfide in the vapor phase in a fixed bed catalyst of activated alumina. Methyl mercaptan is the chief by-product.
- 2. Input Materials

Methanol

Carbon disulfide Catalyst (activated alumina)

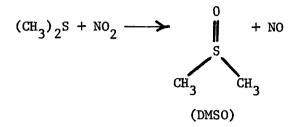
- 3. <u>Operating Parameters</u> Temperature: 370-535°C (698-995°F) Pressure: 414 kPa (4.08 atm)
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Unreacted methanol and carbon disulfide should be present along with some methyl mercaptan and possible H_2S .
- 6. EPA Source Classification Code None
- 7. References

Sittig, M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition, Noyes Development Corp., Park Ridge, N. J., 1969, p. 266.

U. S. Patent 2,930,816 (March 29, 1960).

INDUSTRIAL ORGANIC CHEMICALS

Dimethyl Sulfoxide (NO₂ oxidation of (CH₂)₂S)



 Function - Dimethyl sulfide is oxidized with a dimethyl sulfoxide solution of nitrogen dioxide in a reactor at 40-50°C. The reactor contents pass into a 100°C zone where dimethyl sulfide is sparged from the crude product with nitrogen. The crude dimethyl sulfoxide (DMSO) is then neutralized and distilled.

The flow of nitrogen dioxide into the reactor is kept insufficient to oxidize all of the dimethyl sulfide so that all the NO_2 is converted to NO, which is insoluble in DMSO and escapes the exitgas stream. This stream passes through a heat exchanger to condense some of the dimethyl sulfide for recycle back to the reactor. The gases remaining are conducted to a second reactor where excess NO_2 converts the residual sulfide to the sulfoxide. The gases from this reactor contain substantially no organic matter and are oxidized with oxygen in a third reactor to regenerate the NO_2 . The gases finally pass through a DMSO scrubber to remove nitrogen dioxide prior to venting to the atmosphere.

2. Input Materials

Dimethyl sulfide

Nitrogen dioxide in dimethyl sulfoxide solution

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3. Operating Parameters

Temperature: 20-50°C (68-122°F) Pressure: 101 kPa (1 atm)

- 4. Utilities not given
- 5. <u>Waste Streams</u> The gas stream which is vented from the DMSO scrubber to the atmosphere will consist of CO₂, O₂, N₂, and ~0.3% nitrogen oxides (NO_x). The liquid stream from the scrubber contains NO₂, but this is recycled back into the process. There could also be emissions of NO, NO₂, N₂O₃, and N₂ from the second and third reactors, where additional conversion was accomplished. Some liquid waste could originate from the neutralization of crude dimethyl sulfoxide.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 19 (1969), p. 332, 333.

U.S. Patent 2,935,533 (May 3, 1960).

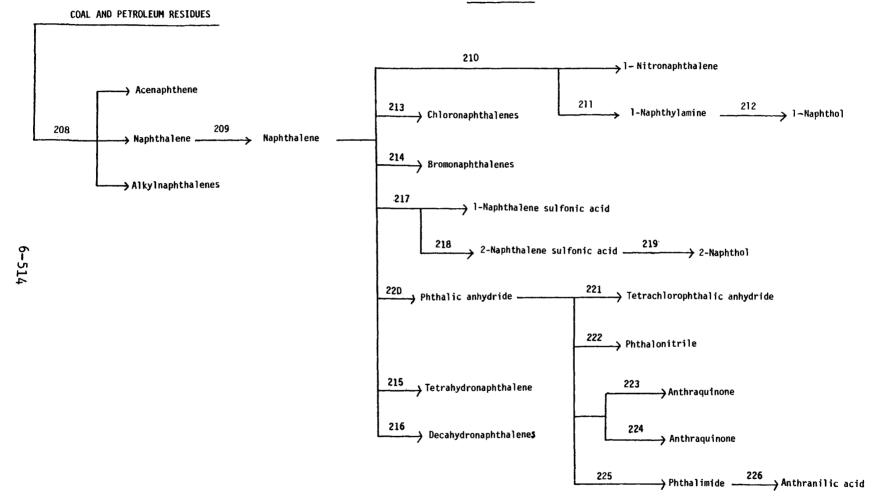
Sittig, M., Organic Chemical Process Encyclopedia - 1969, 2nd Edition, Noyes Development Corp., Park Ridge, N.J., 1969, p. 268.

<u>Chemical Technology</u>, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 585.

SECTION VI NAPHTHALENE

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NAPHTHALENES



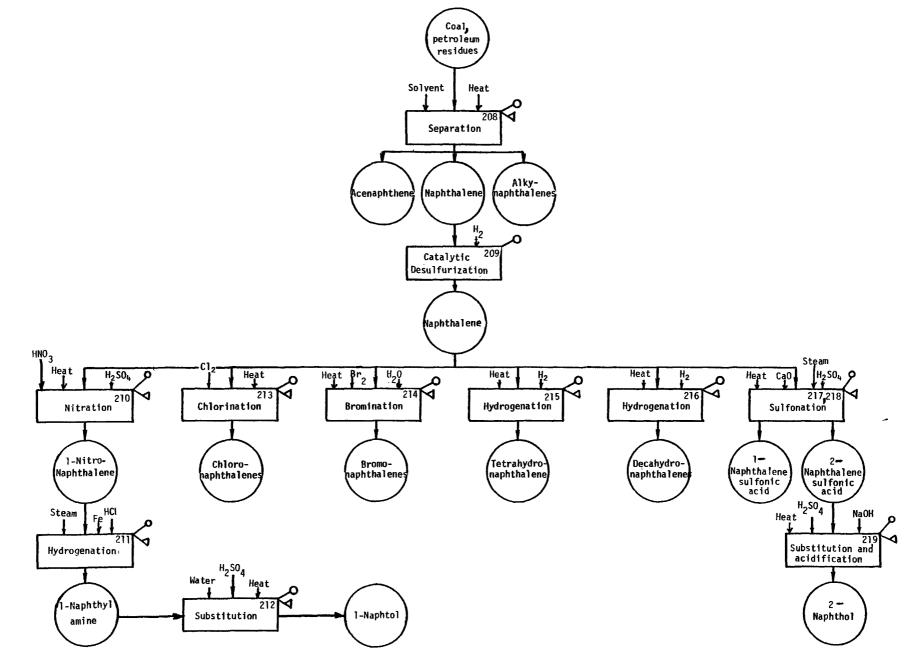


Figure 12. Naphthalene Section Process Flow Sheet

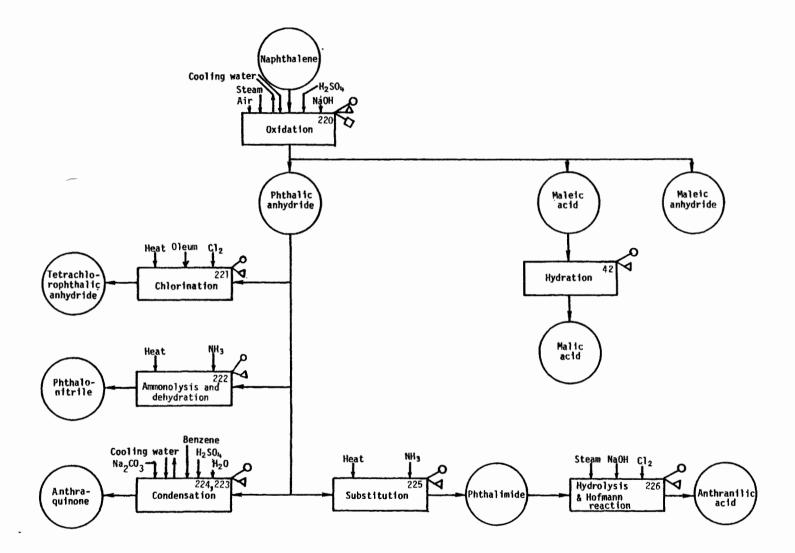


Figure 12. Naphthalene Section Process Flow Sheet (Cont.)

Separation of the Naphthalenes (Alkylnaphthalenes)

 Function - Alkylnaphthalenes are found in coal tar, lignite tar, crude oil, drip-oil, heavy petroleum reformate, and gas oil (4%). The alkylnaphthanes are separated from the naphthalene fractions usually either by fractionation or solvent extraction, or both, depending on the purity desired.

In the separation by fractionation, the coal tar or petroleum fraction feed is sent to a fractionator which produces a naphthalene concentrate, and a middle product of alkylnaphthalenes, and heavy aromatics bottoms. The more common present commercial sources of alkylnaphthalenes are aromatic petroleum fractions of appropriate boiling range 227 - 268°C (440 - 515°F) cut.

The solvent extraction process consists of first distilling the feed to get a middle cut in the 204 - 285°C (400 - 550°F) from the light cycle oil cut. A solvent extraction process known as the Unisorb process is then used to separate the naphthalene homologs (alkylňapthalenes) from the lower aromatics. An extract is produced containing over 85% of the naphthalene homologs (including acenaphthene) from the charge stock while rejecting lower aromatics.

The process contains a fixed absorbent bed which is operated isothermally and at constant pressure.

2. Input Materials

coal tar light cycle oils catalytic gas oils drip-oil reformer bottoms

- 3. Operating Parameters not given
- 4. Utilities not given
- 5. <u>Waste Streams</u> The air vent streams may contain paraffins or olefins as well as low boiling aromatics and solvent vapors. The solvents commonly used in solvent extraction of alkylnaphthalenes are furfural and sulfur dioxide.
- 6. EPA Source Classification Code None
- 7. References

Brownstein, A. M., "U.S. Petrochemicals, Technologies, Markets, and Economics," The Petroleum Publishing Company, Tulsa, Oklahoma, 1972, pp. 213-215.

Kirk-Othmer, Encyclopedia of Chemical Technology," 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 13 (1967), pp. 678-690.

Broughton, D. B. and Hardison, L. C., "Unisorb Extracts Naphthalene Homologs," Hydrocarbon Proc. and Petrol. Refiner, <u>1962</u>, 41(5), 125-128.

PROCESS NO. 209

Desulfurization of Hydrocarbons

$$RCH_2SH + CuCl_2 \longrightarrow (RCH_2S)_2 + CuCl$$
(1)

$$\operatorname{CuC1} + \operatorname{O}_2 \longrightarrow \operatorname{CuC1}_2 + \operatorname{CuO}$$
 (2)

$$RCH_2SH + H_2 \xrightarrow{cobalt} RCH_3 + H_2S$$

 Function - Hydrocarbon feeds from petroleum sources may contain significant amounts of sulfur containing compounds principally hydrogen sulfide and mercaptans. If these stocks are to be used in reactions involving catalysts, which are "poisoned" by sulfur compounds, these compounds must then be removed.

There are three methods of treating hydrocarbon feeds to eliminate the undesirable sulfur compounds. These may be classified as 1) oxidation, 2) catalytic desulfurization and 3) extraction.

<u>Oxidation</u> - Mercaptans are converted to disulfides by exposing the hydrocarbon stream to cupric chloride, CuCl₂. The copper salt may be deposited on an inert substrate and used as a slurry or as a fixed catalytic bed. Sulfur compounds are converted to the inactive disulfides, but are still present in the feed. CuCl₂may be regenerated with air either during or after the reaction.

<u>Catalytic desulfurization</u> - Mercaptans are converted to the lower boiling hydrocarbons by loss of hydrogen sulfide. Hydrogen and a cobalt molybdate or alumina catalyst are used. Oxygen and nitrogen compounds behave similarly to sulfur compounds and thus this catalytic desulfurization process has become important in the upgrading of reformer feed stocks. Commercial processes use temperatures of 350-450°C with pressures up to 1500 psig (100 Kg/cm²).

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Extraction - In some cases, the sulfur containing organics are extracted and recovered from the hydrocarbon stock by adding an organic solvent to the caustic soda (or potash) which is being used as the extraction liquid. The solution is subsequently regenerated by air blowing to oxidize mercaptans to disulfides.

2. Input Materials

Naphthalene feed Hydrogen Catalyst - cobalt molybdate

3. Operating Parameters

Temperature 350-450°C (662-842°F)

Pressure up to 10.34 MPa (102 atm)

Catalyst cobalt molybdate

4. Utilities

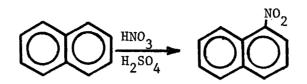
Not given

- 5. <u>Waste Streams</u> Hydrogen sulfide, ammonia, mercaptans
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Chemical Technology, Barnes and Noble, New York, N.Y., Vol. 4

(1972), p. 55-56.

1-Nitronaphthalene



- 1. <u>Function</u> 1-Nitronaphthalene is prepared by nitrating naphthalene with mixed acid at 50-60°C. The organic phase is separated and washed with hot water until free of acids. The product contains about 0.5-1% 2,4-dinitronaphthalene and 3% 2-nitronaphthalene. These are easily removed by crystallization or by sweating (partial melting). The nitration of naphthalene gives a 94% yield of the 1-isomer. The relatively small amount of 2-isomer is easily removed with the other by-products by crystallization from alcohol.
- 2. Input Materials

Naphthalene

Mixed Acids (1 part 62% HNO_3 + 3 parts 80% H_2SO_4).

3. Operating Parameters

Temperature: 50-60°C (122-140°F)

Pressure: 100 KPa (1 atm)

- 4. Utilities Not given
- <u>Waste Streams</u> Air vent streams may contain oxides of nitrogen. Waste streams from the washing and purification processes contain nitric and sulfuric acids, naphthalene, α-nitronaphthalene, β-nitronaphthalene, 2,4-dinitronaphthalene, and alcohols.
- 6. EPA Source Classification Code None

7. <u>References</u>

Kirk and Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 83.

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<u>Ibid</u>., Vol. 13 (1967) p. 704.

Howe, A. P. and Hass, H.B., Ind. Eng. Chem., 38, 251, (1946).

Astle, M. J., <u>Industrial Organic Nitrogen Compounds</u>, Reinhold Publishing Corp., New York, N.Y., 1961, p. 320-21.

- Function 1-Naphthylamine is prepared by the catalytic reduction of 1-nitronaphthalene with iron powder and hydrochloric acid. The product mixture is made alkaline and 1-naphthylamine is distilled out with superheated steam. The yield in this process approximates 96%. By-products of this reaction are 2-naphthylamine, 1,5-naphthalene diamine and 1,1'-binaphthylamine.
- 2. Input Materials

1-Nitronaphthalene Iron powder Hydrochloric acid (dilute)

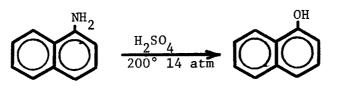
- 3. <u>Operating Parameters</u> Temperature: 80°C Pressure: 100 kPa (1 atm)
- 4. Utilities Not available
- <u>Waste Streams</u> Air vent streams would include HCl vapor and hydrogen.
 Waste water streams contain hydrochloric acid, iron salts (including chlorides), some 1-naphthylamine and 1-nitronaphthalene.
- 6. EPA Source Classification Code None
- 7. References

Kirk and Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 83.

Chemical Technology, Barnes and Noble, New York, N.Y., Vol. 4

(1972), p. 520.

1-Naphthol (from 1-naphthylamine)



- 1. <u>Function</u> The best and most economical process for the production of 1-naphthol is the hydrolysis of 1-naphthylamine in aqueous sulfuric acid at 200°C and 14 atm. pressure. The yield is 95% and the product is pure. The purity of the product gives this process a distinct advantage over the alkali fusion of the sulfonic acid derivative, the method of choice for 2-naphthol, since the product purity from this process is often too low for many applications.
- 2. Input Materials

1-Naphthylamine 1.06 kg/kg product Sulfuric acid (aqueous)

3. Operating Parameters

Temperature - 200°C (392°F)

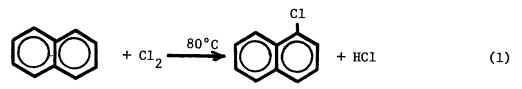
Pressure - 1.42 MPa (14 atm)

- 4. Utilities not given
- <u>Waste Streams</u> Effluents would contain ammonium sulfate, sulfuric acid, 1-naphthylamine and 1-naphthol.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition. Interscience Publishers, New York, N.Y., Vol. 13 (1967) p. 717.

Chemical Technology, Barnes and Noble, New York, N.Y., Vol. 4 (1972) p. 326.

CHLORONAPHTHALENES



 <u>Function</u> - Commercial quantities of 1-chloronaphthalene and mixtures of polychloronaphthalenes are produced by passing chlorine gas into molten naphthalene (80°C). If 1-chloronaphthalene production is favored, catalysts are not normally required.

If a polychloronaphthalene mixture is the desired product, ferric or antimony chloride catalyst must be added to the reaction mixture to promote chlorine addition. Chlorination is begun at 80°C, and the temperature is slowly raised as the reaction proceeds. During the process, the chlorination mixture is continually agitated.

When the desired point has been reached, the chlorination mixture is neutralized by stirring in the molten state with aqueous alkali, washed with water, and dried under vacuum.

2. Input Materials

Naphthalene

Chlorine

Sodium hydroxide

Water

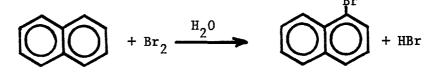
3. Operating Parameters

Temperature - <u>></u> 80°C (176°F) Pressure - not given

Catalyst - for polychloronaphthalenes $FeC1_3$ or $SbC1_3$ (0.5%)

- 4. <u>Utilities</u> Not given
- 5. <u>Waste Streams</u> Wastewater streams from washing operations probably contain sodium chloride, sodium hydroxide, and traces of naphthalene and chlorinated naphthalenes. Chlorine gas may be discharged from various processing equipment.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964) p. 300. Bromonaphthalenes



- 1. <u>Function</u> «-Bromonaphthalene and lesser amounts of dibromonaphthalenes are produced by the interaction of naphthalene and bromine in carbon tetrachloride or water. Iron catalysts are required if carbon tetrachloride serves as the reaction medium. Hydrogen bromide by-product is allowed to escape, preferably being washed by incoming raw material. The crude product is then dried and fractionated, giving «-bromonaphthalene in 72 75% yield.
- 2. Input Materials

Naphthalene - 0.82 - 0.86 kg/kg product Bromine

Water or carbon tetrachloride

3. Operating Parameters

Temperature: 100°C (212°F) Pressure: not given Catalyst: iron (in CC1₆)

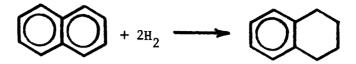
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Air vent streams contain hydrogen bromide, the principal by-product of the reaction. Carbon tetrachloride will be present in the air vent streams from solvent recovery systems, when this solvent is used as the reaction medium. Waste streams will contain HBr, naphthalene, and some bromonaphthalenes when water is used as the solvent medium. Sodium bromide will be present in waste water when caustic soda is used to neutralize the HBr absorbed in the water.

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6. <u>EPA Source Classification Code</u> - None

7. <u>Reference</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 775. Tetrahydronaphthalene



 Function - 1,2,3,4-Tetrahydronaphthalene, more commonly known as tetralin, is produced exclusively by the catalyic hydrogenation of naphthalene. This reduction is carried out at 150°C* in the presence of nickel or modified nickel catalysts.

Since active nickel catalysts are poisoned by sulfur compounds, represented predominatly in naphthalene by thianaphthene, commerical naphthalene must be desulfurized prior to hydrogenation. This is accomplished by treatment with sodium or by a catalytic dehydrosulfurizing process.

2. Input Materials

Naphthalene (desulfurized) Hydrogen

- 3. <u>Operating Parameters</u> Temperature: 150°C (302°F) Pressure: 100 - 200 KPa (1 - 2 atm) Catalyst: nickel or modified nickel
- 4. Utilities Not given

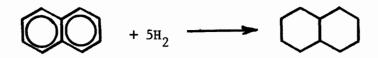
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 Heat-exchanges are necessary to control the temperature of this exothermic reaction, since destructive hydrogenation occurs at high temperatures.

- 5. <u>Waste Streams</u> Air vent streams from the reactor contain hydrogen and may have small quantities of tetrahydronaphthalene and naphthalene. When the product is purified by extractive distillation the air vent streams may contain tetrahydronaphthalene, naphthalene and some solvent (diethylene glycol for example).
- 6. EPA Source Classification Code None

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 13 (1967), p. 676-77. Decahydronaphthalenes



- L. <u>Function</u> Commercial decahydronaphthalene, a mixture of cisand trans-isomers more commonly known as Decalin, is prepared by the catalytic hydrogenation of naphthalene.* The reaction may be carried out in the fused-state (above 100°C) or in the liquid phase at 2.5 - 4.0 MPa (25 - 40 atm) and 200 - 260°C. Both process variations employ copper or nickel catalysts.
- 2. Input Materials

Naphthalene (desulfurized) Hydrogen

3. Operating Parameters

Temperature: fused state - >100°C (212°F)

liquid phase - 200 - 260°C (232-500°F)

Pressure: fused state - not given

liquid phase - 2.5 - 4.0 MPa (25-40 atm)

Catalyst: copper or nickel

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Air vent streams from the reactor will contain hydrogen and some naphthalene and decahydronaphthalene. Air vent streams from the purification system contain naphthalene decahydronaphthalene and solvent when extractive distillation is used to purify the product.
- The naphthalene feed is desulfurized by the methods discussed in Process No. 209.

6. <u>EPA Source Classification Code</u> - None

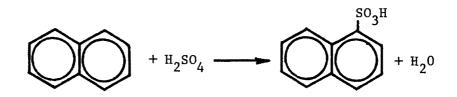
7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 13 (1967), p. 677.

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1-Naphthalenesulfonic Acid



- <u>Function</u> Commercially, 1-naphthalenesulfonic acid is prepared by sulfonating naphthalene with 98% sulfuric acid below 60°C. Isolation is accomplished by liming, conversion of the calcium salt to the sodium salt by soda ash, and drying. The technical product contains about 77.5% 1-naphthalenesulfonate, 10.2% 2-naphthalenesulfonate, 5.7% disulfonate, 2.7% sodium sulfate, and 3.7% water.
- 2. Input Materials

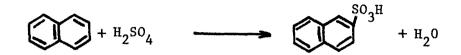
Naphthalene Sulfuric acid (98%) Lime Soda ash

- 3. <u>Operating Parameters</u> Temperature - <60°C (140°F) Pressure - 101 kPa (1 atm)
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Air vent streams from the reactor will contain some sulfur dioxide and small quantities of naphthalene. The overhead gases from the concentrator contain sulfur dioxide and naphthalene. Calcium sulfate and calcium carbonate are recovered from neutralization and washing steps. Waste wash water contains some sulfuric and naphthalene sulfonic acids.

- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 13 (1967), p. 700. <u>Chemical Technology</u>, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 597.

2-Naphthalenesulfonic acid



 Function - 2-Naphthalenesulfonic acid is commercially prepared by treating naphthalene with about one part of 93-96% sulfuric acid at 160°C.

1-Naphthalenesulfonic acid, which constitutes about 15% of the crude product, is hydrolyzed back to naphthalene by steam, and the latter is recovered by steam distillation. The sulfonation mixture is then added to water, and 2-naphthalenesulfonic acid is precipitated as the sodium salt by the addition of sodium chloride.

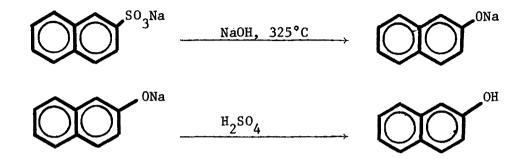
2. Input Materials

Naphthalene Sulfuric acid (93-96%) Sodium chloride Water

- <u>Operating Parameters</u>
 Temperature 160°C (320°F)
 Pressure Not given
- 4. Utilities Not given
- <u>Waste Streams</u> Sodium chloride, sodium sulfate, and caustic acid may be present in process wastes.

- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 13, (1967), p. 700. 2-Naphthol (from 2-naphthalenesulfonic acid)



- 1. <u>Function</u> In commercial practice, 2-naphthol is prepared by fusing the sodium salt of 2-naphthalenesulfonic acid with sodium hydroxide in a cast-iron or nickel-steel kettle at 325°C. The melt is run into cold water, acidified with sulfuric acid, and the free 2-naphthol is separated. The product is washed well with water, distilled <u>in vacuo</u>, and sublimed. The yield is almost 80% of the theoretical.
- 2. Input Materials

2-Naphthalenesulfonic acid (sodium salt) - 1.80 kg/kg product Sodium hydroxide

Sulfuric acid

Water

- 3. <u>Operating Parameters</u> Temperature: 325°C (617°F) Pressure: not given
- 4. Utilities Not given
- 5. <u>Waste Streams</u> The waste water from washing operations probably contains quantities of sodium sulfate, naphthalenesulfonic acids, and naphthols.

6. EPA Source Classification Code - None

7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 13 (1967) p. 718. Phthalic Anhydride (from naphthalene)

$$2 \bigcirc 0 + 90_2 \text{ (air)} \longrightarrow 2 \bigcirc 0 + 4H_20 + 4CO_2$$

 <u>Function</u> - As of January 1, 1975, 36% of the U.S. capacity for phthalic anhydride production was based on naphthalene feedstock. Both petroleum naphthalene (>80°C) and desulfurized coal-tar naphthalene (78°) are converted to phthalic anhydride by vapor-phase air oxidation in the presence of a vanadium pentoxide catalyst.

There are three processes in use for the air oxidation of naphthalene. Two of these include a fixed catalyst bed process and these are adaptable to both naphthalene and o-xylene feed stocks. The third process involves a fluidized catalyst bed and has been applied only to naphthalene. A significant by-product of all three processes is maleic anhydride and maleic acid. Small amounts of benzoic acid are recovered from the fixed bed processes.

The most widely used oxidation processes are the fixed bed processes. These differ in the catalyst composition employed and the temperature range of operation. The original process employed a catalyst consisting of 65% V_2O_5 , 30% MoO₃ and 5% CuO or Mn₃O₄. It operated at 400-475°C and gave yields of phthalic anhydride of approximately 65%.

The von Heyden process, a low-temperature, fixed-bed air oxidation, also accounts for considerable naphthalene-based phthalic anhydride production. Reaction temperatures are maintained in the 350-360°C range with 4 - 5 sec contact time. The catalyst is usually vanadium

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pentoxide on silica with 20-30% potassium sulfate. Yields in the neighborhood of 82% are obtained by this process with limited byproduction of maleic anhydride, maleic acid, etc.

The third process employs an air-fluidized bed of V_2O_5 into which is injected naphthalene in vapor form. The bed is maintained at 340-380°C and 1 atmosphere. The air/feed ratio can be maintained at 2 to 3x a lower value than in the fixed bed system. It is not possible to use o-xylene as a feedstock in this system and as a result the use of this system is decreasing as the difficulty in obtaining naphthalene feedstock increases. Yields from this process approximate 85%. The vaporous effluent in all these processes is passed through heat exchangers where phthalic anhydride crystallizes and deposits on the walls. Heat is then applied and the crude product is melted out and collected. Using this procedure 98-99% of the phthalic anhydride in the effluent is recovered.

The crude product is purified by a chemical soak in sulfuric acid and caustic followed by a heat soak at 150-250°C. This heat treatment removes water and other impurities such as maleic acid and anhydride as well as benzoic acid. The residual phthalic anhydride is vacuum distilled in batch or continuous operation.

2. <u>Input Materials</u> - Basis - 1 metric ton phthalic anhydride Naphthalene (>80° or desulfurized) 1,250 kg (2,756 lbs) Air (15°C, 59°F) 26,000 m³ (918, 181 ft³) Sulfuric acid Sodium hydroxide

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Water

3. Operating Parameters

	Temperature:	High temperature, fixed bed -	400-475°C (752-887°F)
		Von Heyden	350-360°C (662-680°F)
		Fluidized bed	340-380°C (644-716°F)
	Pressure:	Von Heyden	48-55 kPa (0.47-0.54 atm)
		Fluidized bed	101 kPa (1 atm).
	Catalyst:	High Temperature, fixed bed	65° V ₂ 0 ₅ , 30% мо0 ₃ , 5%
			(CuO or Mn ₃ 0 ₄)
		Von Heyden	V ₂ 0 ₅ on SiO ₂ + 20-30%
			κ ₂ so ₄
		Fluidized bed	Finely divided V ₂ 0 ₅
	Reaction Time:	Fluidized bed	19-20 sec
		Von Heyden	4-5 sec
		Fixed bed	0.1-0.6 sec

Water

5.

Cooling, makeup (stream generation), makeup (cooling) - 61,000 gph Electricity Process - 2.0 MW Utilities - 88 kW Fuel - 3.3 dm³/sec average (420 cfh) <u>Waste Streams</u>* Spray scrubber effluent (water) Phthalic anhydride - trace Maleic anhydride - 16.7 Kg/Mg phthalic anhydride Spray scrubber effluent (air)

^{*} These values are characteristic of the first fixed-bed process.

5. Waste Streams (continued)

Naphthalene - trace Phthalic anhydride - 9.5 Kg/Mg phthalic anhydride product Maleic anhydride - 26 Kg/Mg phthalic anhydride Other - 23.7 Kg/Mg phthalic anhydride (assumed to be organic in nature) Phthalic anhydride recovery columns (solid) Phthalic anhydride - 69.3 kg/Mg phthalic anhydride Other - 51 kg/Mg phthalic anhydride (assumed to be organic in nature; specific compound information not available)

- 6. EPA Source Classification Source None
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 8," "Chemical Engineering," July 22, 1974, p. 109.

Sittig, M., <u>Chemicals from Aromatics</u>, Noyes Development Co., Park Ridge, N.J., 1966, p. 50.

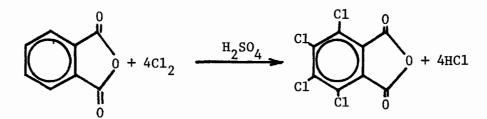
Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 15 (1968), p. 450.

"1971 Petrochemical Handbook," "Hydrocarbon Processing," November 1971, p. 189.

Sittig, M., Pollution Control in the Organic Chemical Industry, Noves Data Corp., Park Ridge, N.J., 1974, p. 186-188.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 658-660.

Tetrachlorophthalic Anhydride



- Function Tetrachlorophthalic anhydride is produced by the hightemperature chlorination of phthalic anhydride in fuming sulfuric acid. Antimony pentachloride may be used as a catalyst.
- 2. Input Materials

Phthalic anhydride

Chlorine

Sulfuric acid (fuming)

- 3. Operating Parameters Not given
- 4. Utilities Not given
- <u>Waste Streams</u> Wastewater from the acid scrubber may contain sodium hydroxide, and traces of phthalic anhydride, and various chlorosubstituted phthalic anhydrides.
- 6. EPA Source Classification Code -None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 15 (1968), p. 446. Phthalonitrile (from phthalic anhydride)



 Function - One competitive route to phthalonitrile involves the vapor-phase reaction of phthalic anhydride and ammonia. This conversion takes place at high temperatures over an alumina catalyst.

Phthalimide and/or phthalamide intermediates are probably involved.

2. <u>Input Materials</u>

Phthalic anhydride

Ammonia

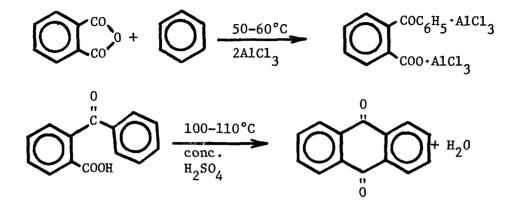
- 3. <u>Operating Parameters</u> Temperature - Not given Pressure - Not given Catalyst - Alumina
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Effluents from the ammonia stripper and/or separator probably contain ammonia, phthalic anhydride, phthalonitrile, and reaction intermediates such as phthalamide and phthalimide.
- 6. EPA Source Classification Code None

7. References

Kirk-Othmer, <u>Encylcopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 15 (1968), p. 447. Throdahl, M. C., Zerbe, R. O., and Beaver, D. J., Ind. Eng. Chem., <u>43</u>, 926 (1951).

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Anthraquinone (solvent method)



 <u>Function</u> - The most frequently used route to anthraquinone involves the condensation of phthalic anhydride and benzene to give o-benzoylbenzoic acid which undergoes ring closure by dehydration. Overall this can be considered a modified Friedel-Crafts reaction. Two general methods are utilized to produce the product, the solvent method and the ball mill method.

In the solvent method, phthalic anhydride is added to a cast-iron kettle containing aluminum trichloride and a large excess of benzene. An aluminum chloride complex of o-benzoylbenzoic acid is formed with an evolution of heat. The temperature is regulated so that it slowly reaches 50-60°C. Hydrogen chloride evolved during the reaction is discharged to a condenser-scrubbing system.

When the evolution of HCl is complete the reaction mass is transferred to an acid proof reactor containing dilute H_2SO_4 which decomposes the complex to o-benzoylbenzoic acid and water soluble aluminum sulfate. The water and benzene solutions are separated and the o-benzoylbenzoic acid recovered by treating the benzene phase with aqueous sodium

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carbonate. The benzene is separated, distilled and recycled. The sodium salt of o-benzoylbenzoic acid is neutralized and filtered out of the aqueous phase.

The o-benzoylbenzoic acid is washed, dried and treated with concentrated H₂SO₄ or oleum at 100-110°C. Practically quantitative yields of high-purity anthraquinone are obtained. If further purification is required it may be done by sublimation.

2. Input Materials

Phthalic anhydride - 0.75 kg/kg product

Benzene

Aluminum chloride (anhydrous)

Sulfuric acid

Sodium carbonate

Sodium hydroxide (HC1 scrubber)

Water

3. Operating Parameters

Temperature: condensation - 50-60°C (122-140°F)

dehydration - 100-110°C (212-230°F)

Pressure: not given

- 4. Utilities Not given
- 5. <u>Waste Streams</u> The principal pollutant sources in this process are most likely wastewater effluents from the HCl scrubber, phase separations, and filtering and washing operations.

Hydrogen chloride scrubber

Sodium chloride and caustic soda are probably present in this waste stream

Aqueous phase separation

The discarded aqueous phase of the aluminum chloride complex decomposition product is likely to contain sulfuric acid as well as various aluminum salts.

Benzene extraction

The extract water probably contains quantities of benzene and other organics, i.e., purification solvents.

Filtering/washing operations

Hydrochloric or sulfuric acid and various sodium salts are probably the principal pollutants in the waste stream.

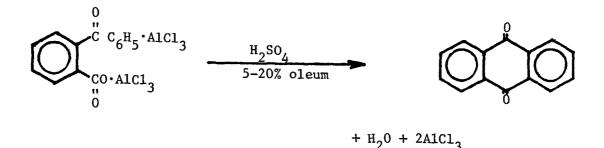
Indeterminate quantities of phthalic anhydride, benzene, and o-benzoylbenzoic acid may be present in all wastewater effluents.

- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Ed., Interscience

Publishers, New York, N.Y., Vol. 2, (1963), p. 435.

Anthraquinone (ball mill method)



1. <u>Function</u> - As mentioned in Process No. 223, the ball mill method is one of two general routes to anthraquinone from phthalic anhydride and benzene. In this process, the reactants are mixed in practically stoichiometrical quantities with only a slight excess of benzene present. Consequently, the product of the condensation reaction is discharged as a dry aluminum chloride complex of o-benzoylbenzoic acid which can be ring-closed directly to anthraquinone by treatment with strong sulfuric acid or 5-20% oleum.

Alternately, the complex may be anhydrously decomposed to o-benzoylbenzoic acid and subsequently dehydrated by the method described in Process No. 223. The yield and quality of the product obtained by this procedure are almost the same as in the solvent method.

However, the ball mill operation has two distinct advantages over the solvent method. Practically no solvent recovery is necessary, and the liberated hydrogen chloride is free of corrosive action since decomposition of the aluminum chloride complex is carried out anhydrously.

2. Input Materials

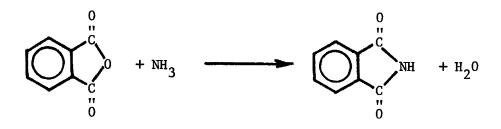
Phthalic anhydride - 0.75 kg/kg product Benzene

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- 2. <u>Input Materials</u> (continued) Aluminum chloride (anhydrous) Sulfuric acid or oleum (5-20%) Aqueous sodium hydroxide (HC1 scrubber)
- 3. Operating Parameters see Process No. 224.
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Wastewater from the HCl scrubber probably contains sodium chloride, sodium hydroxide, and traces of phthalic anhydride and benzene.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Ed., Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 436.

Phthalimide



 Function - On an industrial scale, phthalimide is produced by saturating molten phthalic anhydride with dry ammonia and heating the mixture to 170-240°C under pressure.

Alternately, the cyclic imide can be prepared in 95-97% yield by heating the anhydride with concentrated aqueous ammonia solution and eventually raising the temperature to 300°C. Phthalimide is isolated by evaporating the product solution to dryness.

2. Input Materials

Phthalic anhydride - 1.05 kg/kg product Ammonia (anhydrous or aqueous)

- . . .
- 3. Operating Parameters

Temperature - anhydrous process - 170-240°C (338-464°F) aqueous process - 300°C (572°F)

Pressure - anhydrous process - elevated

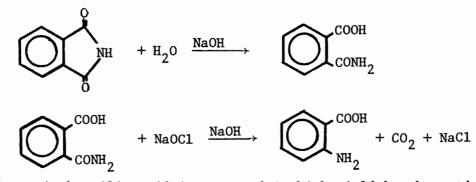
aqueous process - atmospheric

4. Utilities - Not given

- 5. <u>Waste Streams</u> In the anhydrous process, the principal pollutant source is probably the ammonia absorber off-gas, containing ammonia and smaller quantities of phthalic anhydride. In the aqueous process, waste gases from evaporation may also contain quantities of ammonia and phthalic anhydride.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Ed., Interscience Publishers, New York, N.Y., Vol. 15 (1968), p. 447.

Anthranilic Acid



 Function - Anthranilic acid is prepared in high yield by the action of sodium hypochlorite or hypobromite on phthalimide in alkaline solution at 80°C. The ring is opened by hydrolysis and the phthalamidic acid intermediate undergoes the Hofmann reaction.

Anthranilic acid is precipitated on neutralization of the alkaline solution.

In commercial operations, sodium hypochlorite or hypobromite is probably prepared <u>in situ</u> by passing chlorine or bromine into the sodium hydroxide solution.

2. Input Materials

Phthalimide

Sodium hydroxide

Chlorine or bromine

Water

Mineral acid

- <u>Operating Parameters</u>
 Temperature: 80°C (176°F)
 Pressure: not given
- 4. Utilities Not given

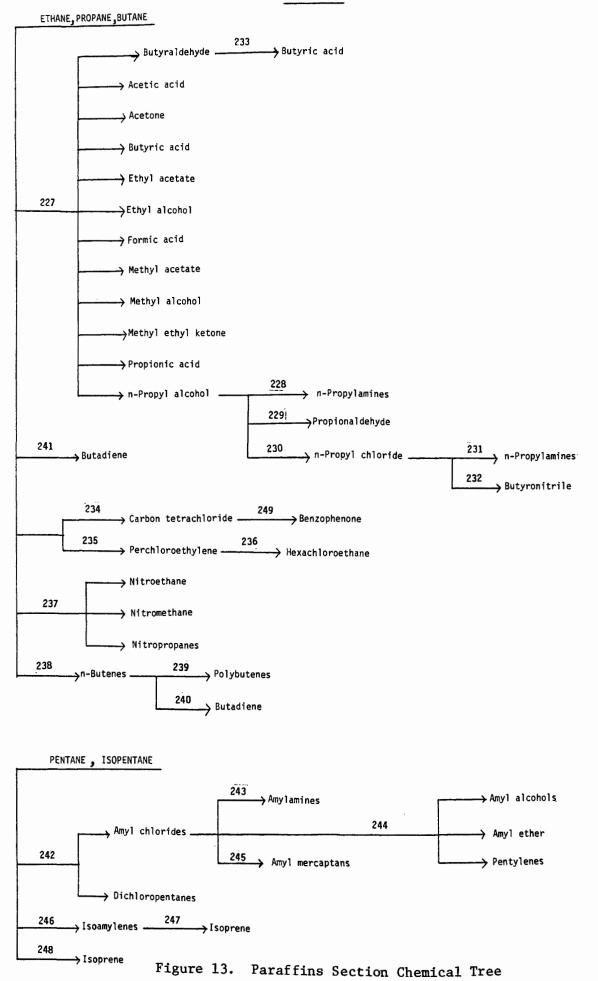
- 5. <u>Waste Streams</u> Hypochlorous acid or the hypobromous acid may be detected in any air vent streams from the reactor. Chlorine and/or bromine will also be present. Waste water streams contain some sodium chloride and small quantities of anthranilic acid.
- 6. EPA Source Classification Code None

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 434.

SECTION VII PARAFFINS

PARAFFINS



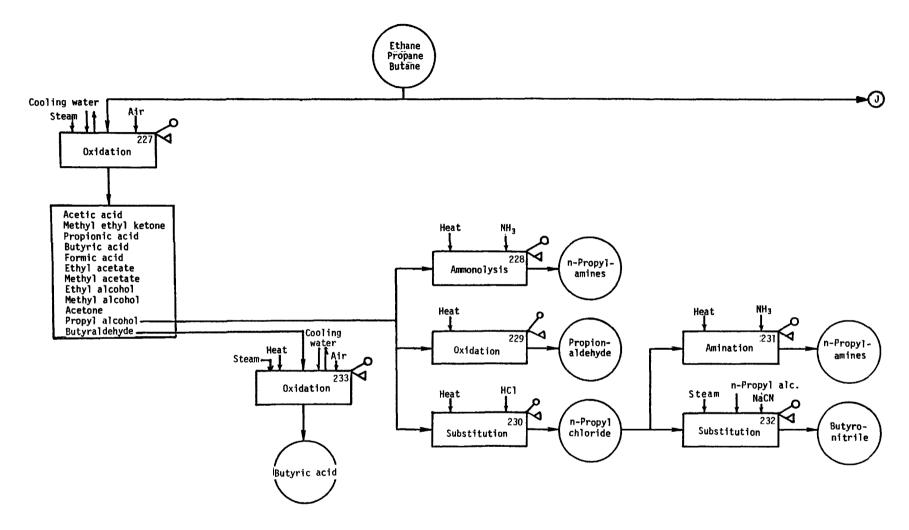


Figure 14. Paraffins Section Process Flow Sheet

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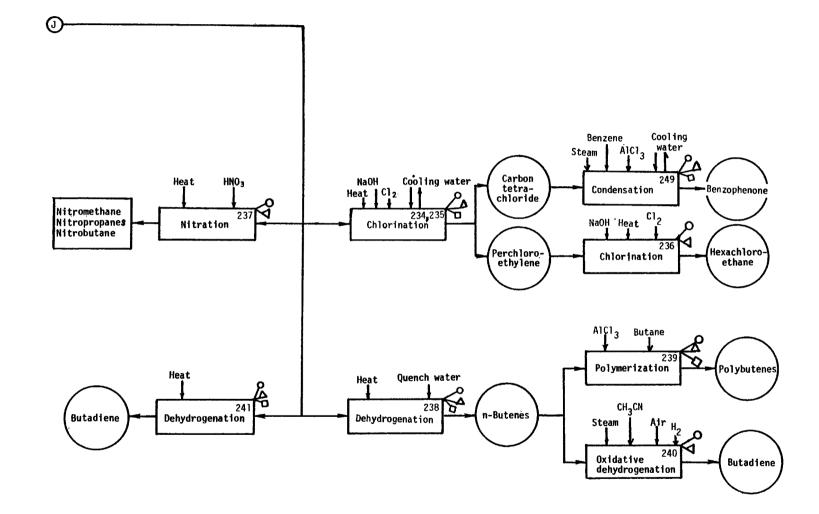


Figure 14. Paraffins Section Process Flow Sheet (Cont.)

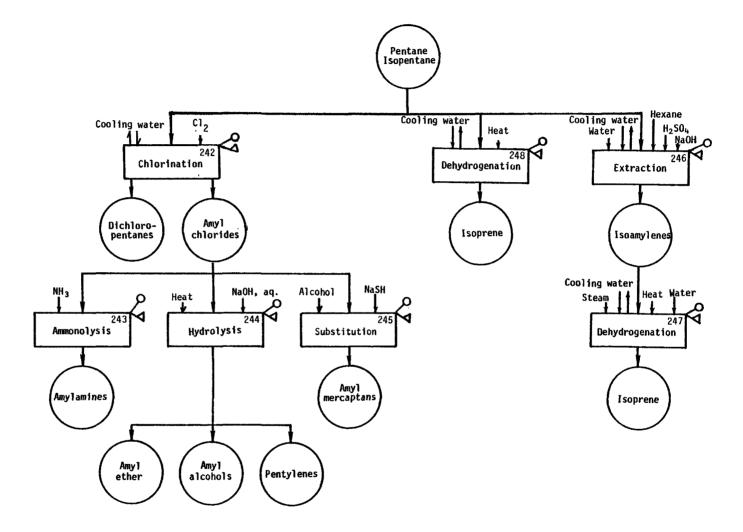


Figure 14. Paraffins Section Process Flow Sheet (Cont.)

Acetic Acid and by-products (oxidation of n-butane)

 $C_4H_{10} + 0_2$ (Air) \longrightarrow $CH_3COOH + by-products$

 <u>Function</u> - The most economical route to acetic acid, and one which accounted for 46% of the total 1973 production in the United States, is the liquid-phase oxidation of a natural gas or light petroleum fraction containing 95% n-butane.

The oxidation of n-butane is carried out at 150-225°C and 5.5 MPa (-800 psig) in the presence of a transition-metal acetate, usually cobalt acetate. Compressed air and liquid butane are fed to a liquid phase reactor. Reaction product is withdrawn, cooled and sent to a decanter for phase separation. The hydrocarbon-rich phase is recycled to the reactor. The aqueous phase is sent to the recovery and purification system. Off-gases primarily nitrogen, oxides of carbon and n-butane, are scrubbed for butane recovery and vented through an expander turbine to recover energy. Low boiling organics are separated from the crude acetic acid by conventional distillation. Recovered by-products include methanol, acetone, n-propyl alcohol and methyl ethyl ketone. Depending on reaction conditions, formic, propionic and butyric acids and their esters (methyl, ethyl) may also be recovered. Azeotropic distillation is used to purify the crude acetic acid to glacial acetic acid.

2. <u>Input Materials</u> - Basis - 1 metric ton products n-Butane^{*} - 1.08 kg/kg acetic acid 965 kg (2127 lbs/ton) Air 3750 m³ (1.32 x 10⁵ ft³/ton)

^{*} The hydrocarbon feed also contains some propane, ethane, isobutane, and other lights.

3. Operating Parameters

Temperature - 150-225°C (302-437°F) Pressure - 5.52 MPa (54.5 atm) Catalyst - cobalt acetate

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Various wastewater streams from the purification section may contain acetic acid and a variety of alcohols, aldehydes, ketones, esters, other organic acids, ethers, and high-boiling impurities. Quantities of butane, propane, ethane, etc., are probably discharged to the atmosphere from the reaction section. No specific information was available.
- 6. EPA Source Classification Code None
- 7. References

Austin, George T., "The Industrially Significant Organic Chemicals -Part 1," "Chemical Engineering," January 21, 1974, p. 128,129.

Ibid., Part 4, April 15, 1974, p. 89,90.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 8 (1965) p. 396,397.

Lowry, R. P. and Aguilo, A., "Hydrocarbon Processing," November, 1974, p. 105. Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 11,12.

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 $\underline{\text{n-Propyl Amines (from n-propyl alcohol)}}$ $CH_{3}CH_{2}CH_{2}OH + NH_{3} \longrightarrow CH_{3}CH_{2}CH_{2}NH_{2} + H_{2}O$ $CH_{3}CH_{2}CH_{2}NH_{2} + CH_{3}CH_{2}CH_{2}OH \longrightarrow (CH_{3}CH_{2}CH_{2})_{2}NH + H_{2}O$ $(CH_{3}CH_{2}CH_{2})_{2}NH + CH_{3}CH_{2}CH_{2}OH \longrightarrow (CH_{3}CH_{2}CH_{2})_{3}N + H_{2}O$

- 1. <u>Function</u> Propyl alcohol reacts with ammonia at moderately high temperature (300-500°C) and pressures of 1-20 MPa (10-200 atm) to yield mono-, di- and tripropyl amines. The mixture of amines formed is thought to be in equilibrium and the yield of each of them can be increased by recycling the others. The product ratio may also be controlled by the ratio of reactants and the operating temperature. A catalyst consisting of activated alumina is commonly used in these reactions. Silica, and magnesium oxide as well as alumina containing Fe_20_3 , $Ti0_2$ and cobalt, nickel and chromium oxides have been used to promote amine formation.
- 2. Input Materials

n-Propyl alcohol

Ammonia

3. Operating Parameters

Temperature: 300-500°C (572-932°F)

Pressure: 1-20 MPA (10-200 atm)

Catalyst: alumina

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste effluents from strippers, separators, etc., may contain ammonia, n-propyl alcohol, and all of the n-propylamines.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 117.

Astle, M.J., <u>Industrial Organic Nitrogen Compounds</u>, Reinhold Publishing Corporation, New York, N.Y., 1961, p. 8-9. Propionaldehyde (from n-propyl alcohol)

$$CH_3CH_2CH_2OH \xrightarrow{Catalyst} CH_3CH_2CHO + H_2$$

- <u>Function</u> Small quantities of propionaldehyde are produced by the dehydrogenation of n-propyl alcohol. This conversion is carried out at 200-300°C in the presence of copper compounds or iron oxide. Reaction equipment is usually stainless steel, but aluminum is also satisfactory.
- 2. Input Materials n-propyl alcohol
- 3. Operating Parameters

Temperature - 200-300°C (392-572°F)

Pressure - Not given

Catalyst - copper compounds (copper chromite) or iron oxide

- 4. <u>Utilities</u> Not given
- <u>Waste Streams</u> Waste gases from this process may contain hydrogen, n-propyl alcohol, and propionaldehyde.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Ed., Interscience Publishers, New York, N.Y., Vol. 16 (1968), p. 550. n-Propyl Chloride (from n-propyl alcohol)

$$CH_3CH_2CH_2OH + HC1 \xrightarrow{ZnCl_2} CH_3CH_2CH_2C1 + H_2O$$

- Function n-Propyl chloride is produced by heating n-propyl alcohol in concentrated hydrochloric acid. Zinc chloride catalyzes the reaction.
- 2. Input Materials

n-Propyl alcohol

Hydrochloric acid (conc.)

3. Operating Parameters

Temperature: not given

Pressure: not given

Catalyst: ZnCl₂

- 4. Utilities Not given
- <u>Waste Streams</u> Water-spent catalyst, propyl chloride, and tars may be present in the separator waste effluents.
- 6. EPA Source Classification Code None
- 7. Reference

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 192, 270.

n-Propyl Amine (from n-propyl chloride)

$$\mathsf{CH}_{3}\mathsf{CH}_{2}\mathsf{CH}_{2}\mathsf{C1} + \mathsf{2NH}_{2} \xrightarrow{} \mathsf{CH}_{3}\mathsf{CH}_{2}\mathsf{CH}_{2}\mathsf{NH}_{2} + \mathsf{NH}_{4}\mathsf{C1}$$

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 + \text{CH}_3\text{CH}_2\text{CH}_2\text{C1} \xrightarrow{\text{NH}_3} (\text{CH}_3\text{CH}_2\text{CH}_2)_2\text{NH} + \text{NH}_4\text{C1}$$

 $(CH_3CH_2CH_2)_2NH + CH_3CH_2CH_2C1 \xrightarrow{NH_3} (CH_3CH_2CH_2)_3^N + NH_4C1$

- 1. <u>Function</u> n-Propyl amine is commercially produced by the reaction of n-propyl chloride and ammonia. The reaction is carried out under pressure at moderately high temperatures (160-170°C). Normally the primary, secondary and tertiary amine derivatives are formed. The primary amine yield may be maximized by operating at excess ammonia concentrations. Yields of secondary and tertiary amines are increased by recycling the primary amine.
- 2. Input Materials

n-Propyl chloride

Ammonia

3. Operating Parameters

Temperature: 160-170°C (320-338°F)

Pressure: 2.7 MPa (27 atm)

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste effluents from the ammonia stripper may contain quantities of ammonia, propyl chloride, and primary, secondary, and tertiary propyl amines.

6. EPA Source Classification Code - None

7. <u>References</u>

Astle, M.J., <u>Industrial Organic Nitrogen Compounds</u>, Reinhold Publishing Corp., New York, N.Y., 1961, p. 5.

Butyronitrile (from n-propyl chloride)

 $\text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{C1} + \text{NaCN} \xrightarrow{\text{aq. CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{OH}}_{\text{Heat}} \text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{CN} + \text{NaC1}$

- Function Butyronitrile is prepared by the reaction of n-propyl chloride and sodium cyanide in aqueous n-propanol.
- 2. Input Materials

n-Propyl chloride Sodium cyanide n-Propyl alcohol Water

- 3. Operating Parameters Not given
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste streams from the purification section probably contain sodium chloride, propyl alcohol, propyl chloride, butyronitrile, and sodium cyanide. Some air emissions of propyl chloride, propanol, and hydrogen cyanide may also occur.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Ed., Interscience Publishers, New York, N.Y., Vol. supplement (1971), p. 598. <u>n-Butyric Acid (oxidation of n-butyraldehyde)</u>

 $^{\mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{CH}_{2}\mathrm{CH}_{2}\mathrm{CH}_{0}} + 1/2 \text{ o}_{2} \xrightarrow{} \mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{CH}_{2}\mathrm{COOH}$

 <u>Function</u> - Some butyric acid is prepared commercially by the oxidation of n-butyraldehyde. In this process, air or oxygen is passed into n-butyraldehyde in the presence of a catalyst such as manganese butyrate or a cobalt salt.

Yields of about 90% are possible over a wide range of temperatures.

2. Input Materials

n-Butyraldehyde - 0.91 kg/kg butyric acid

Air or oxygen

3. Operating Parameters

Temperature: 30-50°C (86-122°F)

Pressure: not given

Catalyst: 0.5% manganese butyrate

Cobalt salts

4. Utilities

Not given

- 5. <u>Waste Streams</u> Although no information was available, some nbutyraldehyde and butyric acid are probably present in the reactor off-gas. Process slops may also be a source of these pollutants, as well as reaction by-products.
- 6. EPA Source Classification Code None

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1964). p. 880.

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 426.

Goldstein, R. F., <u>The Petroleum Chemicals Industry</u>, 2nd Edition, John Wiley and Sons, New York, N.Y., 1958, p. 331. INDUSTRIAL ORGANIC CHEMICALS

PROCESS NO. 234

Carbon Tetrachloride and Perchloroethylene (hydrocarbon chlorinolysis)

 $C_2 - C_4$ Hydrocarbons + $Cl_2 \longrightarrow$ mixed chlorocarbons and chlorohydrocarbons + HCl

 <u>Function</u> - Large quantities of perchloroethylene, carbon tetrachloride, and other chlorohydrocarbons are co-produced by the simultaneous chlorination and pyrolysis of paraffinic hydrocarbons. In commercial practice, this conversion is carried out by reacting ethane, propane, LPG, or natural gas with an excess of chlorine at 500 - 700°C.

Gaseous reaction products are quenched and most organics condensed. Any HCl remaining in the condensed crude is neutralized with dilute caustic, and the product is decanted from the aqueous phase, dried, and distilled.

Light end organics such as carbon tetrachloride and trichloroethylene^{*} are condensed and purified by further distillation. Perchloroethylene, hexachloroethane, and higher-boiling bottoms are separated, and the saleable compounds are neutralized, dried, and inhibited (if an olefinic linkage is present). Depending on economic factors, any of the various products may be recycled to the reactor.

^{*} Generally, trichloroethylene production is favored by lower reaction temperatures, i.e., 300-500°C.

2. Input Materials

Ethane, propane, LPG, or natural gas Chlorine Sodium hydroxide Polymerization inhibiters Water

3. Operating Parameters

Temperature: 500-700°C (932-1292°F)

Pressure: not given

4. Utilities

Not given

- <u>Waste Streams</u> Generally, the same types of pollution would be expected as in Process Nos. 235 and 236.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 2,""Chemical Engineering," February 18, 1974, p. 127.

Ibid, Part 7, June 24, 1974, p. 156.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 132, 199.

"1973 Petrochemical Handbook," "Hydrocarbon Processing," November 1973, p. 114.

Perchloroethylene (chlorination of mixed hydrocarbons)

Hydrocarbons + $C1_2 \longrightarrow mixed$ chlorohydrocarbons

mixed chlorohydrocarbons \longrightarrow CCl₄ + CCl₂=CCl₂ + HCl

 $2CC1_4 \implies CC1_2 = CC1_2 + 2C1_2$

1. <u>Function</u> - Perchloroethylene is now produced from a mixture of hydrocarbons. The usual starting materials are methane, ethane, ethylene, LPG, propane, ethylene dichloride, or process wastes from vinyl chloride manufacture, which are chlorinated to yield saturated chlorohydrocarbons. These are then pyrolyzed to yield mixtures of predominantly trichloroethylene, carbon tetrachloride, and perchloroethylene. The desired product may be separated and the rest returned to the reactor.

The formation of the mixed chlorohydrocarbons is carried out at 100-125°C and 5-10 atm; the pyrolysis is carried out at 400-700°C.

Perchloroethylene is also produced in a modified Deacon process which uses HCl and air:

$$CH_2 = CH_2 + 4HC1 + 20_2 \xrightarrow{300-500 \circ C} Cl_2C = CCl_2 + 4H_2O$$

With an excess of oxygen, the mixed product is typically 5-10% dichloroethylene, 25-35% trichloroethylene, and 50-60% perchloroethylene, which can be separated by fractionation. Fluid catalysts are commonly used; chlorination, oxychlorination and dehydrochlorination may proceed simultaneously in the same vessel.

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In the past, the dominant process started with acetylene and chlorine:

$$\text{HC} \equiv \text{CH} + \text{Cl}_2 \longrightarrow \text{CHCl}_2 \text{CHCl}_2 + \text{CCl}_3 \text{CHCl}_2 + \text{HCl}$$

 $\operatorname{CHCl}_{2}\operatorname{CHCl}_{2} + \operatorname{CCl}_{3}\operatorname{CHCl}_{2} + \operatorname{Ca}(\operatorname{OH})_{2} \longrightarrow \operatorname{CCl}_{2} = \operatorname{CCl}_{2} + \operatorname{CaCl}_{2}$

This process is no longer economical.

2. Input Materials (typical)

Basis - 1 metric ton perchloroethylene and 1,350 kg HCl

Propane, kg 200 (441 1bs)

Chlorine, kg 2,500 (5,512 1bs)

3. Operating Parameters

Step one:

 Temperature, °C
 100-125 (212-257°F)

 Pressure, MPa
 0.507-1.01 (5-10 atm)

 Step two:
 400-700 (752-1292°F)

4. Utilities

Not given

- 5. <u>Waste Streams</u> Although no information was available, mixed chlorohydrocarbons and hydrogen chloride may be present in the waste gases of various production steps. Heavy ends from distillation columns are usually incinerated.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 7," "Chemical Engineering," June 24, 1974, p. 156.

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Hahn, A. V., <u>The Petrochemical Industry - Market and Economics</u>, McGraw-Hill Book Co., New York, N.Y., 1970, p. 312,313.

Faith, W. L., et al., <u>Industrial Chemicals</u>, 3rd Edition, John Wiley & Sons, New York, N.Y., 1965, p. 577,578.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N.Y., 1975, p. 606. Hexachloroethane (from perchloroethylene)

$$\begin{array}{c} c_1 \\ c_1 \\ c_1 \end{array} \xrightarrow{c_1} c_2 \\ c_1 \end{array} + c_1 \xrightarrow{FeC1_3} cc1_3 \\ c$$

 <u>Function</u> - In commercial practice, hexachloroethane is produced by the chlorination of perchloroethylene at 100-140°C. This reaction is carried out in a lead-lined vessel in the presence of ferric chloride.

When 50-60% conversion to hexachloroethane is attained, the reaction is halted. After treatment with alkali to neutralize dissolved hydrogen chloride, the product solution is allowed to crystallize. The crystals are removed by centrifuging, and unreacted perchloroethylene is recovered and recycled to the chlorinator.

2. Input Materials

Perchloroethylene

Chlorine

Sodium hydroxide

Water

3. Operating Parameters

Temperature: 100-140°C (212-284°F)

Pressure: not given

Catalyst: FeCl₃

4. Utilities

Not given

- 5. <u>Waste Streams</u> Waste water from the purification section probably contains sodium chloride, caustic, various chlorinated by-products, and traces of perchloroethylene and hexachloroethane.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 200.

PROCESS NO. 237

$\underline{C_1} - \underline{C_3}$ Nitroparaffins (from propane)

 $CH_3CH_2CH_3 + HNO_3 \longrightarrow C_1 - C_3$ nitroparaffins + oxygenated by-products

1. <u>Function</u> - Propane is oxidized in the vapor phase with 65% nitric acid. The nitration is carried out in a silica-clad stainless steel reactor at 390-450°C and 0.8-1.2 MPa (8-12 atm). Approximately 40% of the nitric acid is converted to nitroparaffins, the remainder acts as an oxidizing agent, resulting in the oxygenated by-products, and is reduced to nitric oxide (NO). This is reoxidized to nitrogen dioxide which is utilized to produce additional nitroparaffins. The combined yield of HNO₃ to organic nitrates is 90%.

The temperature affects the reaction rate of reaction, the product composition (high temperature favors 1-nitro compounds), and the yield of oxidation products. High pressure increases rate but not product composition. The yield of nitromethane and 2-nitropropane may be increased at the expense of the other nitroalkanes by the use of 0.03-0.2 moles of an oxygenated sulfur compound.

The nitroalkanes, aldehydes and ketones are condensed leaving unreacted propane and nitric oxide in the gas phase. Propane is separated and recycled, the NO is oxidized with air to NO_2 which is absorbed in water to produce HNO_3 . This nitric acid solution is brought up to strength by the addition of concentrated HNO_3 and returned to the process. The aldehydes and ketones are separated from the nitroalkanes by solvent extraction with chlorinated aromatics. The nitroalkanes are separated and purified by fractional distillation.

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2. Input Materials

Propane - 0.68 - 0.91 kg/kg product Nitric acid - 0.98 - 1.30 kg/kg product Water Air

3. Operating Parameters

Temperature: 370-450°C (698-842°F)

Pressure: 0.8-1.2 MPa (8-12 atm)

4. Utilities

Not given

- 5. <u>Waste Streams</u> Waste water from washing operations probably contains a number of by-product aldehydes, ketones, acids, alcohols, and olefins. These same pollutants plus carbon monoxide, NO_x, and propane may be present in waste gases from separators and other purification equipment.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 13 (1967), p. 873-874.

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 546-550.

n-Butenes (dehydration of n-butane)

 $^{\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \longrightarrow \text{ n-C}_4\text{H}_8 + \text{H}_2}$

1. <u>Function</u> - In the Phillips process, n-butenes are produced by the dehydrogenation of n-butane to serve as intermediates en route to butadiene.^{*} The feed, preferably 98% n-butane, is dried carefully over bauxite and charged to externally heated tubular reactors filled with alumina-chromia catalyst. The dehydrogenation is carried out at 566-593°C and 108-239 kPa (1-20 psig) with 30% n-butane conversion per pass and 80% selectivity to n-butenes. The process operates cyclically, alternate reactors being used one hour for dehydrogenation and one hour for catalyst regeneration.^{**}

Hydrogen, $C_1 - C_3$ hydrocarbons, and other conversion by-products are separated from the reactor effluent by fractionation. The remaining C_4 hydrocarbon mixture is separated by extractive distillation with aqueous furfural or acetonitrile in two fifty-plate columns. Unreacted n-butane is collected overhead, washed with water, and recycled. The n-butenes remain in the solvent bottoms, from which they are separated by subsequent distillation and washed with water. Recovery of n-butenes as a 90-95% concentrate usually runs on the order of 80-90%.

n-Butenes produced by this process may also be used in the preparation of other derivatives.

^{**} This is carried out at 791 kPa (100 psig) with an air-flue gas mixture containing 2-3% oxygen.

2. Input Materials

n-Butane (98%) - 1.44-1.62 kg/kg product Furfural or acetonitrile

Water

3. Operating Parameters

Temperature: 566-593°C (1050-1099°F)

Pressure: 108-239 kPa (1-2.3 atm)

Catalyst: alumina-chromia

Space Velocity: 700

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Furfural or acetonitrile and various C_4 hydrocarbons are probably present in air and wastewater emissions from extractive distillation and washing operations. Quench waters from the dehydrogenation section may also contain C_4 hydrocarbons as well as residue gas, tars, and oils.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Ed., Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 834.

Friedman, L., Womeldorph, D.E. and Stevenson, D. H., Proc. Am. Petrol. Inst., Sec. III, 38, 202-218, 1958.

Polybutenes

1. <u>Function</u> - Commercial polybuteness are viscous, tacky liquids with molecular weights ranging from 300-3,000. They are produced by the aluminum chloride-catalyzed polymerization of dried, desulfurized butane/ butyleness refinery streams obtained from catalytic or thermal cracking operations. The isobutylene in the feed is polymerized to the greatest extent, so the product is composed predominantly of polyisobutylenes with indeterminate but minor quantities of poly(n-butenes) and insignificant amounts of n- and isobutane.

The yield of polybutenes from this process is about 83%, based on butylene feedstock. Unreacted butanes and the butylenes may be recycled or returned to the refinery.

2. Input Materials

Butane/butylenes refinery stream butylenes - 1.2 kg/kg product

3. Operating Parameters

Temperature - Not given

Pressure - Not given

Catalyst - A1C13

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Air emissions from this process may contain quantities of C₄ hydrocarbons, dimers, trimers, etc., and polymerization solvents, i.e., alcohols, ethers, alkyl halides. Spent AlCl₃ catalyst and reaction by-products may be present in solid or liquid process wastes. However, no specific information was available.

- 6. EPA Source Classification Code None
- 7. References
 - Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Ed., Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 946-55.

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<u>Ibid</u>., Vol. 14 (1967).

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PROCESS NO. 240
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Butadiene (oxidative dehydrogenation of n-butenes)

 $n-C_4H_8 \xrightarrow{catalyst} CH_2 = CHCH = CH_2$

 <u>Function</u> - Since 1971, the Phillips process has employed an oxidative dehydrogenation in the production of butadiene from n-butenes. In this process, a compressed air/steam mixture is heated, mixed with n-butene, and passed over the oxidative dehydrogenation catalyst.

The C_4 components are recovered and the butadiene is extracted and purified by the methods described in Process No. 59.

The significant attribute of this process is the savings in fuel: oxidative dehydrogenation is an exothermic rather than an endothermic process, and so requires significantly less energy than other dehydrogenation processes.

2. Input Materials

n-Butenes - (90-95%) Air - 10% of butylene feed Water - (18 vols/vol butadiene) Hydrogen - (acetylenics removal) Furfural or acetonitrile

3. Operating Parameters

Temperature - 620-675°C (1148-1247°F) Pressure - low partial pressures Space velocity - 400 vols/hr per volume catalyst Catalyst - Ca, Ni, PO₄

4. Utilities - Not given

5. <u>Waste Streams</u> - Waste flows from butadiene production facilities were 417 m³/Gg (100 gal/ton) of product.

The principal pollutant sources should be the quench waters containing tars, oils and soluble hydrocarbons and the solvent extract and wash waters (if acetonitrile or furfural is used) containing acetonitrile, furfural and C_4 hydrocarbons. Some air emissions of furfural or acetonitrile may also occur.

pH: 8-9

TOC: 100-200 g/m³ Filtered COD: 250-375 g/m³ Suspended solids: 200-500 g/m³ Total solids: 3-4 kg/m³

- 6. EPA Source Classification Code None
- 7. References

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, pp. 164-167. Waddams, A. L., <u>Chemicals from Petroleum</u>, 3rd Edition, John Murray Ltd., London, 1973, pp. 156-157.

Butadiene (Houdry process)

 $CH_3CH_2CH_2CH_3 \xrightarrow{catalyst} n-C_4H_8 + CH_2=CH-CH=CH_2$

1. <u>Function</u> - In the Houdry process, 95+% n-butane is dehydrogenated in one step to a mixture of butenes and butadiene. Fresh feed and recycle C₄ hydrocarbons are preheated to 593°C and passed over an activated alumina catalyst bed impregnated with 18-20% chromic oxide. The reactors are brick-lined horizontal drums operating at pressures of 13.8-20.7 kPa (0.14-0.2 atm) and a space velocity of about 2 (liquid volume of feed per hour per volume of catalyst space).

Butadiene is separated from the reactor effluent by the methods described in Process No. 59, and unreacted butane and butenes are recycled. Depending on economic considerations, Houdry units can be run to maximize production of butadiene or butenes. Maximum production of butadiene corresponds to a yield of 57-63%.

2. Input Materials

n-Butane (95+%) - 1.7-1.9 kg/kg butadiene Hydrogen (acetylenics removal) Furfural or acetonitrile

3. Operating Parameters

Temperature - 593°C (1099°F) Pressure - 13.8 - 20.7 kPa (0.14-.20 atm) Catalyst - alumina with 18-20% chromic oxide Space Velocity - 2 (see above)

4. Utilities - Not given

5. <u>Waste Streams</u> - A typical waste water flow from a butadiene production facility was 417 m³/Gg (100 gal/ton) of product.

The principal sources of pollutants should be the quench waters containing tars, oils, and soluble hydrocarbons and the solvent extract and wash waters (if acetonitrile or furfural are used as extractants) containing acetonitrile or furfural and C_4 hydrocarbons. Some air emissions of furfural or acetonitrile may also occur. TOC: 100-200 g/m³ Filtered COD: 250-375 g/m³

Suspended solids: $200-500 \text{ g/m}^3$

Total solids: 3-4 kg/m³

- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 800.

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N.Y., 1975, p. 167-168. Amy1 Chlorides (from pentane/isopentane)

 $C_5H_{12} + C1_2 \longrightarrow C_5H_{11}C1 + HC1$

 Function - Mixtures of isomeric amyl chloride are produced by the continuous vapor-phase chlorination of a n-pentane-isopentane refinery cut. In this process, the pentane feed is dried with hydrogen chloride to prevent corrosion of the steel equipment, combined in excess with chlorine gas, and passed through a heated pipe still. Conversion takes place in the absence of light and catalysts.

The mixed vapors from the reactor are cooled rapidly and passed through a series of four continuous fractionation columns. Hydrogen chloride and most of the pentane are stripped in the first two columns. Amyl chloride is taken overhead and polychloropentanes from the bottom of the third column. Any residual pentane is removed from the amyl chloride in the fourth column. With additional equipment, dichloropentane may be isolated from the polychloropentane mixture as a saleable by-product.

2. Input Materials

Pentane/isopentane

Chlorine

- 3. Operating Parameters Not given
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Process leaks may result in the discharge of hydrogen chloride, chlorine, pentanes, and various C₅ chlorohydrocarbons to the atmosphere. No specific information was available.

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6. EPA Source Classification Code - None

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7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Ed., Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 375. Amyl Amines (from amyl chloride)

$$C_5H_{11}C1 + 2NH_3 \longrightarrow C_5H_{11}NH_2 + NH_4C1$$

$$c_{5}H_{11}NH_{2} + c_{5}H_{11}C1 + NH_{3} \longrightarrow (c_{5}H_{11})_{2}NH + NH_{4}C1$$

 $(c_5H_{11})_2NH + c_5H_{11}C1 + NH_3 \longrightarrow (c_5H_{11})_3N + NH_4C1$

 Function - One commercial route to amyl amines involves the reaction of ammonia and amyl chloride.

As in all reactions between ammonia and alkyl halides, quantities of di- and tri- substituted amines are also formed.

2. Input Materials

Amyl chloride

Ammonia

- 3. <u>Operating Parameters</u> Not given
- 4. Utilties

Not given

- 5. <u>Waste Streams</u> Effluents from the ammonia stripper may contain amyl chloride, ammonia, and various amyl amines. Ammonium chloride and heavier organics are probably present in some waste stream from the purification section, but no specific information was available.
- 6. EPA Source Classification Code None

7. <u>References</u>

Astle, M. J., <u>The Chemistry of Petrochemicals</u>, Reinhold Publishing Co., New York, N. Y., 1956, p. 245.

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Amy1 Alcohols (from amy1 chlorides)

$$C_5H_{11}C1 + NaOH \frac{Oleic}{acid} C_5H_{11}OH + NaCl$$

1. <u>Function</u> - Isomeric amyl alcohols are produced by the high-temperature hydrolysis of mixed amyl chlorides. This continuous hydrolysis is carried out with aqueous sodium hydroxide in the presence of sodium oleate catalyst. In most process variations, the reaction slurry is passed through two digesters. Amyl alcohols, pentylenes, chlorides, and minor amounts of amyl ether distill overhead from the second digester and brine is drawn from the bottom. The remaining slurry is recycled to the first digester so that the initial charge of oleic acid, which is converted to sodium oleate, does not need constant replenishment.

Pentylenes and unreacted amyl chlorides are stripped from the alcohol by steam distillation, and the chlorides are recycled. The alcohol is fractionated into commercial compositions and sold along with the pentylene and amyl ether by-products.

2. Input Materials

Amyl chlorides, mixed Sodium hydroxide Water Oleic acid

3. Operating Parameters

Temperature: not given Pressure: not given

Catalyst: oleic acid

4. Utilities

Not given

5. <u>Waste Streams</u> - The principal pollutant source in this process is probably the waste water from the brine decanter, containing sodium chloride, sodium hydroxide, and traces of amyl alcohols, amyl chlorides, pentylenes, and amyl ether. All of these organics may also be present in the waste water from the amyl alcohol recovery column.

6. EPA Source Classification Code - None

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963) p. 375. Amyl Mercaptans (from amyl chloride)

$$C_{5}H_{11}C1 + NaSH \xrightarrow{alcohol} C_{5}H_{11}SH + NaCl$$

- <u>Function</u> A mixture of isomeric amyl mercaptans is produced by the interaction of amyl chloride and sodium or potassium hydrosulfide in alcohol.
- 2. Input Materials

Amyl chloride

Sodium or potassium hydrosulfide

Solvent alcohol

- 3. <u>Operating Parameters</u> Not given
- 4. Utilities

Not given

- 5. <u>Waste Streams</u> Indeterminate quantities of sodium or potassium chloride, amyl chloride, amyl mercaptans, sodium or potassium hydrosulfide, the solvent alcohol, and reaction by-products such as diamyl sulfide may be present in process wastes.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 20 (1969), p. 212-13.

<u>Ibid</u>., Vol. 2 (1963), p. 375.

Isoamylenes (from C, hydrocarbons)

 Function - Isoamylenes (2-methyl-1-butene and 2-methyl-2-butene) are extracted from a catalytically cracked C₅ gasoline stream with 65% aqueous sulfuric acid. This extraction is carried out in multiple absorption stages at temperatures of 0-10°C.

The isoamyl alcohols formed dissolve in the aqueous phase and are washed with caustic and water to remove residual acid. This aqueous phase is separated and contacted with hexane or a similar solvent at 50° C to reconvert the isoamyl alcohols to isoamylenes. After caustic and water washings, hexane is stripped from the solution to recover the isoamylene concentrate. Recovery from the C₅ hydrocarbon feed is about 22.5%.^{*} However, this figure may be as low as 7.5%, depending on the amylene concentration of the feed.

2. Input Materials **

C₅ hydrocarbons - 3.72 kg/kg isoprene Sulfuric acid - 8.50 kg/Mg isoprene Sodium hydroxide - 10.0 kg/Mg isoprene Hexane - 31.5 kg/Mg isoprene

[&]quot;The C₅ hydrocarbons feedstocks usually contain about 30% isoamylene by weight, but concentrations may be as low as 10%. About 75% of the isoamylene in the feed is recovered.

^{**} The data given is based on isoprene production for which the isoamylene serves as an intermediate.

3. Operating Parameters

Temperature - extraction - 0-10°C (32-50°F) Hexane treatment - 50°C (122°F)

Pressure - not given

- 4. Utilities see Process Nos. 235 and 236.
- 5. Waste Streams **

Amylene recovery section - separation vessel (water)

Sodium hydroxide - 3.05 kg/Mg isoprene

Sodium sulfate - 14.0 kg/Mg isoprene

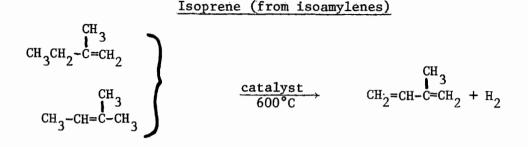
Amylene recovery section - amylene recovery column (water)

n-Hexane - 19.0 kg/Mg isoprene

- 6. EPA Source Classification Code None
- 7. <u>References</u>

"1973 Petrochemical Handbook," "Hydrocarbon Processing," November, 1973, p. 101.

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1. <u>Function</u> - One of the most popular routes to isoprene involves the dehydrogenation of isoamylenes extracted from C_5 gasoline (see Process No. 246). In this process, the amylene feed and a C_5 recycle stream from a downstream purification unit are mixed with steam passed to a catalytic reactor operating at 600°C and atmospheric pressure. A mixture of iron oxide, K_2CO_3 , and Cr_2O_3 catalyzes the conversion to isoprene with by-production of hydrogen, carbon dioxide, and a variety of $C_2 - C_5$ hydrocarbons.

The C_4 and C_5 hydrocarbons are recovered from the reactor effluent in an absorber-stripper section. The dry gas from the absorber usually serves as fuel gas, typically containing: hydrogen, methane, ethylene, ethane, propylene, propane, butylene, butane, butadiene, isoprene, t-amylenes, piperylenes, other C_5 's and absorber oil. Approximately 322 kg of fuel gas are produced per Mg of isoprene.

Upon leaving the stripper, the overhead product is processed for light ends removal. The light ends (mainly C_4 's) are fed to a debutanizer which recovers the C_4 fraction overhead for use as fuel gas and a bottom product for recycle to the reactor. The bottom product of the light ends column is the crude isoprene, which is fed to a Shell Acetonitrile process unit for purification.

2. Input Materials

Isoamylenes - see Process No. 246.

3. Operating Parameters

Temperature - 600°C (1112°F)

Pressure - 100 kPa (1 atm)

Catalyst - iron oxide, K₂CO₃, Cr₂O₃ mixture

4. Utilities * - basis: 1.15 kg/sec capacity (80 \overline{M} 1b/yr)

Cooling water - 1.05 m³/sec (1.0 M̄ gph) Process water - 16.0 dm³/sec (15,200 gph) Steam - 6.36 kg/sec (50,500 lb/hr) Electrical power - 9.72 EJ (2.7 MW) Fuel - 2.16 m³/sec (275,000 cfh)

5. Waste Streams

Dehydrogenation section - partial condensers (water)

Isoprene - 0.5 kg/Mg product

Amylenes - 1.5 kg/Mg product

Isoprene recovery section - extractive distillation column (air)

Acetonitrile - 5.0 kg/Mg product

- 6. EPA Source Classification Code None
- 7. <u>References</u>

"1973 Petrochemical Handbook Issue," <u>Hydrocarbon Processing</u>, Nov. 1973, p. 140. Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical Processes</u>, Technomic Publishing Co., 1975.

^{*} Includes utilities for isoamylene extraction--Process No. 247.

Isoprene (direct dehydrogenation of isopentane)

$$\begin{array}{c} \overset{\text{CH}_3}{\underset{2}{\text{CH}_2\text{CH}-\text{CH}_3}} \xrightarrow{\text{catalyst}} & \text{CH}_2 = \text{CHC} = \text{CH}_2 \\ & \overset{\text{CH}_3}{\underset{2}{\text{CH}_3}} \end{array}$$

1. <u>Function</u> - A promising, new route to isoprene involves a singlestep, fixed-bed dehydrogenation of isopentane or a C₅ fraction obtained by catalytic cracking. In this process, fresh C₅ feedstock is combined with recycle from the isoprene recovery section and heated to 540-620°C. The dehydrogenation takes place over a chromia-alumina catalyst in a cyclic series of three reactors operating at 74-81 kPa (0.7-0.8 atm) partial vacuum.

The product stream is quenched by direct contact with a quench oil stream and compressed before passing into the recovery section. In the recovery section, a conventional absorber, stripper, and debutanizer system recovers the C_5 compounds which are then charged to the isoprene purification section. The purification section (Shell acetonitrile process) gives isoprene product (99% + pure), 1,3-pentadiene, and recycled isopentane-pentylenes.

This process had been used for the manfacture of isoprene only on a pilot plant scale. Yields of 51.5% based on isopentane and 58.6% based on a C_5 gasoline fraction have been reported.

2. Input Materials

C₅ hydrocarbons

Isopentane - 2.06 kg/kg isoprene

 C_5 gasoline fraction ~1.76 kg/kg isoprene

3. Operating Parameters

Temperature: 540-620°C (1004-1148°F) Pressure: 74-81 kPa (0.72-0.81 atm) Catalyst: chromia-alumina Space velocity: 1.5-3.5 hr⁻¹

4. Utilities

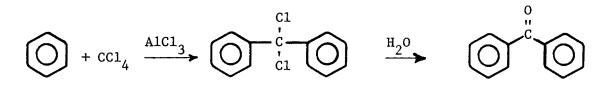
Not given

- 5. <u>Waste Streams</u> Generally, the same types of pollution would be expected as in Process No. 247.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

1

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 12 (1967), p. 75.

Benzophenone



1. <u>Function</u> - Benzophenone is manufactured principally by the Friedel-Crafts reaction of benzene and carbon tetrachloride. Carbon tetrachloride and anhydrous aluminum chloride are charged to a jacketed agitated, iron vessel and thiophene-free benzene is fed in over a period of three to five hours with cooling. The hydrogen chloride evolved is removed by an absorption tower that is coupled with a settling tank where carbon tetrachloride is recovered.

The temperature of the mixture is allowed to rise to $35^{\circ}C$ (95°F) for 0.5 hour after the benzene has been added. The viscous mass is transferred to a still containing water, heated to boil with a steam injector, and held at that temperature by the heat of reaction. The vapors are fed to the absorption system mentioned above.

The crude benzophenone is vacuum distilled and crystallized from a solvent.

2. <u>Input Materials</u> - Basis: 113.4 kg (250 lb) batch Benzene - 115.7 kg (255 lb) Carbon tetrachloride - 476 kg (1,050 lb) Aluminum chloride - 104.3 kg (230 lb) Water (hydrolysis) - 378.5 dm³ (100 gal)

3. Operating Parameters

Temperature: reaction - 20°C (68°F) final reaction - 35°C (95°F)

Equipment: jacketed, iron reactor

- 4. Utilities Not given
- 5. Waste Streams

Water: Waste streams may contain some acid, small amounts of carbon tetrachloride, some aromatic residues, aluminum chloride hydrolysis products.

Solids: Aluminum hydroxide by hydrolysis of aluminum chloridearomatic complexes, tars from still bottoms, and still bottoms from recovery of recrystallizing solvent.

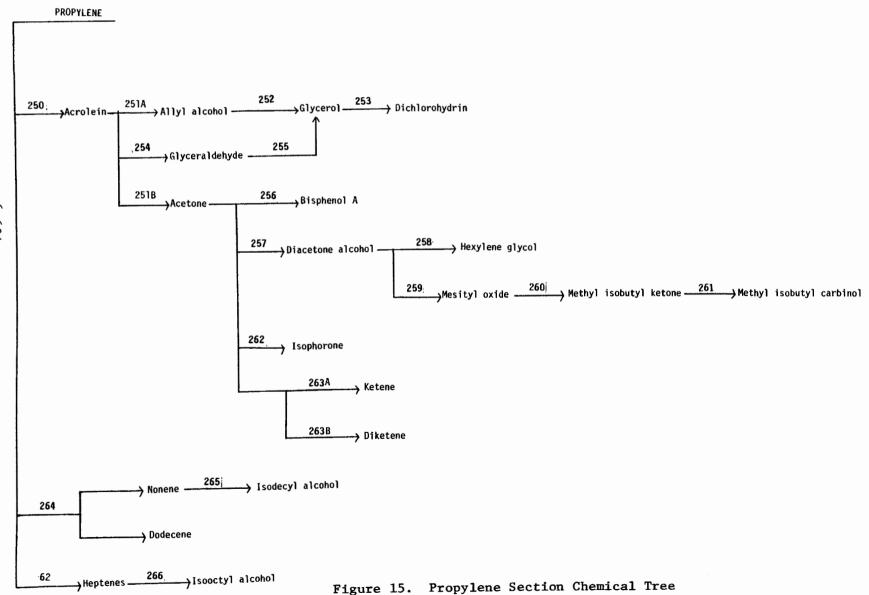
Air: Possible hydrogen chloride vapors.

- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 3 (1964), p. 439-444.

SECTION VIII PROPYLENE

PROPYLENE



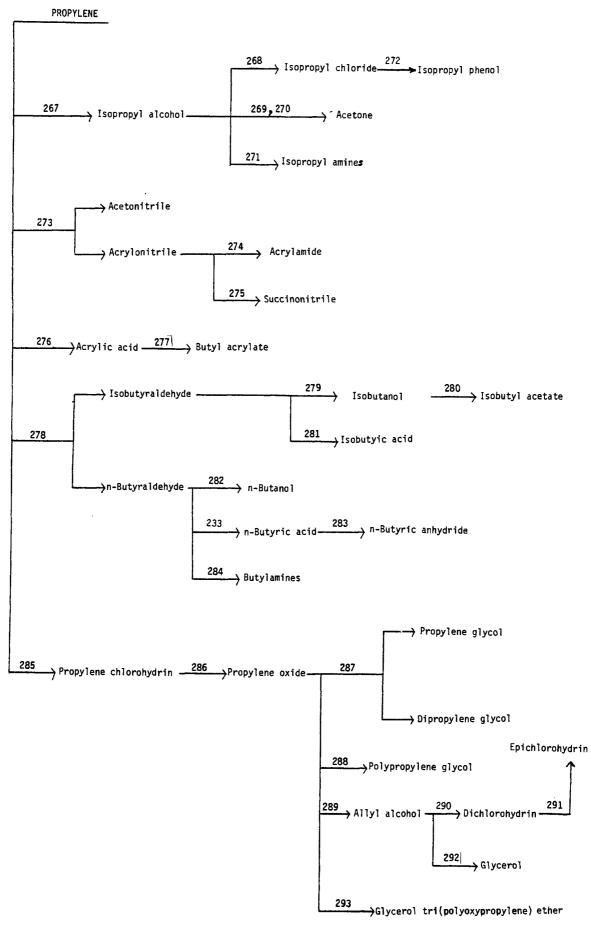
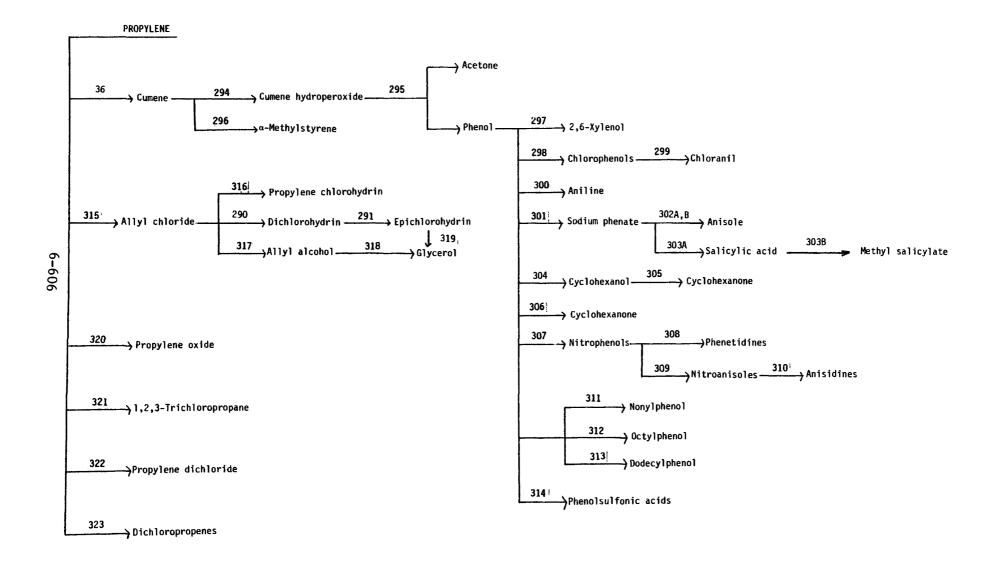


Figure 15. Propylene Section Chemical Tree (Cont.)



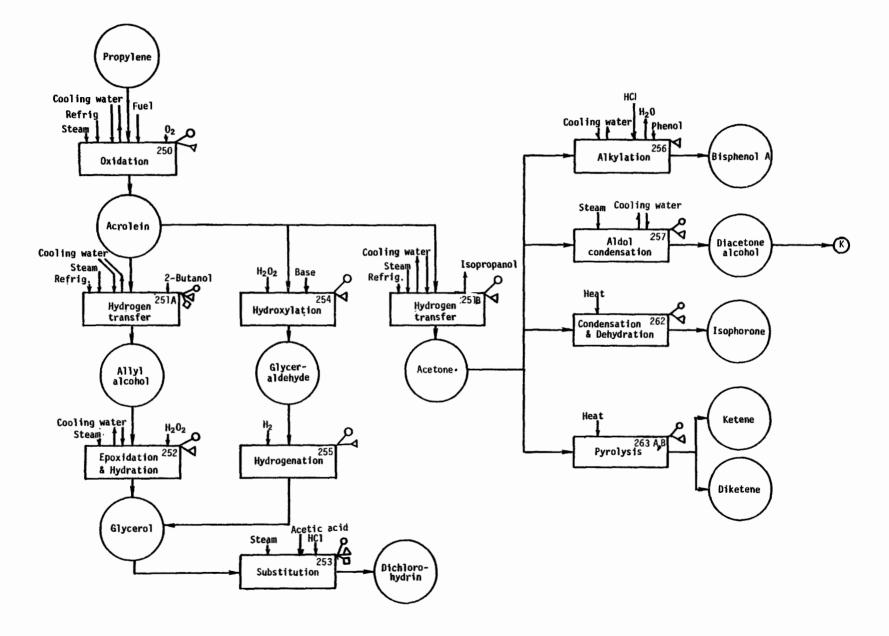


Figure 16. Propylene Section Process Flow Sheet

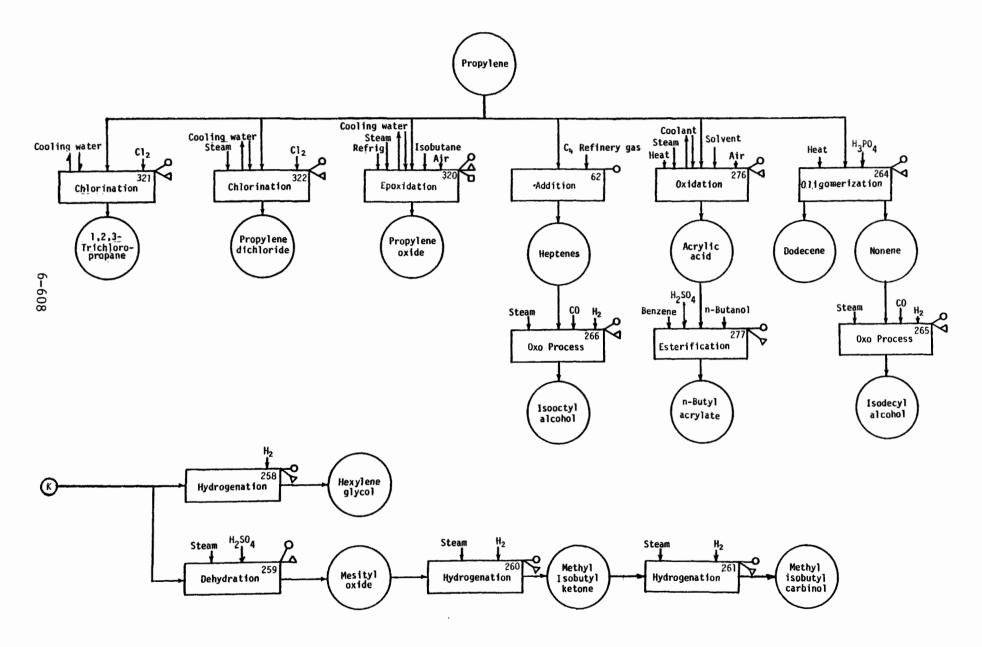


Figure 16. Propylene Section Process Flow Sheet (Cont.)

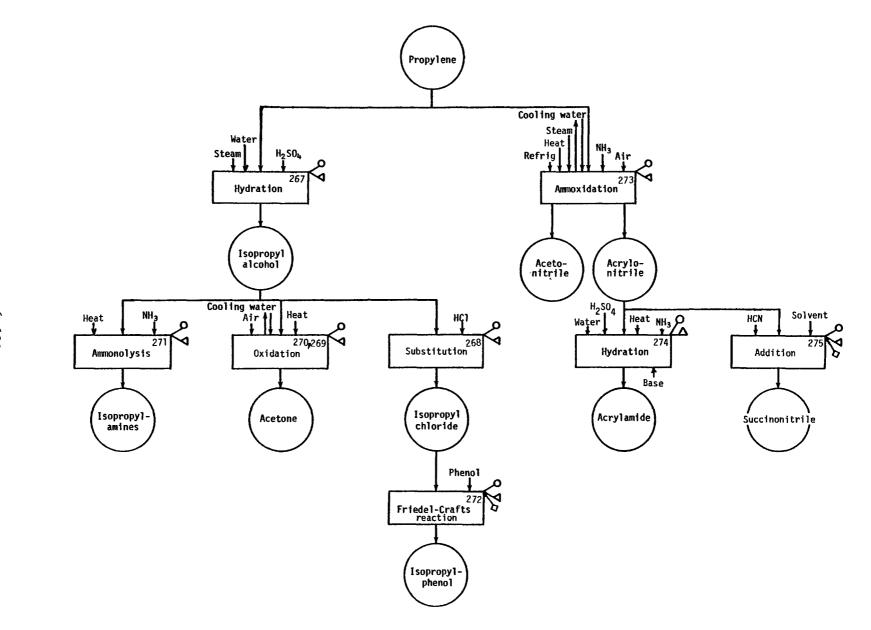


Figure 16. Propylene Section Process Flow Sheet (Cont.)

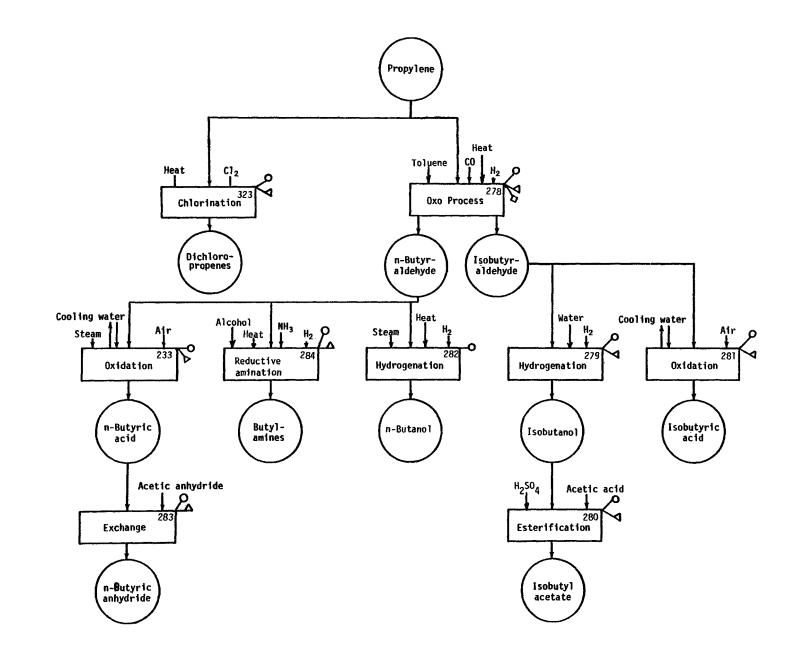


Figure 16. Propylene Section Process Flow Sheet (Cont.)

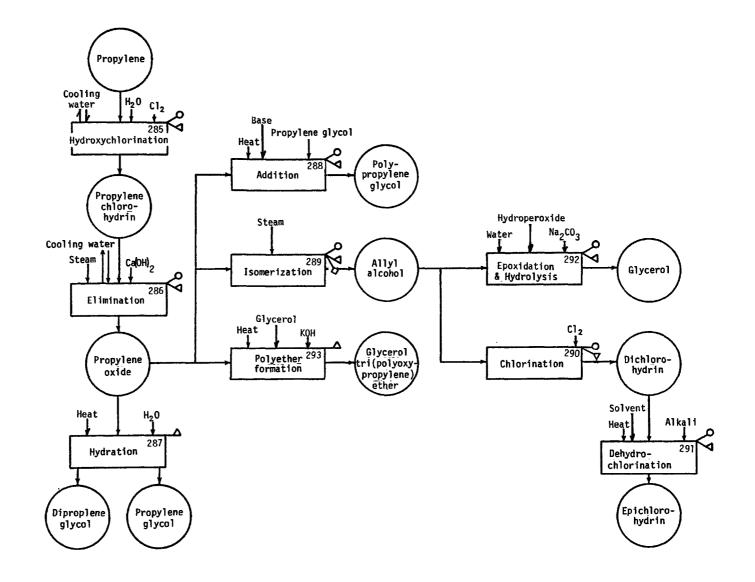
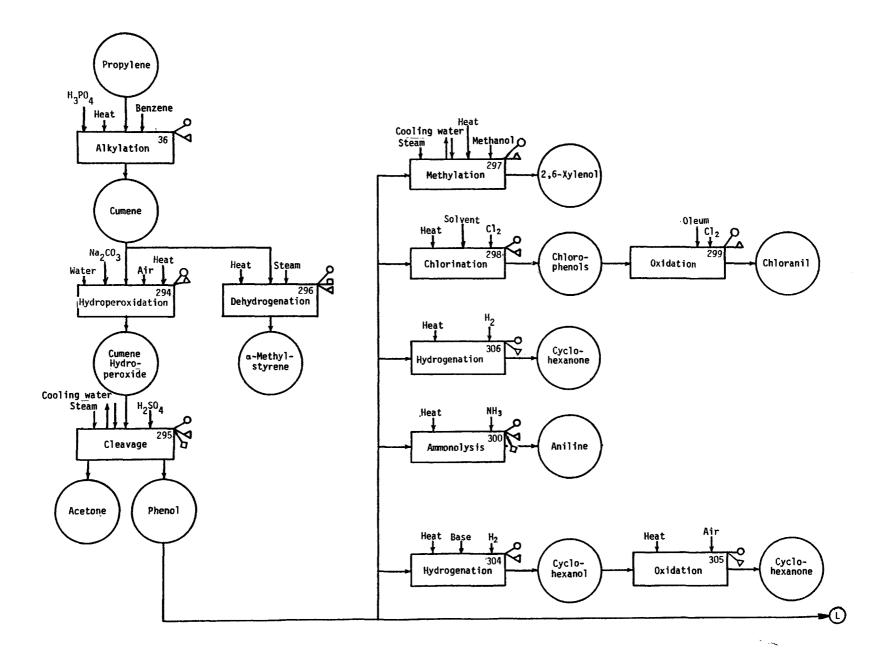
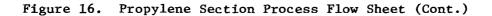


Figure 16. Propylene Section Process Flow Sheet (Cont.)





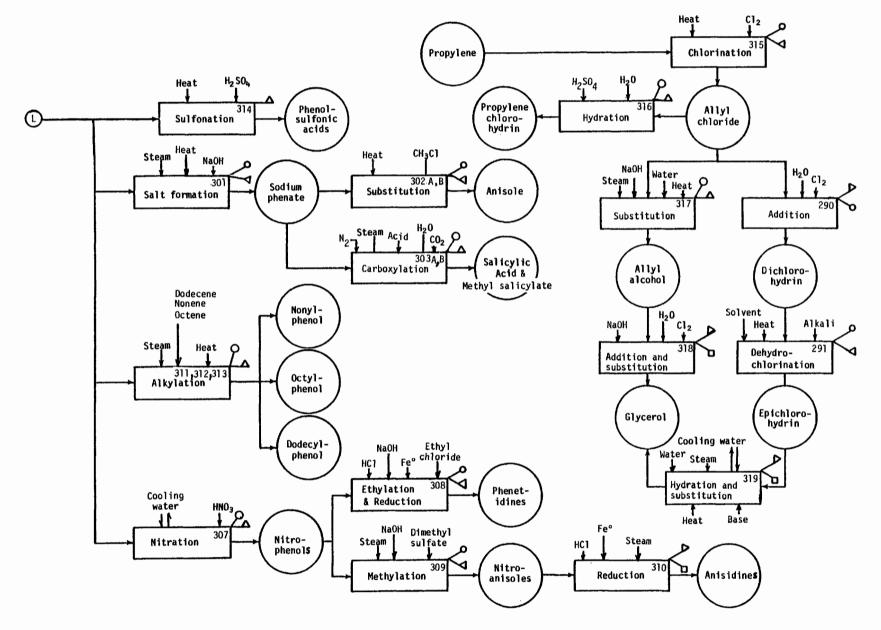


Figure 16. Propylene Section Process Flow Sheet (Cont.)

Acrolein

$$CH_2 = CH - CH_3 + 0_2 \longrightarrow CH_2 = CH - CH + H_2 0$$

- Function Acrolein is produced by a limited vapor-phase oxidation of propylene in the presence of a catalyst. Oxygenated by-products complicate the product recovery and purification.
- 2. Input Materials

Propylene (98%) - 1.161 Mg/Mg (2,322 1b/ton) product

3. Operating Parameters

Temperature - 290-380°C (550-720°F) Pressure - 410-580 kPa (4.05-5.72 atm) Flow rates - not given Size of equipment - not given - fixed bed reactor Types of catalysts - copper-oxide and bismuth-molybdenum

- 4. <u>Utilities</u> Basis 9.1 Gg/yr (20 M lb/yr) capacity Cooling water - 378 dm³/s (6,000 gpm) Steam - 4.1 Mg/hr (9,100 lb/hr) Power - 12.3 GJ (3,430 kWh) Fuel - 350 kW (1.2 M Btu/hr)
- 5. Waste Streams

Propylene recovery section - propylene absorber off-gas Propylene - 71 kg/Mg (142 lb/ton) product Propane - 3.5 kg/Mg (7 lb/ton) product Carbon monoxide - 73.5 kg/Mg (147 lb/ton) product

6. EPA Source Classification Code - None

7. References

Muller, R. G., "Glycerine and Intermediates," Report No. 53, Stanford Research Institute, Menlo Park, California, 1969.

U. S. Patent 2,451,485 and 2,846,842.

Hancock, E. G., <u>Propylene and Its Industrial Derivatives</u>, John Wiley and Sons, New York, N.Y., 1973, p. 23.

Chemical Technology, Barnes and Noble Books, New York, N.Y.,

Vol. 4 (1972), p. 364-427.

Ally1 Alcohol; Acetone (from acrolein)

$$CH_2 = CH - CH + R - CH_2OH \longrightarrow CH_2 = CH_2 - CH_2OH + R - CH$$

$$CH_2 = CH - CH + R_1 - CH - R_2 \longrightarrow CH_2 = CH_2 - CH_2OH + R_1 - C - R_2$$

 Function - Acrolein undergoes hydrogen transfer with either a primary or secondary alcohol in the presence of a metal alkoxide catalyst to form allyl alcohol and the aldehyde or ketone that corresponds to the donor alcohol.

It is not possible for all manufacturers to use the optimum alcohol donor. Alcohols used and the corresponding by-products are: ethyl alcohol (acetaldehyde), n-propyl alcohol (propionaldehyde), isopropyl alcohol (acetone), and secondary (2-) butanol (methyl ethyl ketone). 2-Butanol is a typical example of an alcohol which gives high allyl alcohol selectivity while producing a valuable by-product.

2. Input Materials

Acrolein - 1.044 Mg/Mg (2,088 lb/ton) product 2-butanol - 1.310 Mg/Mg (2,621 lb/ton) product

3. Operating Parameters

Temperature - 20-80°C (68-176°F) Pressure - 100 kPa (1 atm) Flow rates - m.g. Types of catalyst - aluminum alkoxides

- 4. <u>Utilities</u> Basis: 8.7 Gg/yr (19.2 M lb/yr) capacity Cooling water - 156 dm³/s (2,473 gpm) Steam - 14.06 Mg/hr (31,000 lb/hr) Power - 922 MJ (256 kWh) Refrigeration - 29°C (-20°F) - 700 kW (2.4 M Btu/hr) Nitrogen - 140 dm³/hr (5 scfh)
- 5. Waste Streams -

Product recovery and purification - light ends column (water)

Acrolein - 1.25 kg/Mg (25 1b/ton) product

Methyl ethyl ketone - 12.5 kg/Mg (25 1b/ton) product - some 2-butanol

Product recovery and purification - heavy ends column (water)

Butanol - 7.5 kg/Mg (15 1b/ton) product

Allyl alcohol - 5 kg/Mg (10 1b/ton) product

Polymer - 53.5 kg/Mg (107 1b/ton) product

Aluminum hydroxide - 82 kg/Mg (164 1b/ton) product

Trace quantities of acrolein, hydroquinone, and methyl ethyl ketone, and 2-butanol

- 6. EPA Source Classification Code None
- 7. References

Muller, K. G., "Glycerine and Intermediates," Report No. 58, Stanford Research Institute, Menlo Park, California, 1969.

Waddams, A. L., <u>Chemicals from Petroleum</u>, 3rd Edition, John Murray, London, 1973, p. 131.

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4, (1972), pp. 287,388.

Glycerin (from allyl alcohol)

$$CH_2 = CHCH_2OH + H_2O_2 \longrightarrow CH_2 - CHCH_2OH$$

$$\overset{\text{CH}_2 \text{-}\text{CH}-\text{CH}_2\text{OH}}{\swarrow} \xrightarrow{\text{CH}-\text{CH}_2\text{OH}} + \overset{\text{H}_2\text{O}}{\longrightarrow} \overset{\text{HOCH}_2\text{CH}-\text{CH}_2\text{OH}}{\underset{\text{OH}}{\overset{\text{I}}{\longrightarrow}}}$$

- 1. <u>Function</u> Allyl alcohol is epoxidized with hydrogen peroxide to form glycidal which is hydrated to glycerin. The overall process may be considered a hydroxylation catalyzed by tungstic acid. The epoxidation reaction occurs in a three-section reactor maintained at 45°C for a period of 1.1 hours per section. The product glycidal is purified, then hydrated in a tubular reactor, with a 10 minute residence time, at 145°C.
- 2. Input Materials

Allyl alcohol - 746.5 kg/Mg (1,493 lb/ton) product Hydrogen peroxide - 447 kg/Mg (894 lb/ton) product Caustic soda - 9 kg/Mg (18 lb/ton) product

3. Operating Parameters

Temperature: 45°C (3-section reactor), 145°C (tubular reactor) Pressure: not given Flow rates: not given Size of Equipment: not given Types of Catalysts: tungstic acid

- 4. <u>Utilities</u> Basis: 11.65 Gg/yr (25.7 M lb/yr) capacity Cooling water - 86.69 dm³/s (1,374 gpm) Steam - 1.1 MPa (10.8 atm) -20.487 Mg/hr (45,167 lb/hr) 380 kPa (3.75 atm)-11.747 Mg/hr (25,898 lb/hr) Power - 510 MJ (141 kWh) Makeup Water - 3.6 dm³/s (57 gpm)
- 5. <u>Waste Streams</u>

Hydroxylation section - allyl alcohol recovery column - to flare (air) Allyl alcohol - 6 kg/Mg (12 lb/ton) product Butanol - 2 kg/Mg (4 lb/ton) product Acrolein - 20 kg/Mg (40 lb/ton) product Miscellaneous light impurities - 22 kg/Mg (44 lb/ton) product Glycerin recovery and purification - light ends column (water) Allyl alcohol - 4 kg/Mg (8 lb/ton) product Glycerin - 3.5 kg/Mg (7 lb/ton) product Miscellaneous light impurities - 23.5 kg/Mg (47 lb/ton) product

- 6. EPA Source Classification Code None
- 7. References

Muller, K. G., "Glycerine and Intermediates," Report No. 58, Stanford Research Institute, Menlo Park, California, 1969. Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, John Wiley and Sons, New York, N.Y., 1975, p. 436. Hancock, E. G., <u>Propylene and Its Industrial Derivatives</u>, John Wiley and Sons, New York, N.Y., 1973, p. 24-25.

PROCESS NO. 253

Dichlorohydrin (from glycerol)

 $HOCH_2CHOHCH_2OH + 2HC1 \longrightarrow C1CH_2CHC1CH_2OH$ or $C1CH_2CHOHCH_2C1 + 2H_2O$

 Function - In the past, dichlorohydrin has been produced by the interaction of crude glycerol and an excess of hydrogen chloride. This reaction is normally carried out at 100-160°C in a 4% solution of acetic acid.

The major by-products of this reaction are water, polyglyceride, and a mixture of acetates. Polyglyceride formation may be inhibited by lower reaction temperatures (~ IOO°C), although this necessitates HCl recycling. Vacuum distillation is normally sufficient to reduce acetate production.

2. Input Materials

Glycerol - 0.79 kg/kg dichlorohydrin

Hydrogen chloride - excess

Water

3. Operating Parameters

Temperature - 100-160°C (212-320°F)

Pressure - Not given

Catalyst - acetic acid - 16 g/kg dichlorohydrin

4. Utilities - Not given

- 5. <u>Waste Streams</u> Various waste streams may be present depending on the purification procedures employed (different reaction temperatures require different purification techniques). However, tars, acetic acid, various acetates, dichlorohydrin, and other halides from the surge-tank wastes are probably the principal pollutants.
- 6. EPA Source Classification Code None

7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 314.

Glyceraldehyde (from acrolein)

 $CH_2 = CHCHO + H_2O_2 \xrightarrow{pH8} CH_2 - CHCHO + H_2O$ $CH_2 - CH - CHO + H_2O \longrightarrow HOCH_2CHOHCHO$

 Function - Synthetic glyceraldehyde is prepared by the hydroxylation of acrolein via glycidaldehyde intermediate. If pH is maintained at 8 during the reaction, acrolein and hydrogen peroxide combine to form glycidaldehyde.

The intermediate is then hydrolyzed to give nearly quantitative yields of glyceraldehyde.

In some cases, acrolein may be converted directly to glyceraldehyde by treatment with hydrogen peroxide in the presence of $0_{s}0_4$ catalyst.

2. Input Materials

Acrolein - 0.65 kg/kg glyceraldehyde

Hydrogen peroxide

Water

3. Operating Parameters

Temperature - Not given Pressure - Not given

pH - 8

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Wastewater from the separator may contain small quantities of acrolein, hydrogen peroxide, glycidaldehyde, and glyceraldehyde.

6. <u>EPA Source Classification Code</u> - None

7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 261. Glycerol (hydrogenation of glyceraldehyde)

 $\text{HOCH}_2\text{CHOHCHO} + \text{H}_2 \xrightarrow{\text{Ni}^{\circ}} \text{HOCH}_2\text{CHOHCH}_2\text{OH}$

- <u>Function</u> One route to glycerol starts with propylene involving intermediates of acrolein, glycidaldehyde, and glyceraldehyde. The final intermediate, glyceraldehyde, is converted to glycerol by hydrogenation in the presence of nickel catalyst.
- 2. Input Materials

Glyceraldehyde

Hydrogen

3. Operating Parameters

Temperature - 200°C (392°F)

Pressure - Not given

Catalyst - Nickel

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Air vent streams would contain hydrogen gas. Purification by vacuum distillation separates glyceraldehyde and glycerol. Vents from purification system contain glycerol, waste water streams would contain glycerol and some glyceraldehyde. Because of the low vapor pressures of the reactants and products the process should be essentially free of air pollution.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 261-262. Bisphenol-A (from phenol & acetone)

$$2c_6H_5OH + CH_3COCH_3 \xrightarrow{CH_3} c(c_6H_4OH)_2 + H_2O$$

 Function - 2,2-Bis(4-hydroxyphenyl)propane, also known as bisphenol-A, is produced by reacting phenol with acetone in the presence of acid catalyst.

A number of by-products are formed in conjunction with the main reaction. The earlier processes eliminated these impurities by batchwise crystallization, while the new process, the Hooker process, employs a continuous distillation and extractive crystallization under pressure to purify the product.

Phenol and acetone at a molar ratio of approximately 3 to 1 are mixed, saturated with hydrogen chloride gas, and sent to the reaction vessel. Reaction conditions are about 40°C, close to atmospheric pressure, with a mercaptan used as a catalyst. The crude product is stripped of HCl and water of reaction. The overhead is decanted into an organic phase (consisting mainly of phenol which is recycled) and an aqueous phase. The latter goes on to an HCl recovery unit, and water is sent to disposal.

Bottoms from the stripper are sent to a series of purification distillation chambers, where excess phenol, isomers, and heavy ends are removed from the system for either recycle or disposal. Distillate from the last chamber is sent to the extraction operation, which produces a slurry of pure crystals. The filtrate from the centrifuge

is partially recycled to the crystallizer, and the remainder is concentrated in an evaporator to produce liquid bisphenol-A.

2. Input Materials

Phenol - 862.5 kg/Mg (1725 lb/ton) product (excluding recycled excess) Acetone - 265.9 kg/Mg (531.7 lb/ton) product

3. Operating Parameters

Temperature: 40°C (104°F) Pressure: Near atmospheric Flow Rates: Not given Catalysts: HCl, and mercaptan

4. Utilities

Water (process) - 250 kg/Mg (500 1b/ton) product (gross cooling) - 197 Mg/Mg (394,000 1b/ton) product

- 5. <u>Waste Streams</u> Aqueous waste streams are produced by the hydrogen chloride recovery unit, the crystallizer, and the final evaporator. Total water flow 458.8 dm³/Mg (133.6 gal/ton) product COD 17.1 kg/Mg (34.2 lb/ton) product TOC 5.2 kg/Mg (10.3 lb/ton) product Phenol 7.1 kg/Mg (14.2 lb/ton) pressure
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Anon., "Development Document for Effluent Limitations Guidelines and Standards of Performance: Organic Chemical Industry," Contract No. 68-01-1509, prepared for Environmental Protection Agency, June 1973.

Sittig, M., "Pollution Control in the Organic Chemical Industry," Pollution Technology Review No. 9, Noyes Data Corporation, 1974, p. 85-87.

Diacetone Alcohol (condensation of acetone)

 $2(CH_3)_2^{CO} \longrightarrow (CH_3)_2^{COHCH_2^{COCH_3}}$

 Function - Diacetone alcohol is prepared by the aldol condensation of acetone flowing over a solid alkali or alkaline earth catalyst in a fixed-bed catalytic reactor. The reaction is normally carried out near room temperature or below.

To secure good yields it is necessary to remove the diacetone alcohol as fast as it is formed.

Once the product solution is out of contact with the catalyst, the dimer has little tendency to revert to acetone and accumulates. Acetone, being more volatile, is continually removed by distillation and recycled. Acetone-free diacetone alcohol is obtained by fractional distillation under vacuum.

2. Input Materials

Acetone

3. Operating Parameters

Temperature - 10-23°C (50-73°F) Pressure - Not given

Catalyst - Ba(OH)₂ or similar compounds

- 4. Utilities Not given
- <u>Waste Streams</u> Some acetone and diacetone alcohol may be present in air emissions from various processing equipment.

- 6. EPA Source Classification Code None
- 7. References

Austin, G. T., "The Industrially Significant Chemicals - Part 7," "Chemical Engineering, June 24, 1974, p. 153.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Technomic Publishing Co., 1975, p. 309.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 165-166. Ibid., Vol. 12 (1967).

Hexylene Glycol

 $(CH_3)_2 COHCH_2 COCH_3 + H_2 \xrightarrow{CAT.} (CH_3)_2 COHCH_2 CHOHCH_3$

 Function - Hexylene glycol is commercially prepared by the hydrogenation of diacetone alcohol.

In normal plant procedure, acetone is the raw material, undergoing preliminary condensation to diacetone alcohol.

2. Input Materials

Diacetone alcohol (from acetone - 1.2 kg/kg hexylene glycol) Hydrogen

- 3. Operating Parameters Not given
- 4. <u>Utilities</u>

Not given

- 5. <u>Waste Streams</u> Air vent streams from the reactor contain hydrogen and acetone. Off-gas streams from the purification process contain acetone and some diacetone alcohol.
- 6. <u>EPA Source Classification Code</u> None
- 7. <u>References</u>

Hancock, E. G., Propylene and Its Industrial Derivatives, John Wiley and Sons, Inc., New York, 1973, p. 258. Mesityl Oxide (dehydration of diacetone alcohol)

 $(CH_3)_2 COHCH_2 COCH_3 \xrightarrow{\Delta} (CH_3)_2 C=CHCOCH_3 + H_2 O$

- Function Mesityl oxide is commercially produced by dehydrating diacetone alcohol at 100°C in the presence of sulfuric acid.
- 2. Input Materials Diacetone alcohol and H₂SO₄
- 3. Operating Parameters

Temperature - 100°C (212°F)

Pressure - Not given

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Wastewater from the dehydration column may contain some acetone and diacetone alcohol.
- 6. EPA Source Classification Code None
- 7. References

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical Processes</u>, Technomic Publishing Co., 1975.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 12 (1967) p. 136.

Waddams, A. L., <u>Chemicals From Petroleum</u>, 3rd Edition, John Murray Publishers, Ltd., London, Eng., 1973, p. 126. Methyl Isobutyl Ketone (hydrogenation of mesityl oxide)

 $(CH_3)_2 C = CHCOCH_3 + H_2 \longrightarrow (CH_3)_2 CHCH_2 COCH_3$

<u>Function</u> - Methyl isobutyl ketone is made commercially by the selective catalytic hydrogenation of the olefinic linkage in mesityl oxide. The reaction may be run in the vapor phase at 150-170°C and 100 kPa (1 atm) or in the liquid phase at 60-130°C and 1-25 atm. Copper or Raney nickel catalysts are used.

In normal plant procedure, acetone is the raw material undergoing conversion to diacetone alcohol, mesityl oxide, and finally methyl isobutyl ketone (see Process Nos. 257 and 259). Methyl isobutyl carbinol is a by-product of this reaction.

2. Input Materials

Mesityl oxide

Hydrogen

3. Operating Parameters

Vapor Phase - Temperature: 150-170°C (302-338°F) Pressure: 100 kPa (1 atm)

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Air emissions from the purification section may contain mesityl oxide, methyl isobutyl ketone, methyl isobutyl carbinol, and other by-products.
- 6. EPA Source Classification Code None

7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 7," "Chemical Engineering," June 24, 1974, p. 153.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical Processes</u>, Technomic Publishing Co., 1975, p. 309.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 12 (1967), p. 134.

PROCESS NO. 261

Methyl Isobutyl Carbinol (from methyl isobutyl ketone)

 $(CH_3)_2CHCH_2COCH_3 + H_2 \xrightarrow{catalyst} (CH_3)_2CHCH_2CHOHCH_3$

 Function - Methyl isobutyl carbinol is produced on a commercial scale by the hydrogenation of methyl isobutyl ketone.

It is also isolated and collected as a by-product of methyl isobutyl ketone synthesis (see Process No. 260).

2. Input Materials

Methyl isobutyl ketone

Hydrogen

3. Operating Parameters

Temperature: 150-190°C (302-374°F)

Pressure: 345-689 kPa (3.4-6.8 atm)

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Some air emissions may be present. The probable pollutants are methyl isobutyl ketones, methyl isobutyl carbinol, and reaction by-products.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Astle, M. J., <u>The Chemistry of Petrochemicals</u>, Reinhold Publishing Co., New York, N.Y., 1956, p. 202, 228.

Hahn, A. V., <u>The Petrochemical Industry</u>, McGraw-Hill Book Co., New York, 1970, p. 367.

7. <u>References</u> (continued)

Hancock, E. G., <u>Propylene</u>, John Wiley and Sons, New York, 1973, p. 258-259.

Isophorone (vapor-phase condensation of acetone)



1. Function

Isophorone is prepared by the vapor phase condensation of three molecules of acetone in the presence of an alkaline catalyst. A liquid phase condensation may also be employed. In the vapor phase process, acetone is passed over calcium oxide, hydroxide,or carbide at 350°C and atmospheric pressure to give isophorone, water and by products such as: diacetone alcohol and mesityl oxide. The isophorone is purified by vacuum distillation.

2. Input Materials - Acetone

3. Operating Parameters

Vapor phase Temperature: 350°C (662°F) Pressure: 100 kPa (1 atm) Catalyst: CaO, Ca(OH)₂ or CaC₂

Liquid phase

Temperature: 140-170°C (284-338°F)

Pressure: not given

4. Utilities - not given

- 5. <u>Waste Streams</u> Air emissions from purification operations may contain unconverted acetone, mesityl oxide, diacetone alcohol, other reaction by-products and isophorone.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963) p. 166.

Sherwood, P. W., "Petroleum Refiner," 33 (12), 144 (1954).

Ketene (pyrolysis of acetone)

$$(CH_3)_2 CO \xrightarrow{600°C} CH_2 CO + CH_4$$

- 1. <u>Function</u> On a commercial scale, ketene is prepared by the straight pyrolysis of acetone. In the noncatalytic process, acetone is heated to 600°C where it cracks to ketene and methane. Ketene is a highly reactive material, unstable in storage. It is manufactured only for captive use in further synthetic operations. Ketene dimerizes spontaneously and is a commercial by-product of ketene synthesis.
- 2. Input Material Acetone
- 3. Operating Parameters

Temperature - 650-670°C (1202-1238°F)

Pressure - not given

Contact time - 0.25-5 sec.

- 4. Utilities Not given
- 5. <u>Waste Streams</u> The off-gas from the reactor should contain large quantities of methane, and smaller amounts of acetone and possibly acetic acid (reaction of ketene and water).
- 6. EPA Source Classification Code None
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 1," "Chemical Engineering," January 21, 1974, p. 129. Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 12 (1967), p. 91.

7. <u>References</u> (continued)

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N.Y., 1975, p. 18. Diketene (dimerization of ketene)

 Function - Diketene is a commercial by-product of ketene synthesis from acetic acid (see Process No. 105) or acetone (see Process No. 263A). The dimerization occurs spontaneously.

For description of the other items see Process No. 263A.

INDUSTRIAL ORGANIC CHEMICALS

Nonene and Dodecene (oligomerization of propylene)

$$3CH_2 = CHCH_3 \xrightarrow{H_3^{PO}_4} C_9^{H_{18}}$$

$$4CH_2 = CHCH_3 \xrightarrow{H_3PO_4} C_{12}H_{24}$$

 <u>Function</u> - Nonene and dodecene are coproduced when a C₃ refinery stream (40-60% propylene/propane) is oligomerized in the presence of a phosphoric acid catalyst at 200°C and 3.45-6.89 MPa.

In some cases, the oligomerization is done with the intention of producing gasoline, from which cuts of nonene and dodecene can be fractionated. In other cases, the tetramer and/or trimer are the primary products desired and the oligomerization is carried out in such a way as to maximize production of both or either of these. For instance, if the demand for dodecene exceeds the quantity contained in a once-through oligomerization product, some or all of the dimer and trimer are recycled to increase or maximize production of the tetramer.

The trimer and tetramer cuts that are fractionated from the oligomerization product are not pure trimer and tetramer, but are mixtures of olefins that consist principally of polypropylene having average molecular weights corresponding to those of nonene and dodecene.

2. Input Materials

Propylene^{*} (component of C₃ Refinery Gas)

^{*} The figures presented represent maximized production of nonene and dodecene.

- Input Materials (continued)
 For nonene 1.21 kg/kg
 For dodecene 1.27 kg/kg
- 3. Operating Parameters

Temperature: 200°C (392°F)

Pressure: 3.45-6.89 MPa (34-68 atm.)

Catalyst: H₃PO₄

- 4. <u>Utilities</u> Not given
- 5. <u>Waste Streams</u> Since all of the co-products of nonene and dodecene manufacture are utilized, there are no process wastes to be dealt with, except spent phosphoric acid catalyst. However, propylene, nonene, dodecene, and other olefins may be leaked to the atmosphere by various processing equipment.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Technomic Publishing Co., 1975, p. 335. Isodecyl Alcohol (oxo process)

 $c_{9}H_{18} + co + H_{2} \longrightarrow c_{9}H_{19}CHO$

1. <u>Function</u> - Isodecyl alcohol, actually a mixture of trimethyl heptanols, is prepared from nonene by the oxo process. In this process, a mixed stream of nonylenes is combined with synthesis gas at 160°C and 1.38 MPa (137 atm) in the presence of cobalt naphthenate catalyst to produce a mixture of C₁₀ aldehydes.

The intermediate aldehydes are then hydrogenated to isodecyl alcohol at 150°C and 10.0 MPa (100 atm) over a nickel or copper chromite catalyst:

 $C_9H_{18}CHO + H_2 \longrightarrow C_9H_{19}CH_2OH$

Purification is carried out in the manner described in Process Nos. 278 and 282. Yields in the neighborhood of 64% are obtained.

2. Input Materials

Nonene - 1.25 kg/kg product Synthesis gas Hydrogen

3. Operating Parameters

Aldehyde Production Temperature: 160°C (320°F) Pressure: 13.8 MPa (137 atm) Catalyst: Cobalt naphthenate

- 3. <u>Operating Parameters</u> (continued) Hydrogenation Temperature: 150°C (302°F) Pressure: 10.0 MPa (100 atm) Catalyst: Ni or Cu chromite
- 4. <u>Utilities</u> Not given
- 5. <u>Waste Streams</u> Generally, the same types of pollution would be expected as in Process Nos. 187 and 188.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 3," "Chemical Engineering," March 18, 1974, p. 92.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 14 (1967), p. 373-89. Isooctyl Alcohol (from heptene)

 $C_7H_{14} + CO + H_2 \longrightarrow C_7H_{15}CHO$

 $C_7H_{15}CHO + H_2 \longrightarrow C_7H_{15}CH_2OH$

 <u>Function</u> - Isooctyl alcohol, actually a mixture of isomeric C₈ alcohols, is manufactured by the oxo process. Heptene and synthesis gas are reacted at 150°C and 20.7 MPa (3000 psi) in the presence of a cobalt carbonyl catalyst, to yield a mixture of intermediate octaldehydes.

After separation, the octaldehydes are hydrogenated to isooctyl alcohol at 150°C and 10.0 MPa (100 atm) over a nickel chromate catalyst.

The intermediate aldehyde and the crude alcohol product are purified by the methods described in Process Nos. 278 and 282. This process gives a 57% yield based on heptene.

2. Input Materials

Heptene - 1.33 kg/kg product

Synthesis gas

Hydrogen

3. Operating Parameters

Temperature: 150°C (302°F)

Pressure: octaldehyde production - 20.7 MPa hydrogenation - 10.0 MPa

Catalyst: octaldehyde production - cobalt carbonyl hydrogenation - nickel chromate

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Generally, the same types of pollution would be expected as in Process Nos. 187 and 188.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 14 (1967). p. 373-89.

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 6," "Chemical Engineering," May 27, 1974, p. 106. 2-Propanol (Isopropyl Alcohol; Indirect Hydration Process)

 $\begin{array}{rcl} CH_{3}CH=CH_{2} &+ & H_{2}SO_{4} &\longrightarrow & (CH_{3})_{2}CHOSO_{3}H \\ (CH_{3})_{2}CHOSO_{3}H &+ & H_{2}O &\longrightarrow & CH_{3}CHOHCH_{3} \\ CH_{3}CH=CH_{2} &+ & (CH_{3})_{2}CHOSO_{3}H &\longrightarrow & [(CH_{3})_{2}CH]_{2}SO_{2} \\ [(CH_{3})_{2}CH]_{2}SO_{2} &+ & CH_{3}CHOHCH_{3} &\longrightarrow & (CH_{3})_{2}CHOCH(CH_{3})_{2} &+ & (CH_{3})_{2}CHOSO_{3}H \end{array}$

 Function - The basic reactions of the indirect hydration process for the production of isopropyl alcohol are described in the above formulae.

Crude propylene is scrubbed to remove mercaptans and hydrogen sulfide, distilled to remove higher hydrocarbons and hydrogenated to remove the acetylenics.

The liquefied propylene feed stock is combined with recycled propylene and passed into a sulfuric acid absorption column. Most of the propylene is absorbed. The spent gas containing propylene and propane is scrubbed with caustic and sent to liquefied petroleum gas (LPG).

The extract is sent to the hydrolyzer-stripper where it is diluted with water to obtain the sulfate esters. The ester solution is then stripped with steam to remove the 2-propanol and diisopropyl ether. The alcohol and ether vapors are scrubbed with caustic solution to remove acidic compounds and entrained acid.

The alcohol and ether are separated by distillation, the ether being taken overhead as a water-ether azeotrope. The alcohol-water mixture is distilled and the distillate sent to a dehydrating column where the remaining water is removed azeotropically. The

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ternary azeotrope is condensed and sent to a decanter where two layers are formed. The upper layer consists of alcohol and azeotropic components, the lower layer is water.

2. Input Materials

Refinery propylene stream (>50% propylene) Sulfuric acid (70-80 wt %) Caustic soda Azeotropic agent (benzene, isopropyl ether or ethyl ether)

3. Operating Parameters

Absorber (reactor) temperature: 60-90°C (140-190°F) Absorber (reactor) pressure: 791 kPa-28.6 MPa (7.8-28.3 atm)

- 4. Utilities Not given
- 5. Waste Streams

Air: possible compressor seal leaks, recycle gas line leaks, spent gas vent on reactor would result in propylene emissions. Water: Waste water from dehydration column and crude storage may contain small amounts of isopropyl ether, hydrocarbons, and propanoic acid. Spent caustic soda solution contains caustic soda, sodium sulfate, and 2-propanol. Waste water from the decanter may contain isopropanol and azeotropic components.

- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 16 (1967), p. 568-570.

Kent, J. A., <u>Riegel's Handbook of Industrial Chemistry</u>, Ed., 7th Edition, Van Nostrand Reinhold Company, New York, N. Y., 1974, p. 794.

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Isopropyl Chloride (from isopropyl alcohol)

 $(CH_3)_2$ CHOH + HC1 \longrightarrow $(CH_3)_2$ CHC1 + H₂0

- Function Isopropyl chloride is readily formed by the reaction of isopropyl alcohol and hydrochloric acid.
- 2. Input Materials

Isopropy1 alcoho1

Hydrochloric acid

- 3. Operating Parameters Not given
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Air and water effluents from the separator may contain isopropanol, isopropyl chloride, and hydrogen chloride.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 16 (1968), p. 567.

PROCESS NO. 269

Acetone (oxidation of isopropanol)

 $(CH_3)_2CHOH + 1/2 \ 0_2 \longrightarrow (CH_3)_2CO + H_2O$

 Function - A significant amount of acetone is produced by the catalytic oxidation of isopropyl alcohol. In this process, isopropanol is mixed with air and fed to a reactor maintained at 500°C and 345 kPa (50 psi). Copper or silver catalysts are used.

Reactor products are treated similarly to those from the straight dehydrogenation process.

If run in the liquid phase, this process yields hydrogen peroxide as a by-product.

 $(CH_3)_2CHOH + O_2 \longrightarrow (CH_3)_2CO + H_2O_2$

2. Input Materials

Isopropano1 - 1.15 kg/kg product

Air

3. Operating Parameters

Temperature: 500°C (932°F) Pressure: 345 kPa (3.4 atm) Catalyst: copper or silver

- 4. Utilities Not given
- 5. Waste Streams

Isopropanol stripping still and intermediate flush column (water).

5. Waste Streams (continued)

Water flow - 1.46 m³/Mg product (350 gal/ton) COD - 1.1 kg/Mg product (2.2 lb/ton) BOD - 3.25 kg/Mg product (6.5 lb/ton) TOC - 0.35 kg/Mg product (0.7 lb/ton)

The waste water contains acetone, isopropanol and traces of heavier organics.

Vent on absorber (air) - acetone and isopropanol vapors.

- 6. EPA Source Classification Code None
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 1," "Chemical Engineering," January 21, 1974, p. 130.

Hedley, W. H. et al., <u>Potential Pollutants from Petrochemical</u> Processes, Technomic Publishing Co., 1975.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 161.

Acetone (catalytic dehydrogenation of isopropanol)

$$(CH_3)_2 CHOH \longrightarrow (CH_3)_2 CO + H_2$$

 <u>Function</u> - As of November 1974, 42% of the U. S. capacity for acetone production was based on the dehydrogenation or oxidation (see Process No. 269) of isopropyl alcohol. In the dehydrogenation process, isopropanol is fed to a packed tubular reactor. The reaction takes place at 380°C in the presence of brass or zinc oxide catalyst, with a yield of 95%.

The hot reactor effluent contains acetone, unreacted isopropanol, hydrogen, and minor amounts of by-products, such as propylene and diiospropyl ether. The mixture is cooled and the noncondensable gases are scrubbed with water. Because the resultant gas stream is mainly hydrogen, a part of it can be recycled to control catalyst fouling. The liquids are fractionally distilled taking reconcentrated acetone overhead and a mixture of isopropanol and water as bottoms. In a second fractionating column, the aqueous isopropyl alcohol is concentrated for recycle to the reactor. The water removed may be rejected or reused in the gas scrubber.

- 2. Input Material Isopropanol 1.25 kg/kg acetone
- 3. Operating Parameters

Temperature - 380°C (716°F) Pressure - Not given Catalyst - brass or ZnO

- 4. <u>Utilities</u> Basis: 2.16 kg/sec (150 M lb/yr) capacity Cooling water - 379 dm³/sec (6000 gpm) Makeup water - 6.3 dm³/sec (100 gpm) Power - 1080 MJ (300 kW) Steam - 10.1 kg/sec (80,000 lb/hr) Natural gas - 8.8 MW (30 M Btu/hr)
- 5. <u>Waste Streams</u>

Isopropanol stripping still and intermediate flash column (water),

Water flow - 1.46 m³/Mg product (350 gal/ton)

COD - 1.1 kg/Mg product (2.2 1b/ton)

BOD - 3.25 kg/Mg product (6.5 1b/ton)

TOC - 0.35 kg/Mg product (0.7 1b/ton)

The wastewater contains acetone, isopropanol, and traces of heavier organics.

Vent on absorber (air)

Acetone and isopropanol vapors

- 6. EPA Source Classification Code None
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals - Part 1," "Chemical Engineering," January 21, 1974, p. 129.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical Processes</u>, Technomic Publishing Co., 1975.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 160. Isopropyl Amine (from isopropyl alcohol or acetone)

$$CH_{3}CHCH_{3} + NH_{3} \xrightarrow{A1PO_{4}} CH_{3}CHCH_{3} + H_{2}O$$

$$CH_3CCH_3 + NH_3 + H_2 \xrightarrow{Ni} CH_3-CH-CH_3 + H_20$$

1. <u>Function</u> - Isopropyl amine is made principally by two vapor phase catalytic processes. The first involves the alkylation of ammonia by isopropyl alcohol. This reaction is run at 350°C under a pressure of 100-200 atmospheres using an aluminum phosphate catalyst. An excess (3 to 5x) of ammonia is used in order to promote primary amine formation. Secondary and tertiary amines are by-products and must be separated. The amines appear to be in equilibrium and the secondary and tertiary amines are therefore recycled.

Acetone, ammonia and hydrogen are combined at 140°C and 740 psi over Raney nickel to give a 97% yield of isopropylamine. Secondary and tertiary amines are also present as by-products of this reaction.

2. Input Materials

Isopropyl Alcohol Ammonia Acetone

Hydrogen

3. Operating Parameters

Ammonylsis

Temperature - 350°C (662°F)

Pressure - 10.1-20.3 MPa (100-200 atm)

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3. Operating Parameters (Continued)

Catalyst - Aluminum phosphate

Reductive Ammination

Temperature - 130-180°C (266-356°F)

Pressure - 0.507-10.1 MPa (5-100 atm)

Catalyst - Raney nickel

- 4. Utilities not given
- 5. <u>Waste Streams</u> Waste water streams from strippers may contain ammonia, isopropyl alcohol, acetone, isopropyl amines and more highly substituted amines. Air effluents may contain ammonia, acetone, isopropyl amine and isopropyl alcohol.
- 6. EPA Source Classification Code None
- 7. References

E. G. Hancock, <u>Propylene and Its Industrial Derivatives</u>, John Wiley and Sons, New York, N.Y., 1973, p. 223-234.

A. L. Waddams, <u>Chemicals from Petroleum</u>, 3rd Edition, John Murray Publishers, Ltd., London, 1973, p. 128. Isopropyl Phenols (from isopropyl chloride and phenol)



 <u>Function</u> - Isopropyl phenols are produced by Friedel-Crafts reaction of phenol and isopropyl chloride in the presence of AlCl₃, BF₃, or H₂SO₄ catalyst.

Ortho- and para-isopropylphenol are the primary products, although some polysubstitution does occur.

2. Input Materials

Phenol

Isopropyl chloride

3. Operating Parameters

Temperature: not given

Pressure: not given

Catalyst: A1C1₃, BF₃, or H₂SO₄

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste water from the HCl scrubber should contain sodium chloride and caustic, phenol, isopropyl chloride, spent catalyst, and isopropylphenol. The air effluent may contain HCl, isopropyl chloride, and reaction by-products. Tars from the still bottoms are probably incinerated.
- 6. EPA Source Classification Code None
- 7. References

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 129, 269.

INDUSTRIAL ORGANIC CHEMICALS

PROCESS NO. 273

Acrylonitrile/Acetonitrile (ammoxidation of propylene)

 $CH_2 = CHCH_3 + NH_3 + O_2(air) \longrightarrow CH_2 = CHCN + HCN + CH_3CN + H_2O + CO_2$

1. <u>Function</u> - The entire production of acrylonitrile in the United States is obtained by the ammoxidation of propylene. In this vapor-phase process, refinery propylene (90+%), fertilizer grade ammonia (99.5+%), and air are combined in a fluidized bed reactor at 450°C and 200 kPa (2 atm). The reaction is catalyzed by a Sohio developed product, Catalyst 41 (50-60% bismuth phosphonohydrate on $A1_20_3$), which increases the yield of acrylonitrile and decreases the production of acetonitrile and hydrogen cyanide. Approximately 15 kg of acetonitrile and 75 kg of hydrogen cyanide are produced per Mg of acrylonitrile.

The reactor effluent is scrubbed in a countercurrent absorber, and excess ammonia is neutralized with sulfuric acid. The organic materials are recovered from the absorber water by distillation. Hydrogen cyanide, water, light ends, and high boiling impurities are then removed from the crude acrylonitrile by fractionation at atmospheric pressure. Acetonitrile and hydrogen cyanide are collected as saleable by-products.

2. Input Materials - Basis - 1 metric ton acrylonitrile

Propylene - 1.0 kg/kg product1175 kg (2,590 lbs/ton)Ammonia - 0.5 kg/kg product475 kg (1,047 lbs/ton)Air - 10.0 kg/kg product 6090 m^3 (2.15 x 10^5 ft/ton)Sulfuric acidsmall

3. Operating Parameters

Temperature: 450°C (842°F) Pressure: 200 kPa (2 atm) Reaction Time: 10-20 sec.

4. <u>Utilities</u> - Basis: 2.87 kg/sec capacity (200 M 1b/yr)

Cooling water - 1.89 m³/sec (30,000 gpm) Refrigeration - 907 Mg (1000 tons) Process water - 315 cm³/sec (5 gpm) Electricity - 3.6 GJ (1000 kW) Steam - 25.2 kg/sec (200,000 lb/hr) Inert gas, high pressure - 23.6 dm³/sec (3000 scfh)

- 5. <u>Waste Streams</u> Reaction section absorber off-gases to flare (air) Acrylonitrile - 5.0 kg/Mg product Carbon monoxide - 200 kg/Mg product Propane - 50.0 kg/Mg product Propylene - 100 kg/Mg product Acetonitrile - trace Ammonia - trace
 - Purification section off gas from drying column to flare (air) Hydrogen cyanide - 1 kg/Mg product

Reaction section - neutralizer (water) Wastewater contains ammonium sulfate

Purification section - stripper (water) Wastewater may contain acetonitrile.

- 6. EPA Source Classification Code None
- 7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -

Part 1, "Chemical Engineering," January 21, 1974, p. 131.

"1973 Petrochemical Handbook," "Hydrocarbon Processing," November, 1975, p. 99.

Hedley, W. H., et. al., Potential Pollutants from Petrochemical Processes,

Technomic Publishing Co., 1975.

7. <u>References</u> (continued)

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 46,47. Acrylamide (hydration of acrylonitrile)

 $CH_2 = CHCN + H_2SO_4 \cdot H_2O \longrightarrow CH_2 = CHCONH_2 \cdot H_2SO_4$ $CH_2 = CHCONH_2 \cdot H_2SO_4 \xrightarrow{H_2O} CH_2 = CHCONH_2 + H_2SO_4$

 <u>Function</u> - The hydration of acrylonitrile to acrylamide sulfate followed by dilution accounts for most acrylamide production at the present time. This reaction is carried out at 155-175° by adding acrylonitrile to sulfuric acid at the concentration corresponding to its monohydrate. Dilution with water converts the acrylamide sulfate intermediate to acrylamide and sulfuric acid.

To prevent hydrolysis to acrylic acid, free acid must be removed from the crude product solution. This is most commonly achieved by neutralization with ammonia or sodium hydroxide to form water-insoluble sulfate salts. The salts are then removed by filtration and the filtrate is concentrated and/or cooled to recover crystals of acrylamide. The mother liquor is frequently purged and recycled to serve as the medium for further neutralization.

The sulfuric acid may be directly separated from the crude product mixture without neutralization. This is accomplished by means of an ion exchange column which separates the product mixture into successive fractions of sulfuric acid, acrylamide-acrylic acid and acrylamide.

In July 1974, one U.S. company began producing acrylamide by the direct hydrolysis of acrylonitrile over special catalysts. A number of catalysts have been developed that allow the hydrolysis

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of acrylonitrile in aqueous solution to yield the acrylamide directly, obviating the need for the separation procedure necessary in the sulfuric acid hydrolysis. These catalysts consit for the most part of activated metallic oxides and are regenerable. These reactions are run at 100°C and it is necessary to include a water soluble inhibitor to prevent polymerization of the acrylamide. In one case where the catalyst was 40% Cu salt - 25.5% Cr the inhibitor used was N-nitroso-N-phenyl hydroxyamine ammonium salt. For a 7% aqueous solution of acrylonitrile 25 ppm was sufficient to inhibit the polymerization.

2. Input Materials

Acrylonitrile - 0.95 kg/kg acrylamide Concentrated sulfuric acid Water

Ammonia or sodium hydroxide

3. Operating Parameters

Temperature - hydrolysis

reaction - 155-175°C (311-347°F)
neutralization 50°C (122°F)
catalytic - 90-105°C (194-221°F)

Pressure - not given

4. Utilities - not given

5. <u>Waste Streams</u> - The principal pollutants from this process should be the impurities removed from the mother liquor following acrylamide separation. Acrylic acid, acrylonitrile, ammonia or caustic soda, inorganic sulfates, and traces of acrylamide may be present in this waste stream. The principal pollutants from the catalytic process are the impurities remaining in the mother liquor following the recrystallization of acrylamide. Unreacted acrylonitrile, inhibitor and some acrylamide are present. Catalyst is recovered by filtration and except for fines does not present a problem.

- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 1., (1963), p. 278-280. U.S. Patent 3,699,194 (1974).

U.S. Patent, 3,689,558 (Dow Chemical 1974).

Succinonitrile (from acrylonitrile)

 $CH_2 = CHCN + HCN \longrightarrow NCCH_2CH_2CN$

- Function Succinonitrile, also known as ethylene cyanide, is manufactured by reacting acrylonitrile with HCN in the presence of a catalyst (~5 wgt % acrylonitrile) and an inert solvent (tertbutyl alcohol). The acrylonitrile is added gradually to prevent polymerization.
- 2. Input Materials

Acrylonitrile

Hydrogen Cyanide

Catalyst: (Triton B) (benzyltrimethylammonium hydroxide)

Solvent: tert-Butyl Alcohol

3. Operating Parameters

Temperature:	55-60° C (131-140°F)
Pressure:	101 kPa (1 atm)
Reaction time:	5 hrs.

- 4. <u>Utilities</u> Not given
- 5. <u>Waste Streams</u> Wastewater streams from the purification section may contain alcohol and smaller quantities of acrylonitrile, hydrogen cyanide, catalyst, and polymers of acrylonitrile.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 6 (1965), p. 641. Acrylic Acid (oxidation of propylene)

$$CH_2 = CHCH_3 + O_2 \longrightarrow CH_2 = CHCHO + H_2O$$
$$CH_2 = CHCHO + 1/2 \quad O_2 \longrightarrow CH_2 = CHCOOH$$

 Function - The fastest-growing route to acrylic acid involves a one-or two-stage oxidation of propylene in the presence of a molybdenum oxide catalyst.

In the two-step process, propylene, steam, and preheated air are fed to the first reactor filled with oxidation catalyst. The temperature is maintained at 330 - 370°C by circulating heat transfer medium. The crude acrolein product is fed directly to the second reactor where it is converted to acrylic acid at 260 - 300°C. The reaction may be run in a single reactor by raising the temperature to 350 - 400°C and using a pressure of 98-196 kPa.

Regardless of the conversion technique, the reactor effluent is introduced to an absorber where acrylic acid is scrubbed as an aqueous solution. Acrylic acid in the solution is then extracted with a solvent. After solvent separation and light ends removal, high purity acrylic acid is obtained at the final rectifier. Some acetic acid by-product may be recovered.

2. Input Materials

Propylene - 0.83 kg/kg acrylic acid

Air

Steam - see utilities

3. Operating Parameters

Temperature: one stage - 350 - 400°C (662-752°F)

two stage - first reactor - 330 - 370°C (626-698°F)

second reactor - 260 - 300°C (500-572°F)

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Pressure: 100 - 200 kPa (1-2 atm.)
    Catalyst: MoO2
4. Utilities * - Basis: 0.31 kg/sec capacity (21.6 M 1b/yr)
    Steam - 3.11 kg/sec (24,700 1b/hr)
    Power - 0.97 GJ (270 kW)
    Cooling water - 379.1 \text{ dm}^3/\text{sec} (6,009 gpm)
    Makeup water - 20.3 dm^3/sec (322 gpm)
    Electricity - 3.9695 (1,100 kWh) metric ton
5. Waste Streams * - Overhead of solvent recovery column (air)
    Acetone - 0.35 kg/Mg product
    Acrolein - 1.85 kg/Mg product
    Ethyl acetate - 1.85 kg/Mg product
    Off-gas from the C<sub>3</sub> recovery system (air)
    Ethyl acetate - 36.8 kg/Mg product
    Propylene - 6.25 kg/Mg product
    Carbon monoxide - 502 kg/Mg product
    Heavy ends from acrylic acid finishing system (water)
    Acrylic acid - 4 kg/Mg product
    Polymers - 20.6 kg/Mg product
    Hydroquinone - 10.65 kg/Mg product
    Bottom from ethyl acetate recovery system (water)
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Acetic acid - 35.7 kg/Mg product

Acrylic acid - 5.9 kg/Mg product

Ethyl acetate - 27.25 kg/Mg product

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^{*} Data is based on the one-step oxidation.

- 6. EPA Source Classification Code None
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 1, Chemical Engineering, January 21, 1974, p. 130,313.

"1973 Petrochemical Handbook," Hydrocarbon Processing, November, 1973, p. 96.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Technomic Publishing Co., 1975.

PROCESS NO. 277

n-Butyl Acrylate (from acrylic acid)

 $CH_2 = CHCOOH + n - C_4H_9OH \longrightarrow CH_2 = CHCOOC_4H_9 + H_2O$

 <u>Function</u> - One competitive process for making n-butyl acrylate involves the direct esterification of acrylic acid with n-butanol.

Sulfuric acid is normally used as the catalyst and benzene is used as a water entrainer to assist in driving the reaction to completion.

2. Input Materials

Acrylic acid

n-Butanol

Benzene

- 3. <u>Operating Parameters</u> Temperature: not given Pressure: not given Catalyst: H₂SO₄
- 4. Utilities not given
- 5. <u>Waste Streams</u> Waste water streams, if present, may contain acrylic acid, sulfuric acid, n-butanol, n-butyl acrylate, and benzene.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 2," "Chemical Engineering," February 18, 1974, p. 126, 127.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 299. n-Butyraldehyde (oxo process)

 $\operatorname{CH}_2 = \operatorname{CHCH}_3 + \operatorname{CO} + \operatorname{H}_2 \longrightarrow \operatorname{CH}_3 \operatorname{CH}_2 \operatorname{CH}_2 \operatorname{CHO}$

1. <u>Function</u> - In the oxo process, propylene is reacted with synthesis gas in the liquid phase at 140-170°C and 20-30 MPa (200-300 atm). An aromatic liquid such as toluene is used as the solvent, and cobalt carbonyl compounds catalyze the reaction. n-Butyraldehyde, isobutyral-dehyde, and some butanol are produced. In modern plants the ratio of n-butyraldehyde to isobutyraldehyde is 4:1. The cobalt catalyst is separated from the crude oxo product and recycled to the reactor without any loss.

The two aldehydes may be hydrogenated and the corresponding alcohols separated by distillation, or the aldehydes may be separated and hydrogenated individually.

The remainder of the product mixture, containing butanols, esters, and heavy ends, is separated in a third column to yield small quantities of butanol and a residue which is used as fuel.

2. Input Materials

Propylene - 0.75 kg/kg n-butyraldehyde Synthesis gas (CO and H₂) Toluene (or other solvents)

3. Operating Parameters

Temperature - 140-170°C (284-338°F) Pressure - 20-30 MPa (197-296 atm) Catalyst - Cobalt carbonyl compound 4. Utilities

Not given

5. Waste Streams

Catalyst recovery section (air, water)

Air vents discharge carbon monoxide, propylene, and propane. Some catalyst recovery systems have a wastewater stream.

Purification section (air)

Various light end by-products may be flared to the atmosphere.

- 6. EPA Source Classification Code None
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 2", "Chemical Engineering," February 18, 1974, p. 126. "1973 Petrochemical Handbook," "Hydrocarbon Processing," November

1973, p. 107.

Hedley, W. H., et. al., <u>Potential Pollutants from Petrochemical Processes</u>, Technomic Publishing Co., 1975. Isobutanol (hydrogenation of isobutyraldehyde)

 $(CH_3)_2CHCHO + H_2 \longrightarrow (CH_3)_2CHCH_2OH$

 <u>Function</u> - Isobutanol is produced by the catalytic hydrogenation of isobutyraldehyde in a process similar to that used to make n-butanol from n-butyraldehyde. The reaction is carried out at 10.0 MPa pressure, and water is added to suppress ether formation.

Some n-butanol is also produced by this reaction due to aldehyde isomerization. The isobutanol, n-butanol, and other by-products are separated by the methods described in Process No. 282.

2. Input Materials

Isobutyraldehyde - 1.10 kg/kg product

Hydrogen

Water

3. Operating Parameters

Temperature: 130-250°C (266-482°F)

Pressure: 10.0 MPa (100 atm)

Catalyst: nickel, copper chromite, or molybdenum sulfide

- 4. Utilities Not given
- 5. <u>Waste Streams</u> The same general types of pollution would be expected as in Process No.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 6," "Chemical Engineering," May 27, 1974, p. 104.

7. References (continued)

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"1973 Petrochemical Handbook Issue," <u>Hydrocarbon Processing</u>, November 1973, p. 107.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Technomic Publishing Co., 1975.

Waddams, A. L., <u>Chemicals from Petroleum</u>, 3rd Edition, John Murray, Ltd., London, England, 1973, p. 205.

Isobutyl Acetate (from isobutanol)

 $CH_{3}COOH + (CH_{3})_{2}CHCH_{2}OH \xrightarrow{H_{2}SO_{4}} CH_{3}COOCH_{2}CH(CH_{3})_{2} + H_{2}O$

- 1. <u>Function</u> Isobutyl acetate is formed by the esterification of acetic acid with isobutyl alcohol in the presence of sulfuric acid. The reaction is carried out at the reflux temperature of the ternary azeotrope of isobutyl alcohol, isobutyl acetate and water. The vapor mixture distilling at this temperature is sent to a separator where the water is separated into an aqueous and alcohol-ester fraction. The alcohol-ester layer is distilled giving an alcohol-ester azeotrope and pure ester.
- 2. Input Material basis 1 kg isobutyl acetate

Isobutyl alcohol .9 kg/kg Acetic acid .94 kg/kg Sulfuric Acid 0.1%

3. Operating Parameters

Temperature:	85-89°C (185 - 192°F)
Pressure:	100 kPa (1 atm.)
Catalyst:	Sulfuric acid

4. Utilities

Not available

5. <u>Waste Streams</u> - Isobutyl alcohol and isobutyl acetate will be emitted from the reflux condenser. Waste water streams from the separator contain acetic acid, dilute sulfuric acid, isobutyl alcohol and isobutyl acetate. Air vent streams from the purification system (distillation) will contain isobutyl alcohol and isobutyl acetate.

- 6. EPA Source Classification Code None
- 7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 2,""Chemical Engineering," February 18, 1974, p. 126.

Faith, W. L., et al., <u>Industrial Chemicals</u>, 3rd Ed., John Wiley and Sons, Inc., New York, 1965, p. 176-78.

Isobutyric Acid (oxidation of isobutyraldehyde)

 $(CH_3)_2$ CHCHO + 1/2 0₂ \longrightarrow $(CH_3)_2$ CHCOOH

 <u>Function</u> - Isobutyric acid is prepared in 95% yield by the air oxidation of isobutyraldehyde at 30-50°C.

The crude product is best purified by azeotropic distillation with water followed by fractional distillation.

In some cases, isobutyl alcohol may be the raw material for this oxidation.

2. Input Materials

Isobutyraldehyde - 0.86 kg/kg product

Air

Water

- 3. <u>Operating Parameters</u> Temperature: 30-50°C Pressure: not given
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste water from distillation procedures may contain isobutyraldehyde, traces of isobutyric acid, and isobutanol, if used as the raw material in the synthesis. Waste gases from the purification section probably contain isobutyraldehyde and/or isobutanol.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1964), p. 880.

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n-Butanol

 $C_3H_7CHO + H_2 \longrightarrow CH_3CH_2CH_2CH_2OH$

 Function - About half of the commercial n-butanol is produced by the hydrogenation of n-butyraldehyde. In nearly all plant processes, the butyraldehyde feedstock is prepared by the oxo-reaction of propylene, so it contains isobutyraldehyde as well (see Process No. 278). In modern processes the hydrogenation reaction tends to isomerize the mixture to n-butanol.

A number of operating parameters have been reported for this reaction. In most cases, the butyraldehyde feed is converted with hydrogen over a fixed-bed catalyst such as nickel, copper chromite, or molybdenum sulfide at 130-250°C and 3-20 MPa (30-200 atm).

The crude n-butanol is purified by rectification in two columns. In the first column, the low boiling impurities, isobutanol and water, are separated as overhead. The higher-boiling impurities are removed in the second column by continuous discharge of the bottoms, product, and pure n-butanol is taken overhead.

2. Input Materials

n-Butyraldehyde (+ some isobutyraldehyde) - 1.09 kg/kg n-butanol Hydrogen 3. Operating Parameters

Temperature - 130-250°C

Pressure - 3-20 MPa (30-200 atm)

Catalyst - nickel, copper chromite, or molybdenum sulfide

- 4. <u>Utilities</u> Not given
- 5. Waste Streams

Hydrogenation reactor (air)

Tail gas vent discharges hydrogen and some organic vapors

Distillation column (organic liquid)

Heavy ends are usually burned.

This process involves no waste water and minimal air pollution.

- 6. EPA Source Classification Code None
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals - Part 2," "Chemical Engineering," February 18, 1974, p. 126.

"1973 Petrochemical Handbook Issue," "Hydrocarbon Processing," November 1973, p. 153.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical Processes</u>, Technomic Publishing Co., 1975.

Waddams, A. L., <u>Chemicals from Petroleum</u>, 3rd Ed., John Murray, Ltd., London, England, 1973, pp. 204-206.

n-Butyric Anhydride

$$2C_{3}H_{7}COOH + (CH_{3}CO)_{2}O \longrightarrow (C_{3}H_{7}CO)_{2}O + 2CH_{3}COOH$$

$$2C_{3}H_{7}COOH + 2CH_{2}CO \longrightarrow (C_{3}H_{7}CO)_{2}O + (CH_{3}CO)_{2}O$$

 <u>Function</u> - Butyric anhydride may be prepared by an exchange between butyric acid and acetic anhydride, or by the spontaneous reaction of butyric acid and ketene.

Since ketene may be synthesized from acetic acid (see Process No. 105), these reactions may be run in conjunction with each other. This system would require an initial input of either acetic acid or acetic anhydride.

2. Input Materials

Butyric acid

Acetic acid or acetic anhydride

- 3. Operating Parameters Not given
- 4. Utilities Not given
- <u>Waste Streams</u> Effluents from separation and purification operations may contain acetic acid, acetic anhydride, unreacted butyric acid, and butyric anhydride.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3. (1964), p. 880. n-Butyl Amines (from n-butyraldehyde)

 $\mathsf{CH}_{3}\mathsf{CH}_{2}\mathsf{CH}_{2}\mathsf{CH}_{2}\mathsf{CH} + \mathsf{NH}_{3} + \mathsf{H}_{2} \longrightarrow \mathsf{CH}_{3}\mathsf{CH}_{2}\mathsf{CH}_{2}\mathsf{CH}_{2}\mathsf{NH}_{2} + \mathsf{H}_{2}\mathsf{O}$

 <u>Function</u> - The most common route to n-butylamine involves the hydrogenation of n-butyraldehyde and alcoholic ammonia. The reaction is carried out at 90-125°C and elevated pressure in the presence of a nickel catalyst.

The yield of n-butylamine is about 80% with smaller amounts of di- and tri-n-butylamine by-products.

2. Input Materials

n-Butyraldehyde - 1.23 kg/kg n-butylamine

Ammonia

Hydrogen

Alcohol (solvent)

3. Operating Parameters

Temperature: 90-125°C

Pressure: ~500-1000 kPa (5-10 atm)

Catalyst: nickel

- 4. Utilities Not given
- 5. <u>Waste Streams</u> The separator effluent may contain quantities of ammonia, n-butyraldehyde, alcoholic solvent, spent catalyst, various butylamines, and by-product n-butanol.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 117, 124..

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7. <u>References</u> (continued)

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Ibid., Vol. 3 (1964), p. 868.

Koddo, N., Chem. Eng., 50(9), 149-68 (1952).

Propylene Chlorohydrin (from propylene)

$$C1_2 + H_20 \implies HOC1 + HC1$$

$$CH_3-CH=CH_2 + HOC1 \longrightarrow CH_3CH-CH_2OH + CH_3CHCH_2C1$$
C1
OH
$$10\% \qquad 90\%$$

1. <u>Function</u> - The bulk of propylene chlorohydrin produced in this country is made by the hydrochlorination of propylene. The method involves passing chlorine, propylene and water into a rubber-lined steel or acid-proof brick reactor at 35-50°C. The chlorine and water react to form hypochlorous acid and hydrochloric acid in a reversible reaction. The olefin is added to the hypochlorous acid at a rate which is maintained to produce a chlorohydrin of 3-5%. More concentrated solutions promote side reactions which yield bis(chloroisopropyl) ether and propylene dichloride.

The vent gases from the chlorohydrin tower are passed through a partial condenser to remove propylene dichloride and bis(chloroisopropyl) ether. The residual gas is scrubbed to remove HCl and in some cases recycled to the tower to recover any residual propylene. The propylene dichloride is purified and sold.

2. Input Materials

Propylene Chlorine

Water

3. Operating Parameters

Temperature: 35-50°C (95-122°F) Pressure: 110-130 kPa (1.14-1.27 atm)

- 4. Utilities not available
- 5. <u>Waste Streams</u> Waste water from scrubbing operations may contain sodium chloride and caustic soda. Reaction by-products, such as bis(chloroisopropyl) ether, may be present in air and waste water emissions from other purification sources. A portion of the recycled propylene may be vented to control the concentration of inert gases in the propylene feed. These emissions may contain ethylene, propylene, butane, hydrogen chloride and chlorine.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 8,""Chemical Engineering," July 22, 1974, p. 111.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 16 (1968), p. 600-602.

Waddams, A. L., <u>Chemicals from Petroleum</u>, 3rd Ed., John Murray, Ltd., London, England, 1973, p. 137, 138. Propylene Oxide (chlorohydrin process)

 $2CH_{3}CHOHCH_{2}C1 + Ca(OH)_{2} \longrightarrow 2CH_{3}CH-CH_{2} + CaC1_{2} + 2H_{2}O$

1. <u>Function</u> - As of July 1973, 70% of the U.S. capacity for propylene oxide production was based on the chlorohydrin process. In normal plant procedure, the propylene chlorohydrin feedstock is synthesized as described in Process No. 285. This dilute chlorohydrin solution is mixed with a 10% slurry of lime and pumped to a steam-heated flash hydrolyzer for conversion to propylene oxide. The reaction is carried out under ambient conditions.

The oxide is flashed out of the reaction zone as quickly as possible to prevent its further hydrolysis to propylene glycol. The lime slurry is used in excess and this excess may be recovered for recycle in thickeners which provide for the removal of the spent calcium chloride brine by decantation. This effluent consists of 5% aqueous CaCl, containing traces of lime and propylene glycol.

The overhead from the hydrolyzer is largely propylene oxide and water. It is contaminated with propylene dichloride, chloroprenes from dehydrochlorination of propylene dichloride, and propionaldehyde from isomerization of propylene oxide. This crude product is purified by fractionation in multiple distillation columns.

2. Input Materials

Propylene chlorohydrin

(from propylene - 0.94 kg/kg propylene oxide) 10% Calcium hydroxide - 1.17 kg/kg product

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- 3. <u>Operating Parameters</u> Temperature: 25°C (77°F) Pressure: ~atmospheric (100 kPa)
- 4. <u>Utilities</u>* Basis 0.72 kg/sec capacity (50 M lb/yr) Cooling water - 259 dm³/sec (4100 gpm) Nitrogen - 23.6 dm³/sec (3000 cfh) Power - 648 MJ (180 kW) Refrigeration - 1.109 Gg (1222 tons) Steam - 7.31 kg/sec (58,000 lb/hr)
- 5. <u>Waste Streams</u>*

Purge gas from caustic absorber (air) Ethane - 8.5 kg/Mg product Butane - 8.5 kg/Mg product Propylene - 8.5 kg/Mg product Hydrogen chloride - 0.5 kg/Mg product Chlorine - 0.5 g/Mg product Off gas from tail gas absorber (air) Propylene oxide - 4.1 kg/Mg product Hydrogen chloride - 0.5 g/Mg product Chloride - 0.5 g/Mg product Water effluent The major waste stream would probably contain calcium chloride and traces of lime and propylene glycol.

6. EPA Source Classification Code - None

Includes Process No. 285

7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 8," "Chemical Engineering," July 22, 1974, p. 111.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> Processes, Technomic Publishing Co., 1975, p. 147-148.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 16 (1968), p. 600.

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PROCESS NO. 287

Mono- and Dipropylene Glycols

 $CH_2OCHCH_3 + H_2O \longrightarrow CH_3CHOHCH_2OH$ $CH_3CHOHCH_2OH + CH_2OCHCH_3 \longrightarrow CH_3CHOHCH_2OCH_2CHOHCH_3$

 <u>Function</u> - Propylene glycol is produced by hydration of propylene oxide under pressure at temperatures up to 200°C. No catalysts are used.

Some dipropylene glycol, tripropylene glycol, and minor quantities of higher glycols are co-produced by the continued reaction of propylene oxide.

The proportion of higher glycols is controlled by the molar ratio of propylene oxide to water in the initial reaction mixture: the greater the dilution, the greater the production of propylene glycol and the higher the cost of recovering the pure products from solution. Usually about 15 moles of water are used per mole of propylene oxide in order to maximize propylene glycol production. This yields about 13% by weight dipropylene glycol and 1.5% tripropylene glycol.

Although most dipropylene glycol is recovered as a by-product of this process, some is produced by reacting propylene glycol with propylene oxide.

2. Input Materials

Propylene oxide

For propylene glycol - 0.77 kg/kg

- 2. <u>Input Materials</u> (continued) For dipropylene glycol - 0.95 kg/kg Water - 3.7 kg/kg product
- Operating Parameters
 Temperature: ~200°C
 Pressure: not given
- 4. Utilities Not given
- 5. <u>Waste Streams</u> The principal pollutant source in this process is waste water flow from the dehydrator, containing quantities of propylene oxide and propylene glycol.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Technomic Publishing Co., 1975.

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 8," "Chemical Engineering," July 22, 1974, p. 110-111.

Polypropylene Glycol

 $CH_{3}CHOHCH_{2}OH + nCH_{2}OCHCH_{3} \longrightarrow HO(C_{3}H_{6}O)_{n+1} H$

 Function - Polypropylene glycol is produced by the base-catalyzed addition of propylene oxide to propylene glycol. The reaction takes place around 150°C.

Commercial polypropylene glycols have molecular weights ranging from 400 to 4000.

2. Input Materials

Propylene oxide

Propylene glycol

3. Operating Parameters

Temperature: 150°C Pressure: Not given Catalyst: KOH or other bases

- 4. Utilities Not given
- <u>Waste Streams</u> The same types of pollution would be expected as in Process No. 287. Spent catalyst may also be present.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 8," "Chemical Engineering," July 22, 1974, p. 110.

Allyl Alcohol (isomerization of propylene oxide)

$$CH_3CH-CH_2 \longrightarrow CH_2=CHCH_2OH$$

- 1. <u>Function</u> Allyl alcohol is produced in 80-85% yield by the catalytic isomerization of propylene oxide. This rearrangement is carried out in the liquid phase in jacketed, stirred tank-type reactors at 200-300°C and 1-25 atm. Both lithium phosphate and lithium arsenate catalysts are used.
- 2. <u>Input Material</u> Propylene oxide 1.21 kg/kg allyl alcohol
- 3. <u>Operating Parameters</u> Temperature: 200-300°C (392-572°F) Pressure: 0.1-2.5 MPa (1-25 atm) Catalyst: lithium phosphate or arsenate
- 4. <u>Utilities</u> Basis 284 g/sec capacity (19.8 M lb/yr) Steam - 1.16 kg/sec (9200 lb/hr) Power - 302.4 MJ (84 kW) Fuel - 1159 MJ (1.1 M Btu/hr) Nitrogen - 157 scm³/sec (20 scfh)
- 5. Waste Streams

Isomerization section - product column (water)

Allyl alcohol - 13 kg/Mg product

plus traces of n-propyl alcohol, tars, and xylene

Catalyst tar removal section - auxiliary liquid column (water)

Terphenyls - 12.5 kg/Mg product

Lithium phosphate - 5 kg/Mg product

Tars - 25.5 kg/Mg product

6. EPA Source Classification Code - None

7. <u>References</u>

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Technomic Publishing Co., 1975, p. 151.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 10 (1966), p. 624.

Dichlorohydrin

$$CH_2 = CHCH_2OH + Cl_2 \longrightarrow ClCH_2 - CHCl - CH_2OH$$
 (1)

$$CH_2 = CHCH_2 C1 + HOC1 \longrightarrow HOCH_2 CHC1CH_2 C1$$
 (2)

 <u>Function</u> - Dichlorohydrin is an intermediate in the production of glycerine. There are two principal processes used in the synthesis of dichlorohydrin. The starting materials in both processes are derived from propylene.

Allyl alcohol is chlorinated with chlorine gas to the dichlorohydrin. The product mixture contains 1,2-dichlorohydrin and 1,3dichlorohydrin which need not be separated if this is the intermediate step in the synthesis of epichlorohydrin.

Allyl chloride is used as the starting material in a continuous chlorohydrination process. Chlorine, water and allyl chloride are fed to a stirred-reactor operating at 30-80°C and atmospheric pressure. The allyl chloride is kept low to inhibit side reactions which form 1,2,3-trichloropropane and chloroethane. The reaction yields a mixture of 1,2- and 1,3-dichlorohydrin in a 70-30 ratio.

The reactor effluent is lead to a separator where the aqueous and organic phases are separated. The aqueous phase is recycled to the reactor after additional chlorine is added. The organic phase is converted to epichlorohydrin.

2. Input Materials

Allyl alcohol

Chlorine

2. Input Materials (continued

Allyl chloride - 0.98 kg/kg epichlorohydrin Chlorine/water - 0.90 kg/kg epichlorohydrin

- 3. <u>Operating Parameters</u> Temperature: 30-80°C (86-176°F) Pressure: 100 kPa (1 atm)
- 4. <u>Utilities</u> Not given
- 5. <u>Waste Streams</u> Vent gases from the reactor may contain allyl alcohol, allyl chloride, chlorine, dichlorohydrin and reaction by products such as propylene dichloride.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 316-317.

Hancock, E. G., <u>Propylene and Its Industrial Derivatives</u>, John Wiley and Sons, New York, N.Y., 1973, p. 24.

Epichlorohydrin (from dichlorohydrin)

 $C1CH_2CHC1CH_2OH + 1/2 Ca(OH)_2 - CH_2-CHCH_2C1 + 1/2 CaCl_2 + H_2O$

 $C1CH_2CHC1CH_2OH + NaOH - CH_2-CHCH_2C1 + NaC1 + H_2O$

 <u>Function</u> - Epichlorohydrin is commercially produced by the dehydrochlorination of dichlorohydrin. In this process, crude dichlorohydrin (see Process No. 290) is treated with a lime slurry or caustic soda in a column-type reactor at 70-100°C and atmospheric pressure. The solvent is trichloropropane.

The crude epichlorohydrin is removed from the reaction mixture as a water azeotrope by steam stripping. Final purification is accomplished by a two-column distillation train.

If the product is to be used in glycerol production, it need not be purified.

2. Input Materials

Dichlorohydrin (crude mixture) Calcium hydroxide - 1.01 kg/kg epichlorohydrin or Sodium hydroxide - 1.09 kg/kg epichlorohydrin

3. Operating Parameters

Temperature: <60°C (<140°F)

Pressure - 101 kPa (1 atm)

4. Utilities

Not given

5. Waste Streams

Tail gas absorber vent (air)

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Chlorine - 0.5 g/Mg product Hydrogen chloride - 0.5 g/Mg product Allyl chloride - 2 kg/Mg product Reactor vent (air) Allyl chloride - 2 kg/Mg product Epichlorohydrin - 1.5 kg/Mg product Trichloropropane - 0.5 kg/Mg product Chlorine - 0.5 g/Mg product Hydrogen chloride - 0.5 kg/Mg product

The major water pollution problem would probably be a slurry containing lime or caustic soda, calcium chloride or sodium chloride, and small amounts of epichlorohydrin.

6. EPA Source Classification Code - None

7. <u>References</u>

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical</u> Processes, Technomic Publishing Co., 1975.

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corp., Park Ridge, N.J., 1974, p. 131, 132.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, p. 335, 336.

INDUSTRIAL ORGANIC CHEMICALS

Glycerol (from peroxidation of ally1 alcohol)

$$CH_2 = CHCH_2OH + (CH_3)_3C - OOH \longrightarrow CH_2 - CH - CH_2OH + (CH_3)_3COH$$

$$\overset{\text{CH}_2\text{-CH-CH}_2\text{OH}}{\xrightarrow{}} + \overset{\text{Na}_2\text{CO}_3}{\xrightarrow{}} + \overset{\text{NOCH}_2\text{-CH-CH}_2\text{OH}}$$

 <u>Function</u> - This process has become competitive with the hydrochlorination of allyl alcohol in the synthesis of glycerin. The trend has been away from chlorination to peroxidation because in the former process the chlorinated products are discarded, for lack of markets, while the products of hydroperoxidation are all saleable.

Allyl alcohol is epoxidized by reaction with a hydroperoxide. The hydroperoxide that is used is chosen carefully so that its degradation product is saleable or useable in an allied process. The hydroperoxides commonly used are t-butyl hydroperoxide (degradation product, t-butylalcohol) and ethyl benzene hydroperoxide (degradation product, phenyl methyl carbinol). The glycidol produced is hydrolyzed to produce glycerin. Although the reactants in this process are more expensive than those in the chlorohydrin-glycerin process, their cost is recoverable since all products are utilized.

2. Input Materials

Allyl alcohol - 0.67 kg/kg glycerol t-Butyl hydroperoxide - 1.1 kg/kg glycerol

3. Operating Parameters

Temperature: 25-30°C (77-86°F)

Pressure: 1.6-3.6 KPa (16-35 atm)

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- 4. Utilities Not given
- 5. <u>Waste Streams</u> Air streams may contain allyl alcohol and degradation products of the hydroperoxide (t-butyl alcohol, for example). Waste water streams may contain allyl alcohol, glycidol, sodium carbonate and t-butyl alcohol or methyl phenyl carbinol depending on the hydroperoxide used.
- 6. EPA Source Classification Code None
- 7. References

R. G. Muller, "Glycerin and Intermediates," Report No. 58, Stanford Research Institute, Menlo Park, California, 1969.

"Hydrocarbon Processing," Nov. 1961, p. 249.

Hedley, W. H. et al., <u>Potential Pollutants From Petrochemical Processes</u>, Prepared for EPA, Final Report MRC-DA-406, Contract 68-02-0226, Dec. 1973, p. 149-150. Glycerol Tri(polyoxypropylene) Ether (GTPE)

HOCH₂CHCH₂ + 3n CH₂-CHCH₃

 $^{\mathrm{CH}_{2}[(\mathrm{OC}_{3}\mathrm{H}_{6})_{n}\mathrm{OH}]-C\mathrm{H}[(\mathrm{OC}_{3}\mathrm{H}_{6})_{n}\mathrm{OH}]\mathrm{CH}_{2}-[(\mathrm{OC}_{3}\mathrm{H}_{6})_{n}\mathrm{OH}]}$

 <u>Function</u> - Glycerol tri(polyoxypropylene) ether is formed by the base-catalyzed reaction of glycerol and propylene oxide. The conversion is normally carried out at 125°C and 446 kPa (4.4 Atm).

Near the end of the reaction, some ethylene oxide is usually added to impart certain desired properties characteristic of polyoxyethylene linkages.

GTPE is prepared in a variety of molecular weights,

2. Input Materials

Glycerol Propylene oxide Ethylene oxide

3. Operating Parameters

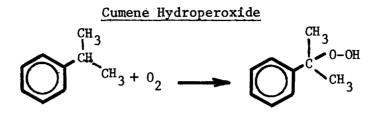
Temperature: 125°C (257°F) Pressure: 446 kPa (4.4 atm) Catalyst: KOH

- 4. Utilities Not given.
- 5. <u>Waste Streams</u> Waste streams from purification operations are likely to contain quantities of propylene oxide, spent catalyst, glycerol, GTPE, and by-products such as propylene glycol.

6. EPA Source Classification Code - None.

7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 6", "Chemical Engineering", May 27, 1974, p. 103.



1. <u>Function</u> - The hydroperoxide is made from cumene by an air oxidation process. A mixture of cumene, water, sodium carbonate, sodium stearate and a small amount of cumene hydroperoxide, which functions as an oxidation initiator, is fed to a liquid phase oxidation vessel. The oxidizing agent is air, and the reaction is carried out at 130°C and 274-446 kPa (2.70-4.40 atm) until 35-50% of the cumene is converted to the hydroperoxide. The oxidation product is distilled so that most of the unreacted cumene goes overhead, and the cumene hydroperoxide to bottom. As of January 1, 1975, almost 91% of synthetic phenol capacity was based on the acid-catalyzed cleavage of cumene hydroperoxide.

2. Input Materials

Cumene

Air Sodium carbonate Sodium stearate Water

3. Operating Parameters

Temperature - 130°C (266°F) Pressure - 274-446 kPa (2.70-4.40 atm)

4. Utilities - Not given

5. <u>Waste Streams</u> - Waste water contains sodium carbonate, sodium stearate, phenol and acetone. The air vents may emit cumene, acetone and traces of mesityl oxide.

Flow	$\frac{Plant 1}{2.33 \times 10^{-3} m^3/kg} (279.6)$ gal/1000 lbs)	<u>Plant 2</u> 1.37 x 10 ⁻³ m ³ /kg (164 gal/ 1000 lbs)
COD	4,700 mg/1 11.1 g/kg	84,304 mg/1 11.4 g/kg
BOD ₅	2,410 mg/1 5.6 g/kg	17,575 mg/1 24 g/kg
TOC	194 mg/1 0.45 g/kg	77,406 mg/1 105.6 g/kg

Lower values for plant 1 due to installation of dephenolizer facilities (steam strippers).

- 6. EPA Source Classification Code 3-01-034-01
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals - Part 1," "Chemical Engineering," January 21, 1974, p. 130.

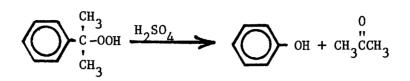
Ibid., Part 8, July 22, 1974, p. 107,108.

"1973 Petrochemical Handbook," "Hydrocarbon Processing," November 1973, p. 158.

"1975 Petrochemical Handbook," "Hydrocarbon Processing," November 1975, p. 170.

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical Processes</u>, Technomic Publishing Co., 1975.

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corp., Park Ridge, N.J., 1974, p. 182,183. Phenol (decomposition of cumene hydroperoxide)



- 1. <u>Function</u> Cumene hydroperoxide decomposes under the influence of sulfuric acid to acetone and phenol. Approximately 88% of the phenol produced in the United States in 1974 was made by this process. The hydroperoxide is usually made from crude cumene and may contain benzene and α -methyl styrene.
- 2. Input Materials

Cumene hydroperoxide

Sulfuric acid

3. Operating Parameters

Temperature - 70-80°C (158-176°F)

Pressure - 50-152 kPa (0.5-1.5 atm)

Catalyst - Sulfuric acid

- 4. Utilities Not given
- 5. Waste Streams

Crude Phenol surge (water)

Cumene trace

Acetone - 4.5 x 10^{-4} kg/kg phenol

Phenol - 7.5 x 10⁻⁵ kg/kg phenol

Evaporator Residue

Acetophenone - .00175 kg/kg phenol Phenol - 7.5 x 10⁻⁴ kg/kg phenol Polymeric matter - 0.11 kg/kg phenol Cumyl phenol - 8.5 x 10⁻⁴ kg/kg phenol 6-699

6. EPA Source Classification Code - None

7. Reference

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N.Y., 1975, pp. 612-613.

Hedley, W. H., et al., "Potential Pollutants from Petrochemical Processes," for Control Systems Laboratory, NERC, Environmental Protection Agency, Contract No. 68-02-0226, Task No. 9, pp. 121-122. α -Methylstyrene (dehydrogenation of cumene)

 $C_{6}H_{5}CH(CH_{3})_{2} \xrightarrow{\Delta} C_{6}H_{5}C(CH_{3})=CH_{2} + H_{2}$

 Function - Most commercial α-methylstyrene is produced by the dehydrogenation of cumene. In a typical operation, a mixture of three parts steam to one part cumene is passed rapidly over an iron oxide catalyst at temperatures of 500-600°C.

The crude dehydrogenation mixture contains cumene and α methylstyrene, as well as small amounts of benzene, toluene, ethylbenzene, styrene, and tars. All of the usable components are separated and purified through a series of fractional distillations and recycled.

2. Input Materials

Cumene

Steam

3. Operating Parameters

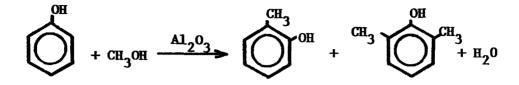
Temperature: 550-600°C (1022-1112°F) Pressure: not given

Catalyst: iron oxide

- 4. Utilities Not given.
- 5. <u>Waste Streams</u> Wastewater streams from the separators and superheater probably contain a variety of heavy-end aromatic hydrocarbons, tars, and spent catalyst. Organic solids from still bottoms are usually incinerated.
- 6. EPA Source Classification Code None.

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 19, (1969) p. 81. 2,6-Xylenol (methylation of phenol)



- Function 2,6-Xylenol is a by-product of the methylation of phenol to produce o-cresol. The xylenol isomer is present in approximately 25% of the yield. Phenol is reacted with methanol at about 300°C and a pressure of 4.13 MPA (41 atm) over an alumina catalyst. Small amounts of meta and para alkylated products are formed as well as some phenyl ethers formed by oxidative coupling. The crude product is separated and purified by crystallization.
- 2. Input Materials

Pheno1

Methano1

Alumina

3. Operating Parameters

Temperature: 300°C (572°F) Pressure: 4.13 MPA (41 atm) Catalyst: Al₂0₃

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Air vent streams would contain methanol and small quantities of phenol. Wastewater effluents from purification operations probably contain small quantities of ethers and m- or p- substituted cresols and xylenols. Unreacted methanol and phenol may also be present in trace amounts.

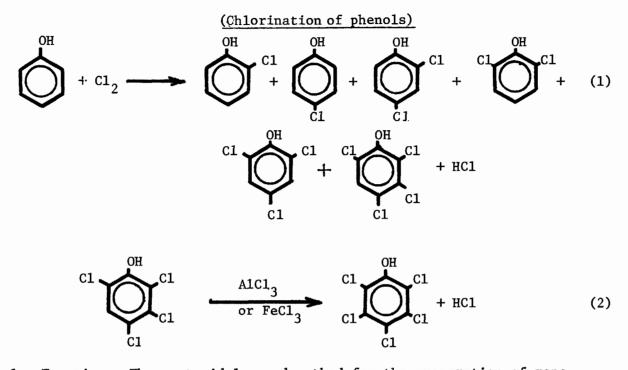
6. EPA Source Classification Code - None

7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 6 (1965) p.

Hahn, A. V., The Petrochemical Industry, McGraw-Hill Book Co., New York, 1970, p. 576-78.

CHLOROPHENOLS



1. <u>Function</u> - The most widely used method for the preparation of monochlorophenols is the direct chlorination of phenol in the absence of a solvent. The product is a mixture of o- and p-chlorophenols with preponderance of the para isomer. The reaction will proceed stepwise to the di-, tri- and tetrachloro- products although the rate slows with each additional atom of chlorine added to the phenol substrate.

The dichlorophenols can be produced by direct regulated action of chlorine in a solvent such as glacial acetic acid or chloroform. Chlorination in aqueous solution gives 2,4,6-trichlorophenol rapidly and quantitatively.

Pentachlorophenol is produced by chlorinating the more highly substituted chlorophenols in the presence of FeCl₃ or AlCl₃ since the rate of chlorination has decreased to the point that the uncatalyzed reaction becomes prohibitably slow.

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The chlorophenols can be separated from unreacted phenol by adding potassium carbonate which reacts with the chlorinated phenols to form the water-soluble salts. Phenol is not basic enough to react and can therefore be extracted from the water solution.

The chlorophenol isomers can be separated by fractional distillation. Pentachlorophenol, 2,4-dichlorophenol, 2,3,4,6-tetrachlorophenol, 2,4,6trichlorophenol and p-chlorophenol are all soluble products. o-Chloro and 2,6-dichlorophenol have no commercial use and are recycled for further chlorination.

2. Input Materials

Pheno1

Chlorine

Potassium carbonate

Aluminum trichloride or ferric chloride

3. Operating Parameters

Temperature - 50-155°C (122-311°F)

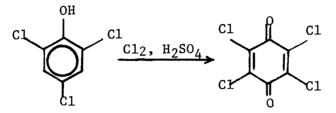
Pressure - not given

Catalyst - for pentachlorination - A1Cl₃ or FeCl₃ (0.05-1.0%)

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste water streams from washing operations and still bottoms probably contain quantities of potassium chloride, HCl, phenol chlorine and chlorophenols. Chlorine, HCl and extraction solvents are present in air emissions.
- 6. EPA Source Classification Code None

7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1968) p. 300. Chloranil (from 2,4,6-trichlorophenol)

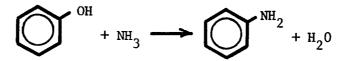


- <u>Function</u> Chloranil or 2,3,5,6-tetrachloro-1,4-benzoquinone is prepared by the action of chlorine and fuming sulfuric acid on 2,4,6-trichlorophenol.
- 2. Input Materials

2,4,6-Trichlorophenol Chlorine Sulfuric acid (fuming)

- 3. Operating Parameters Not given.
- 4. Utilities Not given.
- <u>Waste Streams</u> Effluents from purification operations may contain 2,4,6-trichlorophenol and other chlorophenols, chlorine, sulfuric acid, chloranil and a variety of reaction by-products.
- 6. EPA Source Classification Code None.
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 334. Aniline (ammonolysis of phenol)



- 1. <u>Function</u> Currently, the most economical route to aniline is the ammonolysis of phenol. In this process, ammonia and phenol are preheated and fed to a fixed-bed catalytic reactor where the conversion takes place over alumina. The reactor effluent is partially condensed and unconverted ammonia is compressed and recycled. The water of reaction is removed from the crude aniline stream by distillation, at the same time unreacted phenol distills as an azeotrope with water and is recycled. High purity aniline product is recovered by distillation from heavies. This process offers less by-products than other commercially used processes.
- 2. Input Materials

Phenol - 1.05 kg/kg product Ammonia - 0.20 kg/kg product

3. Operating Parameters

Temperature: not given Pressure: not given Catalyst: alumina

4. Utilities

Not given

5. <u>Waste Systems</u> - Off-gases from the separator may contain hydrogen, nitrogen, and some ammonia. Traces of aniline and phenol may be present in the waste gas from the dryer. The rejected heavies from

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the final distillation could be present in waste water streams, but are probably incinerated. Overall, waste disposal problems are considered minimal.

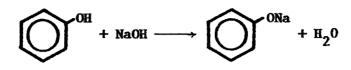
- 6. EPA Source Classification Code 3-01-034-01
- 7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 1, "Chemical Engineering," January 21, 1974, p. 132.

"1973 Petrochemical Handbook Issue," "Hydrocarbon Processing," November 1973, p. 105.

"1975 Petrochemical Handbook", Hydrocarbon Processing," November 1975, p. 114.

Sodium Phenate



- 1. <u>Function</u> In the commercial production of sodium phenate, phenol and a slightly greater than equimolar quantity of hot aqueous sodium hydroxide (concentration about 50%) are mixed in thermocoil autoclaves. The solution is heated to approximately 130°C and is evaporated to dryness, first at atmospheric pressure and in later stages by the application of a vacuum. This operation is sometimes carried out in heated ball mills in order to yield a dry, powdered product.
- 2. Input Materials

Pheno1

50% aqueous sodium hydioxide

3. Operating Parameters

Temperature - 130°C

Pressure - Not given

- 4. Utilities Not given
- 5. <u>Waste Streams</u> The principal source of air pollutions in this process is the evaporation step when a mixture of water vapor and phenol is emitted.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 17 (1968) p. 148.

ANISOLE

$$ONa + CH_3C1 \longrightarrow OCH_3 + NaC1$$
(1)

$$2 \qquad Ona + (CH_3)_2 SO_4 \longrightarrow 2 OcH_3 + Na_2 SO_4 \qquad (2)$$

 Function - Anisole is made by the Williamson reaction which is the alkylation of a phenate salt. The most economical route to anisole is described by equation (1) and involves the reaction of sodium phenate and methyl chloride. An alternate method, utilized more in the past, was based on the use of dimethylsulfate as the alkylating agent (2).

In both methods, the sodium phenate is prepared <u>in situ</u> by combining molten phenol and sodium hydroxide at 45-60°C. The alkylating agent is added and the temperature is then increased to 100°C. The yield in both processes approximates 95%.

2. Input Materials

Phenol (2) 0.92 kg/kg anisole

Sodium hydroxide

- (1) methyl chloride
- (2) dimethyl sulfate
- 3. Operating Parameters

Temperature - 45-100°C (113-212°F) Pressure - not given

4. Utilities - not given

- 5. <u>Waste Streams</u> Waste streams from purification processes may contain sodium chloride or sodium sulfate, depending on the process used, sodium hydroxide, phenol, sodium phenate, anisole and methyl chloride or dimethyl sulfate, depending on the process utilized. Methyl chloride may also be present in the off-gases of various processing equipment.
- 6. EPA Source Classification Code None

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 15 (1968) p. 167.

Salicylic Acid and Methyl Salicylate

 $C_6H_5ONa + CO_2 \longrightarrow C_6H_4(OH)(COONa)$

 $C_6H_4(OH)(COONa) + HC1 \longrightarrow C_6H_4(OH)(COOH) + NaC1$

 <u>Function</u> - In the preparation of salicylic acid, an excess of carbon dioxide at 5 - 6 atm. pressure is charged to a thermocoil autoclave containing dry, powdered sodium phenate (see Process No. 301). The conversion to sodium salicylate requires several hours at 140 - 170°C. Any regenerated phenol is recovered by vacuum distillation.

The crude product is then cooled, dissolved in water, and filtered to remove impurities. Acidification of this sodium salicylate solution with hydrochloric acid or sulfuric acid results in the precipitation of salicylic acid.

Further purification of the technical product to yield USP salicylic acid is achieved by sublimation. In order to eliminate the risk of dust explosions, caused by frictional electricity during this operation, a stream of inert gas (nitrogen with some carbon dioxide) is circulated through the sublimation chamber. The products obtained are USP salicylic acid and a slightly colored technical grade sublimed acid. The yields of technical-grade and USP salicylic acid from this entire process are 88% and 84%, respectively.

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Methyl salicylate is an important commercial product in the perfume and flavoring industries. Production in 1972 was in excess of 5,000,000 pounds. It is produced from salicylic acid, which has been purified by sublimation, by esterification with methyl alcohol in the presence of catalytic amounts of sulfuric acid. The ester product is purified by vacuum distillation with the water and unreacted methanol recycled to the system.

2. Input Materials

Sodium phenate (from phenol - 0.74 kg/kg salicylic acid) Carbon dioxide Water Hydrochloric acid or sulfuric acid

Nitrogen

3. Operating Parameters

Temperature: carboxylation - 140 - 170°C (252 - 338°F) acidification - not given Pressure: carboxylation - 500 - 600 kPa (5-6 atm) acidification - not given

4. Utilities

Based on production of 4,000 pounds of salicylic acid/day Steam - 0.158 kg/sec (1,250 lb/hr) Power - 3,600 MJ (1,000 kWh)

5. <u>Waste Streams</u> - The principal pollutant source in this process should be the waste water stream from centrifuging operations. The mother liquor is likely to contain sodium chloride or sulfate, hydrochloric or sulfuric acid, various reaction by-products, and traces of phenol and salicylic acid. The wash water stream contains salicylic acid, sulfuric acid and methanol. The vent streams from the esterification and distillation steps will contain some methanol.

- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 17, (1968), p. 723-25.

"Phenol," in <u>Chemical Economics Handbook</u>, Stanford Research Institute, Menlo Park, California.

Shreve, R. N., <u>Chemical Process Industries</u>, 3rd Edition, McGraw Hill Book Company, New York, N. Y., 1956, p. 864.

Groggins, <u>Unit Processes in Organic Synthesis</u>, 5th Edition, McGraw Hill Book Company, New York, N.Y., 1958, p. 367. Cyclohexanol (hydrogenation of phenol)

 $C_6H_5OH + 3H_2 \longrightarrow C_6H_{11}OH$

 <u>Function</u> - Some cyclohexanol is produced by the catalytic hydrogenation of phenol. The reaction takes place over active nickel at 70-80°C and elevated pressure.

Cyclohexanone is a by-product of this reaction, and may be removed by condensation with benzaldehyde in the presence of alkali.

2. Input Materials

Pheno1

Hydrogen

Benzaldehyde

Alkali

3. Operating Parameters

Temperature: 70-80°C (126-176°F)

Pressure: not given

Catalyst: activated nickel

- 4. Utilities Not given
- 5. Waste Streams

Some phenol, cyclohexanol, and cyclohexanone may be present in air emissions from purification processes. Wastewater streams, if present, may contain alkali, benzaldehyde, cyclohexanone, and condensation products.

6. EPA Source Classification Code - None

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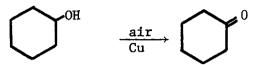
7. <u>References</u>

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Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 6 (1965), p. 684.

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Cyclohexanone (oxidation of cyclohexanol)



- <u>Function</u> Small quantities of cyclohexanone may be produced by passing cyclohexanol over copper catalyst with air at 140°C.
- 2. Input Materials

Cyclohexanol

Air

3. Operating Parameters

Temperature - 140°C

Pressure - Not given

Catalyst - Copper

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste water streams contain sodium hydroxide and dissolved organics. Light ends column vent emits cyclohexane, cyclohexanol and cyclohexanone.
- 6. EPA Source Classification Code None
- 7. References

Hedley, W. H., et al., <u>Potential Pollutants from Petrochemical Processes</u>, Final Report, Contract 68-02-0226, Task 9, December 1973, p. 224.

Waddams, A. L., <u>Chemicals from Petroleum</u>, 3rd Ed., John Murray Ltd., London, England, 1973, p. 136. Cyclohexanone (hydrogenation of phenol)

 OH + $^{2H}_2$ \longrightarrow

 Function - Some cyclohexanone is produced by a hydrogenation reaction similar to that employed to make cyclohexanol from phenol. The distinguishing variation is the milder catalyst used in this process.

Phenol and hydrogen are fed to a hydrogenator, where they are reacted in the liquid phase at 100-200°C and 1-4 atm pressure in the presence of a palladium-on-carbon catalyst. After scrubbing and cooling, the reaction mixture is removed to a distillation column, where high boilers are removed and cyclohexanone is recovered. This method accounts for approximately 20% of the total of cyclohexanone produced commercially in the United States.

2. <u>Input Materials</u> - Basis kg cyclohexanone Phenol - 1.005 kg Hydrogen - 0.64 m³

Palladium-on-charcoal - small

3. Operating Parameters

Temperature - 100-200°C (212-392°F)

Pressure - 101-404 kPa (1-4 atm)

Catalyst - Palladium-on-charcoal

4. Utilities - Not given

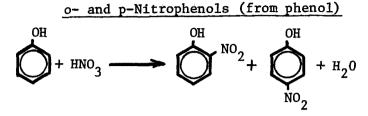
- 5. <u>Waste Streams</u> Air vent systems contain some hydrogen. Waste water from the scrubber will contain phenol, small quantities of cyclohexanol and cyclohexanone. Vents from the overhead take-off system in the distillation process will emit cyclohexanol and cyclohexanone.
- 6. EPA Source Classification Code None
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals - Part 3," "Chemical Engineering," March 18, 1974, p. 92.

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 6 (1965), p. 686.

Waddams, A. L., <u>Chemicals From Petroleum</u>, 3rd Edition, John Murray, London, England, 1973, p. 136.

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, Inc., 1975, p. 306-307.



1. <u>Function</u> - Some o- and p-nitrophenol is produced by the nitration of phenol with dilute nitric acid at low temperatures. The presence of an OH group on the ring activates it and permits a significant amount of oxidation resulting in a relatively large proportion of by-products. The nitration produces the ortho-isomer in about a 4x excess. The overall yield however, is 40% ortho, 13% meta, 14% para, and 33% oxidation products. The more volatile ortho isomer is almost quantitatively stripped from the crude product by steam distillation. The residue is heated and recrystallized in dilute acid to obtain the para isomer.

2. Input Materials

Phenol - for o-nitrophenol - 1.69 kg/kg product for p-nitrophenol - 5.20 kg/kg product total product - 1.28 kg/kg product

Nitric acid (20% aqueous)

3. Operating Parameters

Temperature - ~20°C (~68°F)

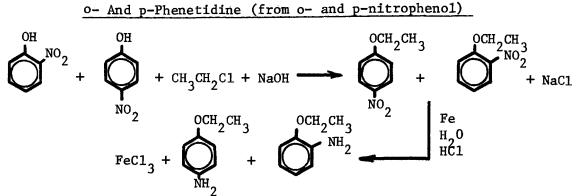
Pressure - 101 kPa (1 atm)

4. <u>Utilities</u>

Not given

- 5. <u>Waste Streams</u> Process waste effluents probably contain a variety of resinous by-products, dinitrophenols and trinitrophenols, oxalic acid, nitric acid, phenol, and small amounts of p-nitrophenol.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 13 (1967), p. 892, 893.



1. <u>Function</u> - Ortho- and para-phenetidine are usually prepared from nitrophenol isomers by ethylation (Williamson Reaction) and reduction. The initial step is the formation of the ethyl-phenyl ether by the displacement of chloride from the ethyl chloride by the o- or para-nitrophenate ion. Either ethyl chloride or diethyl sulfate may be used as the alkylating agent.

The nitrated phenol ether is then reduced to the corresponding amine using iron turnings and hydrochloric acid as the reducing system.

2. Input Materials

o- and p-Nitrophenol Ethyl sulfate or ethyl chloride Sodium hydroxide Hydrochloric acid Iron filings Water

3. Operating Parameters

Alkylation	Reduction
Temperature - 20-30°C (68-86°F)	Temperature - 200°C (392°F)
Pressure - 101 kPa (1 atm)	Pressure - 101 kPa (1 atm)

4. Utilities

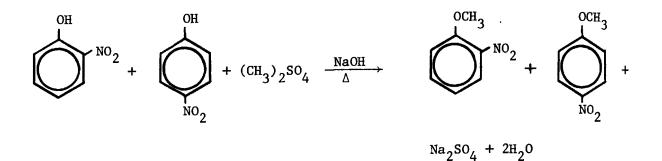
Not given

- 5. <u>Waste Streams</u> Aqueous wastes from separation probably contain sodium chloride, ethyl chloride, ethyl alcohol, nitrophenol and phenetidene isomers, and a variety of reduction by-products. Ethyl chloride, ethyl alcohol, and HCl may be discharged from reactor vents and various types of purification equipment.
- 6. EPA Source Classification Code None

7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New york, N.Y., Vol. 2 (1963), p. 422, 423.

Nitroanisoles (from nitrophenol)



- <u>Function</u> The o- and p-isomers of nitroanisole are produced by methylating the corresponding isomers of nitrophenol with a reagent such as dimethyl sulfate. The reaction is carried out in hot aqueous sodium hydroxide.
- 2. Input Materials

o- and p-Nitrophenol Dimethyl sulfate Sodium hydroxide Water

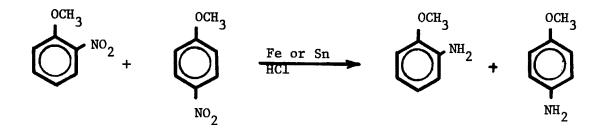
- 3. Operating Parameters not given
- 4. Utilities not given
- 5. <u>Waste Streams</u> Air and water effluents from separation probably contain quantities of sodium hydroxide and sodium sulfate (water only), dimethyl sulfate, and reaction by-products such as methanol.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 15 (1968), p. 148, 168.

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ANISIDINE

(reduction of nitroanisole)



 Function - Ortho- and para-anisidines are produced from o- and pnitroanisole by reduction with tin or iron filings and hydrochloric acid.

The ortho and para isomers are separated by steam distillation.

2. Input Materials

o- and p-Nitroanisole Hydrochloric acid

Tin or iron filings

3. Operating Parameters

Not given

4. Utilities

Not given

- 5. <u>Waste Streams</u> Liquid and/or solid wastes from purification may contain iron or tin salts and other reaction by-products.
- 6. EPA Source Classification Code 3-01-034-01
- 7. References

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Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition,

Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 422.

Nony1pheno1

 $c_{6}H_{5}OH + c_{9}H_{18} \rightarrow HOC_{6}H_{4}C_{9}H_{19}$

 <u>Function</u> - Nonylphenol is commercially prepared by the alkylation of phenol with a mixture of isomeric nonylenes (propylene trimers). The reaction is carried out at 50-100°C and 345 kPa (3.4 atm) in the presence of boron trifluoride catalyst.

The conversion takes place in the liquid phase and yields a mixture of isomers, mostly para- with some 2,4-dinonyl substitution. Both continuous and batch processes are used.

Following alkylation, the crude product is washed several times and heated under vacuum to remove traces of reactants and water. The final purification step is a vacuum distillation at 10-20 mm Hg.

2. Input Materials

Phenol - 0.46 kg/kg product

Nonene - 0.76 kg/kg product

3. Operating Parameters

Temperature: 50-100°C (122-212°F)

Pressure: 345 kPa (3 atm)

Catalyst: BF₃

- 4. Utilities Not given.
- 5. <u>Waste Streams</u> The main source of pollution is the wastewater from the product washing step. The water contains spent catalyst, phenol, and traces of product.

6-728

6. EPA Source Classification Code - None

7. <u>References</u>

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 7", "Chemical Engineering", June 24, 1974, p. 155.

Hedley, W. H., <u>et al.</u>, <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Technomic Publishing Co., 1975.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 908.

Octylphenol

$$c_{6}^{H_{5}OH} + c_{8}^{H_{16}} \longrightarrow HOC_{6}^{H_{4}} c_{8}^{H_{17}}$$

 Function - Octylphenol is prepared by alkylating phenol with isobutylene dimer. The product is a mixture of isomers.

The reaction conditions and purification procedures are similar to those used in nonylphenol production.

2. Input Materials

Phenol

Diisobutylene

H₂SO₄

3. Operating Parameters

Temperature: 120°C (248°F)

Pressure: Not known

Catalyst: H₂SO₄

- 4. Utilities Not given.
- 5. <u>Waste Streams</u> The principal waste stream from this process is the product wash water. This may contain phenol, sulfuric acid and traces of octylphenol.
- 6. EPA Source Classification Code None.
- 7. References

Goldstein, R. F., <u>The Petroleum Chemicals Industry</u>, John Wiley and Sons, Inc., New York, N.Y., 1958, p. 191-2.

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 149.

Dodecy1pheno1

 $C_6H_5OH + C_{12}H_{24} \longrightarrow HOC_6H_4C_{12}H_{25}$

 Function - Dodecylphenol is produced from phenol and propylene tetramer (dodecene), and consists mainly of a mixture of palkylphenols derived from various isomeric branched-chain dodecylenes.

The alkylation process is quite similar to that used to make nonylphenol.

2. Input Materials

Phenol - 0.38 kg/kg product Dodecene - 0.86 kg/kg product

3. Operating Parameters

Temperature: 50-100°C (122-212°F)

Pressure: 345 kPa (3 atm)

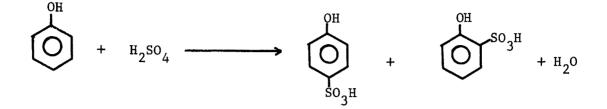
Catalyst: BF3

- 4. Utilities Not given.
- 5. <u>Waste Streams</u> The main source of pollution is the waste water from the product washing step. The water contains spent catalyst, phenol and traces of dodecylphenol.
- 6. EPA Source Classification Code None.
- 7. References

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 7", "Chemical Engineering", June 24, 1974, p. 155. Hedley, W. H., <u>et al.</u>, <u>Potential Pollutants from Petrochemical</u> Processes, Technomic Publishing Co., 1975.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 1 (1963), p. 908.

Phenolsulfonic Acids (from phenol)



 <u>Function</u> - Phenolsulfonic acid is commercially prepared by the direct sulfonation of phenol with concentrated sulfuric acid at 100°C.

The yield based on phenol is approximately 94%. Although the p-isomer predominates (96%), some o-phenolsulfonic acid is also produced.

2. Input Materials

Phenol - 0.57 kg/kg product

Sulfuric acid (conc.) - 0.60 kg/kg product

3. Operating Parameters

Temperature: 100°C (212°F)

Pressure: Not given

- 4. Utilities Not given.
- <u>Waste Streams</u> The principal pollutant from this process should be spent caustic, present in the waste water from caustic washing operations.
- 6. EPA Source Classification Code None.
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 15 (1968), 211 and Vol. 19, (1969) p. 311-18.

Allyl Chloride

$$CH_{3}CH=CH_{2} + Cl_{2} \xrightarrow{500^{\circ}C} ClCH_{2}CH=CH_{2} + HCl$$

 <u>Function</u> - Allyl chloride is made by chlorinating propylene at 400-500°C. At temperatures of 300°C and less, addition to the double bond is the predominant reaction and 1,2-dichloropropane is formed.

The reaction is carried out in an adiabatic reactor designed to provide rapid and intimate mixing. The reaction temperature is controlled by balancing the mole ratio of the feed (usually 4 moles of propylene to one mole of chlorine) and the propylene preheat temperature. The commonly used temperature range is 500-510°C, at 200 kPa (1.9 psig).

2. Input Materials

Propylene - 723 kg/Mg product (71%) Chlorine - 1.323 Mg/Mg product (70%)

3. Operating Parameters

Temperature: 500-510°C (932-950°F)

Pressure: 200 kPa (1.97 atm)

4. Utilities

Not given

5. Waste Streams

Absorber vent (air) Propylene - 13.5 kg/Mg product Ethyl chloride - 13.5 kg/Mg product The water pollution source from the allyl chloride process would probably be spent caustic from the absorber.

6. EPA Source Classification Code - None

7. <u>References</u>

Anon., "Air Pollution from Chlorination Processes," prepared for OPA, Environmental Protection Agency, Contract No. CPA 70-1, March 1972.

Muller, R. G., "Glycerine and Intermediates," Report No. 58, Stanford Research Institute, Menlo Park, California, 1969.

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corp., Park Ridge, N.J., 1974, p. 75,76.

Propylene Chlorohydrin (from ally1 chloride)

 $CH_2 = CH - CH_2C1 + H_2SO_4 \longrightarrow CH_3 - CH - CH_2C1$ $OSO_2OH OH$ $CH_3 - CH - CH_2C1 + H_2O \longrightarrow CH_3 - CH - CH_2C1$

- <u>Function</u> Small quantities of propylene chlorohydrin are produced by the acid catalyzed hydration of allyl chloride. This system yields 1-chloro-2-propanol free of 2-chloro-1-propanol.
- 2. Input Materials

Ally1 chloride

Water

Sulfuric acid

3. Operating Parameters

Temperature - 3.55-4.56 MPa (35-46 atm)

Pressure - 170-240°C (338 - 464°F)

Catalyst - sulfuric acid

4. Utilities

Not given

- 5. <u>Waste Streams</u> Although no specific information was available, wastewater streams from the purification section may contain traces of sulfuric acid, allyl chloride, and propylene chlorohydrin.
- 6. EPA Source Classification Code None

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 310.

G. Frosberg and L. Smith, Acta Chem. Scand., 1, 578 (1947).

Hancock, E. G., <u>Propylene and Its Industrial Derivatives</u>, John Wiley and Sons, New York, N.Y., 1973, p. 225.

INDUSTRIAL ORGANIC CHEMICALS

Allyl Alcohol (from allyl chloride)

 $H_2C=CHCH_2C1 + NaOH \xrightarrow{H_2O} H_2C=CHCH_2OH + NaC1$

1. Function - Some allyl alcohol is prepared from propylene glycol.

One competitive route to allyl alcohol involves the hydrolysis of allyl chloride with dilute (5%) caustic solution. The reaction is run at 150-160° C and a pressure of 1.38 MPa (14 atm).

The alcohol is recovered by injecting steam to form the waterallyl alcohol azeotrope. The water is removed by ternary allyl ether azeotrope. A second distillation then yields pure allyl alcohol. The principal by-product is allyl ether which can be minimized by the addition of dilute caustic solution at a rate such that the pH is maintained in the range 8-11.

2. Input Materials

Allyl chloride

Sodium hydroxide (5% aqueous solution)

Allyl ether

3. Operating Parameters

Temperature: 150-160° C (302-320°F) Pressure: 1.38 MPa (14 atm)

4. Utilities

Not given

5. <u>Waste streams</u> - The principal pollutant sources in this process are probably distillation waste water and solvent handling. Allyl chloride and allyl alcohol, as well as diallyl ether, may be involved. Spent caustic waste streams from the reactor may also contain allyl chloride and allyl alcohol.

6. EPA Source Classification Code

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 1 (1963), p. 588.

Fanbaun, A. W., H. A. Cheney and A. J. Charniavsky, <u>Chem. Eng.</u> Prog., <u>43</u>, 280, (1947).

U.S. Patent 2,318,033.

Astle, M. J., <u>The Chemistry of Petrochemicals</u>, Reinhold Publishing Corp., New York, N.Y., 1956, p. 196-197. Glycerol (from allyl chloride via allyl alcohol) Cl₂ + H₂O HOCl + HCl

 $CH_2 = CHCH_2OH + HOC1 \longrightarrow CH_2OHCHOHCH_2C1$

 Function - Some glycerol is produced from allyl chloride via preliminary hydrolysis to allyl alcohol (see Process No. 317). The allyl alcohol is then chlorohydrinated with aqueous chlorine solution to yield a mixture of monochlorohydrins.

The chlorohydrin intermediates are converted to glycerol in 90% yield (based on allyl alcohol) by hydrolysis with sodium hydroxide:

 $CH_2OHCHOHCH_2C1 + NaOH \longrightarrow CH_2OHCHOHCH_2OH + NaC1$

The crude product is a dilute aqueous solution containing 5% or less of glycerol. To obtain a high purity product, the crude mixture is first concentrated to about 80% glycerol in multipleeffect evaporators. Salt produced by the reaction is removed by centrifuging. Additional concentration of the product, followed by final desalting, yields 98% glycerol. Finally, colored substances are removed by solvent extraction and the product is refined by steam-vacuum distillation.

2. Input Materials

Allyl alcohol - 0.70 kg/kg product Chlorine Water Sodium bicarbonate 10% aqueous solution

3. Operating Parameters

Temperature: hydrochlorination - 14°C (57.2°F) hydrolysis - 150°C (302°F) Pressure: hydrochlorination - 100 KPa (1 Atm) hydrolysis - elevated

- 4. Utilities Not given
- 5. <u>Waste Streams</u> The vents from the acid scrubber may omit hydrogen chloride and chorine. Waste water will contain some sodium salts, allyl alcohol and acids.
- 6. EPA Source Classification Code None.
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 10, (1966) p. 624. Glycerol (from epichlorohydrin)

 $\begin{array}{c} \text{CH}_2\text{OCHCH}_2\text{C1} + \text{H}_2\text{O} \longrightarrow \text{HOCH}_2\text{CHOHCH}_2\text{C1} \\ \text{HOCH}_2\text{CHOHCH}_2\text{C1} + \text{NaOH} \longrightarrow \text{CH}_2\text{OCH} \text{ CH}_2\text{OH} + \text{H}_2\text{O} + \text{NaC1} \\ \begin{array}{c} \text{CH}_2\text{OCHCH}_2\text{OH} + \text{H}_2\text{O} \longrightarrow \text{HOCH}_2\text{CHOHCH}_2\text{OH} \\ \end{array}$

 <u>Function</u> - The production of glycerol from epichlorohydrin involves a series of three reactions carried out at 157-180°C and 1.14 MPa (11.2 Atm). First, epichlorohydrin is hydrated to monochlorohydrin in basic solution.

Glycerol chlorohydrin is then dehydrochlorinated to glycidol by treatment with caustic.

In the final reaction, glycidol is hydrated to glycerol.

Pipe reactors are used in this process with residence times of 7-9 minutes. The crude glycerol product is purified in the manner described in Process No. 318

2. Input Materials

Epichlorohydrin - 1.05 kg/kg product Sodium hydroxide - 0.49 kg/kg product Sodium carbonate - 73.0 g/kg product Toluene - 6.0 g/kg product HC1 - 83.5 g/kg product

3. Operating Parameters

Temperature: 157-180°C (315-356°F) Pressure: 1.14 MPa (11.2 Atm) Residence time: 420-540 sec.

- 4. <u>Utilities</u> Basis: 0.361 kg/sec capacity (25.2 M lb/yr) Cooling water - 124 dm³/sec (1960 gpm) Power - 547.2 MJ (152 kWh) Steam (300 psi) - 4.10 kg/sec (32,520 lb/hr) (2.07 MPa) Process water - 3.03 dm³/sec (48 gpm)
- 5. Waste Streams -

Glycerol purification section - second effect evaporator (water) Glycerol - 4.5 kg/Mg product

Glycerol purification section - centrifuge (solid) Sodium chloride - 431 kg/Mg product

Glycerol purification section - centrifuge (solid) Sodium chloride - 431 kg/Mg product

Glycerol purification section - film evaporator (water) Glycerol - 9.5 kg/Mg product Sodium chloride - 82.5 kg/Mg product Miscellaneous impurities - 61 kg/Mg product

Glycerol purification section - toluene recovery column (water) Toluene - 4.5 kg/Mg product

Glycerol purification section - light ends column (water) Glycerol - 0.95 kg/Mg product Toluene - 1.55 kg/Mg product

- 6. EPA Source Classification Code None.
- 7. <u>References</u>

Hedley, W. H., <u>et al.</u>, <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Technomic Publishing Co., 1975.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 10 (1966), p. 624. Propylene Oxide (peroxidation of propylene)

$$2(CH_3)_3CH + \frac{3}{2}O_2 \longrightarrow (CH_3)_3COOH + (CH_3)_3COH,$$

 $(CH_3)_3COOH + CH_2=CHCH_3 \longrightarrow CH_2-CHCH_3 + (CH_3)_3COH$

 Function - Increasing quantities of propylene oxide are now being produced by the peroxidation of propylene. The organic peroxygen carrier is usually t-butyl hydroperoxide, formed by the liquid-phase air oxidation of isobutane at 125-150°C and 3.55 MPa (35 Atm) in the presence of soluble molybdenum catalysts.

t-Butyl alcohol is the principal by-product of this reaction and also functions as a product.

After separation, the t-butyl hydroperoxide is used to oxidize propylene to propylene oxide and is reduced in the process to tbutyl alcohol. Tungsten, vanadium, or molybdenum catalyst systems catalyze this liquid-phase epoxidation.

It has been reported that the yield of propylene oxide from propylene is about 93% of the theoretical. However, this process yields considerably more t-butyl alcohol than propylene oxide (2.2 kg/kg propylene oxide).

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2. Input Materials
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Propylene - 0.78 kg/kg propylene oxide Isobutane \sim 3 kg/kg product

Air

3. Operating Parameters

Temperature: isobutane oxidation - 125-150°C (257-302°F) epoxidation - not given Pressure: isobutane oxidation 3.55 MPa (35 Atm) epoxidation - not given Catalyst: tungsten, vanadium, or molybdenum ([Mo(CO)₂] systems Utilities - 100 kg/sec capacity (70 \overline{M} 1b/yr) 4. Cooling water - $1.89 \text{ m}^3/\text{sec}$ (30,000 gpm) Refrigeration - 454 Mg (500 tons) Electricity - 3600 MJ (1000 kW) Steam - 12.6 kg/sec (100,000 1b/hr) at 4.14 MPa (40.8 Atm) Inert gas - 23.6 sdm^3/sec (300 scfh) 5. Waste Streams Hydroperoxide preparation section - absorber (air) Isobutane - 3.5 kg/Mg product n-Butane - 0.5 kg/Mg product Propylene oxide recovery section - vent from vaporizing column (air) Propylene - 10 kg/Mg product Solvent recovery section - evaporator waste (liquid and (solid) Toluene - 1.0 kg/Mg product Heavy ends - 50.0 kg/Mg product Propylene oxide purification section - off gas from column to flare (air) Ethylene oxide - 2.0 kg/Mg product Acetalahyde, etc. - 3.5 kg/Mg product EPA Source Classification Code - None. 6.

7. References

Hedley, W. H., <u>et al.</u>, <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Technomic Publishing Co., 1975. <u>1,2,3-Trichloropropane</u> (from propylene)

$$H_3^{C-CH=CH_2} + 2Cl_2 \longrightarrow ClCH_2 - CH - CH_2 Cl + HCl_2$$

- Function 1,2,3-Trichloropropane is made by chlorinating propylene at low temperature (25-40° C). The principal product of this reaction is propylene dichloride. In the absence of a catalyst however 20 percent of the product is 1,2,3-trichloropropane. The products are easily separated by distillation.
- 2. Input Materials

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Propylene
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Chlorine

Propylene dichloride

3. Operating Parameters

Temperature: 25-40° C (77-104°F)

Pressure: 100 KPa (1 atm)

- 4. Utilities Not available
- 5. <u>Waste streams</u> Overhead gas streams contain chlorine, propylene, hydrogen chloride some propylene dichloride.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Astle, M. J., <u>The Chemistry of Petrochemicals</u>, New York, N.Y., Reinhold Publishing, 1956, p. 60-62.

PROCESS NO. 322

Propylene Dichloride

 $H_3CCH=CH_2 + Cl_2 \longrightarrow CH_3CHC1CH_2C1$

1. <u>Function</u> - Propylene dichloride is produced as a by-product of the propylene chlorohydrin process for the synthesis of glycerin. Some may also be produced as a by-product of the chlorination of propylene to produce allylchloride. Propylene dichloride does not itself have industrial uses however it may be easily cracked to produce carbon tetrachloride and perchloroethylene.

The chlorine necessary to react with the propylene is present as a result of the equilibrium HOC1 + HC1 $\stackrel{\rightarrow}{\leftarrow}$ C1₂ + H₂0. The formation of propylene dichloride is promoted when the olefin concentration in the propylene chlorohydrin process falls too low or when the chlorohydrin concentration exceeds 5-6% in the system. Under the usual operating conditions 0.1 kg of propylene dichloride is formed per kg of propylene oxide.

2. Input Materials

Propylene

Chlorine

Water

3. Operating Parameters

 Temperature:
 30-40° C (86-104°F)

 Pressure:
 100 KPa (1 atm)

4. Utilities*

Cooling water	259dm ³ /sec (4100 gpm)
Nitrogen	23.6 dm^3/sec (3000 cfh)
Power	648 MJ (180 KW)
Refrigeration	1.109 Gg (1222 tons)
Steam	7.31 Kg/sec (58,000 1b/hr)

- 5. <u>Waste Streams</u>* Propylene dichloride is a by-product of propylene chlorohydrin production and as such the waste streams will be identical to this process. Air vent streams contain propylene and chlorine. Waste water contains HCl, HOCl, some chlorohydrin.
- 6. EPA Source Classification Code None.
- 7. References

Waddams, A. L., <u>Chemicals from Petroleum</u>, 3rd Edition, John Murray, London, 1973, p. 137-138.

Astle, M. J., <u>The Chemistry of Petrochemicals</u>, Reinhold Publishing Corp., New York, 1956, p. 60-61.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5 (1964), p. 2-3.

*See propylene chlorohydrin waste streams.

Dichloropropenes

$$CH_2 = CHCH_3 + 2Cl_2 \longrightarrow CHC1 = CHCH_2C1 + CH_2 = CHCHCl_2 + 2HCI_3$$
90% 10%

 Function - 1,3-Dichloropropene and 3,3-dichloropropene are the chief secondary products of allyl chloride manufacture, which involves the high-temperature reaction of propylene and chlorine.

The dichloropropene yield may be increased by using an excess of chlorine or smaller amounts of propylene. Chlorination at temperatures below 300°C yields the addition product, 1,2-dichloropropane.

The reaction is carried out in the vapor phase under conditions similar to those used in the production of allyl chloride, temperature 500-510°C (932-950°F) and 142-284 kPa (1.4-2.8 atm). The propylene is preheated to 250-350°C (482-662°F) to prevent the addition of chlorine to the double bond on mixing. The product ratio can be controlled to some extent by the ratio of reactants charged. The use of excess chlorine to increase the product ratio of 1,3-dichloropropene to allyl chloride is limited, however, by the possibility of over chlorination of the propylene.

The product mixture is separated by passing the effluent gas stream into an HCl absorption column. Next the gas is passed into an organic absorbing solvent to remove propylene. The chlorinated propylenes are separated by fractional distillation.

2. <u>Input Materials</u> - Basis - 1 kg product

Propylene - 0.723 kg/kg

Chlorine - 1.32 kg/kg

3. Operating Parameters

Temperature: preheater - 340°C (650°F)

reactor - 500-510°C (932-950°F)

Pressure: 142-284 kPa (1.4-2.8 atm)

- 4. <u>Utilities</u> Not given
- 5. <u>Waste Streams</u> The principal sources of pollution are the air vent stream on the absorber which may emit propylene and the waste water from the absorber which contains spent caustic.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Astle, M. J., <u>The Chemistry of Petrochemicals</u>, Reinhold Publishing Corp., New York, 1956, p. 60-61.

Hedley, W. H., et al., "Potential Pollutants from Petrochemical Processes," prepared for Control Systems Laboratory, NERC, Environmental Protection Agency, Contract No. 68-02-0226, Task No. 9, 1973, p. 136.

SECTION IX TOLUENE

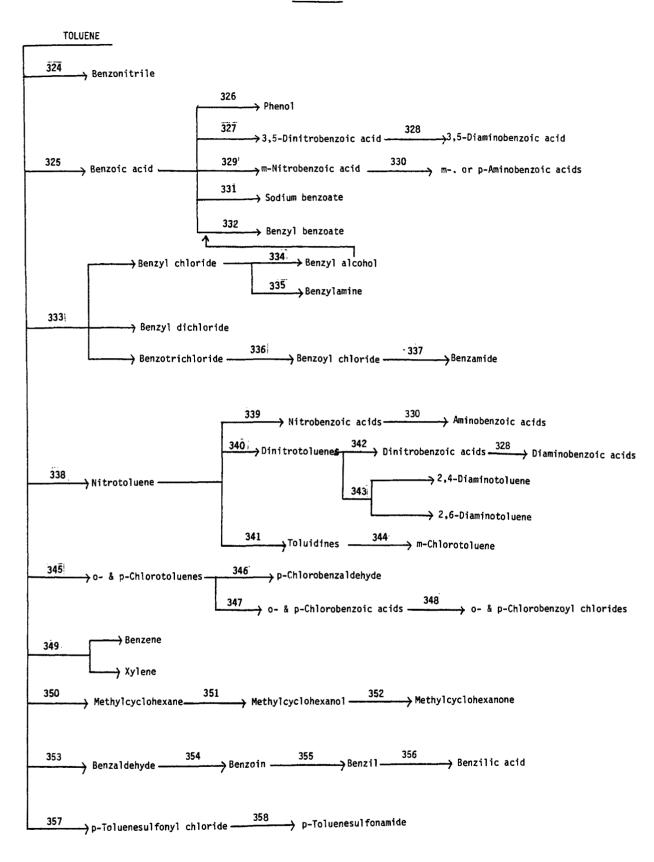
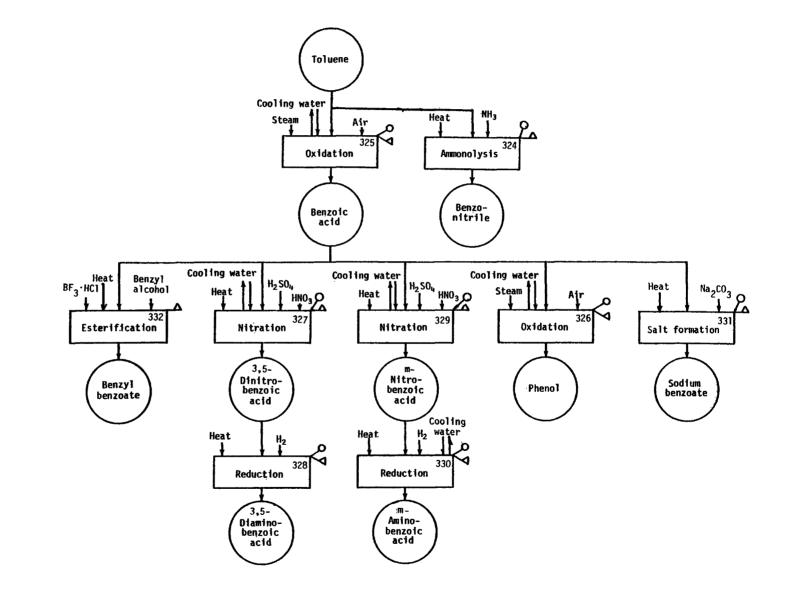


Figure 17. Toluene Section Chemical Tree



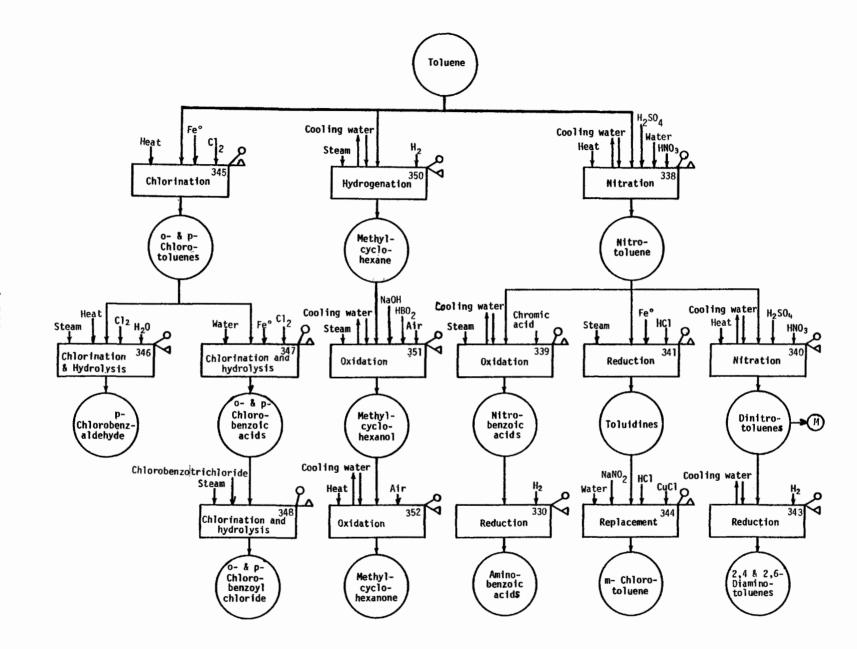


Figure 18. Toluene Section Process Flow Sheet (Cont.)

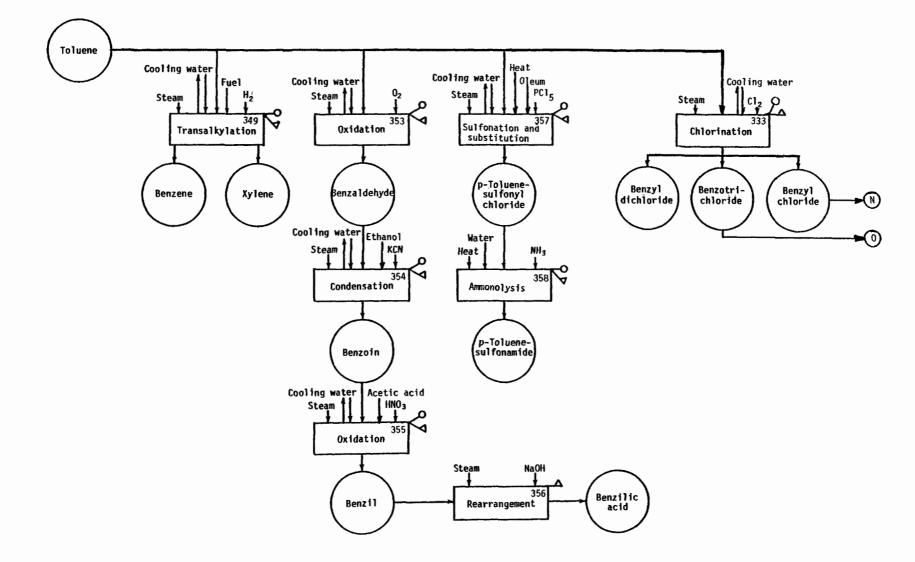


Figure 18. Toluene Section Process Flow Sheet (Cont.)

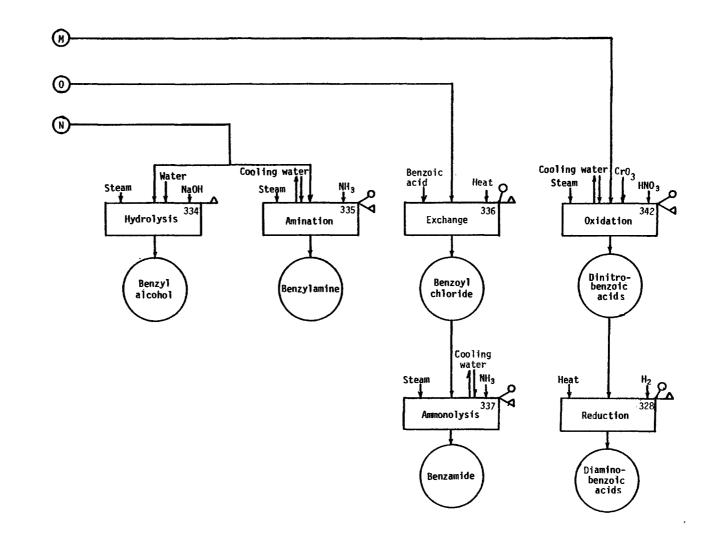
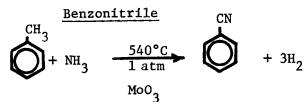


Figure 18. Toluene Section Process Flow Sheet (Cont.)

INDUSTRIAL ORGANIC CHECMICALS



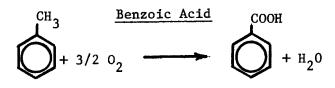
- 1. <u>Function</u> Benzonitrile is produced in the United States chiefly by the ammonolysis of toluene in the vapor phase. The reaction takes place in a reactor that consists of a shell containing a catalyst chamber heated with a heat transfer medium from outside the shell. Benzonitrile produced in each pass is stripped from the exit gases which are recycled with makeup toluene and ammonia. The optimum operating conditions are described as employing molybdenum oxide on alumina as a catalyst, maintaining temperature between 524-552°C, and operating at pressures of 1 atm. of less. Conversion per pass ranges from 5-10%. Overall yields from 60-85% based toluene are reported.
- 2. <u>Input Materials</u> Basis: 1 kg benzonitrile Toluene - 0.89 kg Ammonia - 0.16 kg

MoO₃ catalyst - quantities not given

- 3. <u>Operating Parameters</u> Temperature: 524-552°C (975 - 1025°F) Pressure: 101 KPa (1 atm) or less Yield: 60-85% based on toluene
- 4. Utilities Quantities not given
- 5. <u>Waste Streams</u> Off gases contain ammonia, hydrogen cyanide and toluene. Air vent streams from the purification system would contain toluene.
- 6. EPA Source Classification Code None

7. <u>Reference</u>

Astle, M.J., <u>Industrial Organic Compounds</u>, Reinhold Publishing Corporation, New York, 1961, p. 227-228.



 <u>Function</u> - The preferred industrial process in the manufacture of benzoic acid, in the United States, is the air oxidation of toluene.

The reaction is carried out in the liquid phase at 110 - 150°C at pressures of 273 - 490 kPa (2.7 - 5 atm) using a cobalt salt usually the naphthenate as the catalyst. The heat of reaction is controlled by refluxing toluene and water-jacketed cooling. Water of reaction is removed from condensed off gas before the toluene is returned to the reactor heel. Material in the autoclave heel continously overflows to a stripper where toluene is recycled. The bottoms, which contains the crude benzoic acid, are sent to a crystallizer, or a distillation tower. Yields of relatively purematerial of 90% based on toluene are cited.

2. Input Materials - Basis 1 kg benzoic acid.

Toluene .83 kg/kg

Air 1.71 kg/kg

Cobalt naphthenate .008 - .024 kg/kg

3. Operating Parameters

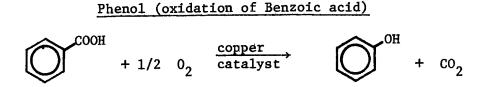
Temperature: 110 - 150°C (230-302°F) Pressure: 273 - 490 kPa (2.7 - 5 atm) Catalyst: 0.1 - 0.3% of toluene

- 4. <u>Utilities</u> Based on 100 M lb/yr capacity Water - .545 m³/sec (518,000 gPh) Steam - 5.93 kg/sec. (47,000 lbs/hr) Power 2,320
- 5. <u>Waste Streams</u> Air vent stream from the purification contains toluene, some benzaldehyde and some benzyl alcohol. The air vent from the separator (centrifuge) contains toluene vapors. The waste water contains benzoic acid, benzaldehyde and benzyl alcohol.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1967), p. 420-439.

Sittig, M., Organic Chemical Process Encyclopedia, 2nd Edition, Noyes Development Corporation, Park Ridge, New Jersey, 1969, p. 101.

Hedley, W.H. et. al., <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Final Report, Contract 68-02-0226, Task 9, MRC-DA, 406, December 1973, p. 111-112.



 <u>Function</u> - Benzoic acid is melted in biphenyl, mixed with a small amount of manganese-promoted cupric benzoate and fed to an oxidizer (reactor). A mixture of air and steam is sparged into the reactor, where the benzoic acid is oxidized to phenol.

Purification is accomplished by distillation. Phenol and water are taken off overhead and benzoic acid is taken from the column bottom and returned to the reactor. The bottoms may be extracted first, to recover organics for recycle. The phenol and water are separated by azeotropic distillation.

2. Input Materials

Benzoic acid

Air

Catalyst

3. Operating Parameters

Temperature - 230°C (446°F) Pressure - 138-172 kPa (1.36-1.7 atm) Mn-cupric benzoate - not given

4. Utilities - Not given

5. Waste Streams

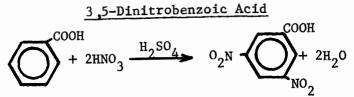
Centrifuged separator (solid) Tar -0.10 kg/kg phenol (204 lb/ton) Phenyl benzoate -0.0015 kg/kg phenol (3.1 lb/ton) 5. Waste Streams (continued)

Acetone -0.0018 kg/kg phenol (3.6 1b/ton) Manganese benzoate -0.005 kg/kg phenol (10 1b/ton) Copper benzoate -0.002 kg/kg phenol (4.3 1b/ton) Separator effluent Toluene -0.0011 kg/kg phenol (2.14 1b/ton)

- 6. EPA Source Classification Code None
- 7. References

Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley & Sons, New York, N.Y., 1975, p. 618-619.

Hedley, W. H., et al., "Potential Pollutants from Petrochemical Processes," Prepared for Environmental Control Systems Laboratory, NERC, Environmental Protection Agency, Contract No. 68-02-0226, Task No. 9, 1973, p. 111-112. INDUSTRIAL ORGANIC CHEMICALS

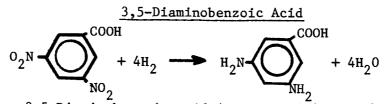


- Function 3,5-Dinitrobenzoic acid is primarily manufactured by nitrating benzoic acid with a mixture of fuming nitric and sulfuric acids. The sulfuric acid forms a hydrated molecule and removes the water of reaction. The nitration occurs at elevated temperatures (70-90°C).
- 2. <u>Input Materials</u> Basis: 1 kg 3,5-dinitrobenzoic acid Benzoic acid - 0.6 kg HNO₃ - 0.6 kg (99+% acid) H₂SO₄
- 3. <u>Operating Parameters</u> Temperature: 70-90°C (158 - 194°F) Pressure: atmospheric
- 4. Utilities

Quantities not given

- 5. <u>Waste Streams</u> Off gas will contain oxides of nitrogen and some sulfur dioxide. Waste water from the purification process contains nitric and sulfuric acids, benzoic acid and some 3,5-dinitrobenzoic and 3-nitrobenzoic acid.
- 6. EPA Source Classification Code None
- 7. References

Astle, M.J., <u>Industrial Organic Nitrogen Compounds</u>, American Chemical Society Mongraph Series, Reinhold Publishing Corporation, New York, 1961, p. 334.



- 1. <u>Function</u> 3,5-Diaminobenzoic acid is commercially produced by the catalytic reduction of dinitrobenzoic acid. The process is similar to that used to manufacture m,p-aminobenzoic acids. The reaction occurs in the liquid phase at about 1 atmosphere pressure. The hydrogen is fed in large excess to a slurry of catalyst, dinitrobenzoic acid and water at temperatures greater than 85°C. The product acid is then filtered to remove catalyst and cooled to precipitate the product.
- 2. <u>Input Materials</u> Basis: 1 kg diaminobenzoic acid

Dinitrobenzoic acid - 1.5 kg Hydrogen - >0.03 kg Catalyst - quantities not given

3. Operating Parameters

Temperature: 85°C (185°F) Pressure: 100KPa (1 atm) Catalyst: Pd, Cu, Pt, or Ni

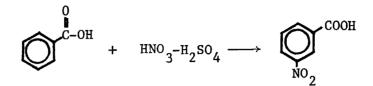
4. Utilities

Not given

- 5. <u>Waste Streams</u> Off-gas from the reactor contains hydrogen. Waste water contain 2,5-dinitrobenzoic acid and 3,5-diaminobenzoic acid.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3, (1964) pp. 435-436.

m-Nitrobenzoic Acid



 <u>Function</u> - The product of the nitration of benzoic acid is m-nitrobenzoic acid with the principal byproduct being ortho-nitrobenzoic acid. Almost no p-nitrobenzoic acid is formed and the ortho isomer can be minimized by proper selection of the reaction temperature.

The rate of reaction increases with temperature, however the amount of m-isomer decreases with temperature while the amount of ortho isomer increases. The operating temperature must be a compromise between optimum rate of production and purity of product.

The reaction is carried out in sulfuric acid and a maximum in rate of nitration is found at 89-90% sulfuric acid.

2. Input Materials

Benzoic acid

Nitric acid

Sulfuric acid

3. Operating Parameters

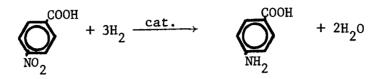
Temperature - 25-45°C Pressure - Atmospheric Sulfuric acid - 90%

- 4. Utilities Not given
- <u>Waste Streams</u> Air vent streams contain oxides of nitrogen.
 Waste water streams will contain benzoic acid, some m-nitrobenzoic acid.
- 6. EPA Source Classification Code None

7. <u>References</u>

Hoggett, J. G., Moodie, R. B., Penton, J. R., and Schofield, K., <u>Nitration and Aromatic Reactivity</u>, Cambridge University Press, London, 1971, pp. 16, 18, 151, 160, 178.

m-or p-Aminobenzoic Acids



 <u>Function</u> - These acids are manufactured chiefly by the reduction of m.or p-nitrobenzoic acids by catalytic hydrogenation or, less frequently, by reduction with tin or iron and HCl. One patent for p-aminobenzoic acid claims an 85% yield when hydrogenating p-nitrobenzoic acid with a Pt or Pd catalyst in water.

A thin slurry of p-nitrobenzoic acid and catalyst in water is agitated at about 800 RPM and held at 85°C. Hydrogen is then introduced until no more absorption is noted and the p-nitrobenzoic acid dissolves as the reaction proceeds. The partial pressure of H_2 is from 200-700 mm Hg in the atmospheric pressure process. The product acid is filtered and cooled to precipitate a 99% product. The mother liquor from precipitation is reused in the next batch.

- 2. <u>Input materials</u> Basis: 1 kg of aminobenzoic acid Nitrobenzoic acid (m-, or p-) - 1.2 kg H₂ - >0.04 1.2 kg Catalyst: Pt, Mi, Pd, or Cu - quantities not given
- 3. Operating parameters

Temperature: 85°C

Pressure: atmospheric

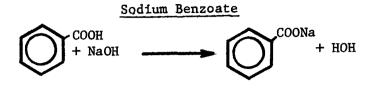
Agitation: 800 RPM

4. Utilities

Quantities not given

- 5. <u>Waste streams</u> The off gas from the hydrogenation reactor contains hydrogen, when iron powder and hydrochloric acid is used hydrogen chloride is present in the off gas. Waste wash water from the centrifuge contains aminobenzoic acid, ferric chloride and HC1. The product contains some m-or p-nitrobenzoic acids.
- 6. EPA Source Classification Code
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publisher, New York, N.Y., Vol. 3 (1967) p. 434-436.



- Function Sodium benzoate is generally produced by the addition of benzoic acid to a hot solution of sodium carbonate or sodium hydroxide. The resulting solution is treated with charcoal or, in some cases, potassium permanganate, and is filtered and dried.
- 2. <u>Input Materials</u> Basis: 1 kg sodium benzoate Benzoic acid - 0.85 kg NaOH - >0.3 kg NagCO₃ (alternate) - >0.74 kg Charcoal - quantity not given

KMnO₄ - quantity not given

- 3. <u>Operating Parameters</u> Quantities not given
- 4. Utilities

Quantities not given

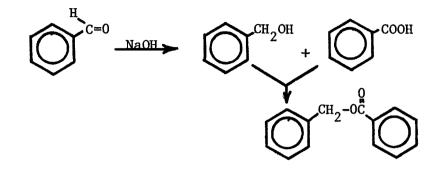
- 5. <u>Waste Stream</u> Waste water streams contain sodium hydroxide or sodium carbonate and water use to wash the benzoate product contains NaOH, Na₂CO₃, NaHCO₃ and some sodium benzoate. There will be some carbon dioxide in the off-gas.
- 6, EPA Source Classification Code

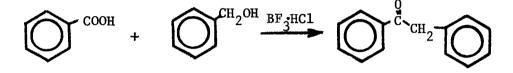
None

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1967), p. 433.

Benzyl Benzoate





- <u>Function</u> Benzyl benzoate is produced commercially by two routes. The most commonly used commercial process is the Cannizaro reaction in which benzaldehyde, catalyzed by sodium hydroxide, undergoes an oxidation-reduction reaction giving benzyl alcohol and benzoic acid. These compounds undergo an esterification catalyzed by the NaOH to produce benzyl benzoate. The second process involves a direct esterification of benzoic acid and benzyl alcohol catalyzed by a boron trifluoride hydrochloric acid complex. The reactions
 are carried out at 75-90°C at 1 atm pressure.
- <u>Input Materials</u> Basis: 1 kg benzyl benzoate (benzaldehyde route)

Benzaldehyde - 2 kg

NaOH catalyst/reactant - quantities not given

3. Operating Parameters

Temperature: 75-90°C (167-194°F)

Pressure: 100 kPa (1 atm)

Catalyst: NaOH or any strong base

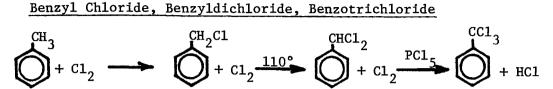
4. <u>Utilities</u>

Quantities not given

- 5. <u>Waste Streams</u> Waste water contains sodium hydroxide, sodium benzoate and some benzaldehyde. No significant quantities of air pollutants would result from this process.
- 6. EPA Source Classification Code None

7. References

Shreve, R. N., <u>Chemical Process Industries</u>, McGraw-Hill Book Co., New York, 1967, p. 512.



 Function - The chlorination of toluene to the three products, mono-, di-, and tri-chloromethyl benzene, can be considered as a single process since the extent of chlorination cannot be exactly controlled.

The use of excess toluene will result in a predominance of benzyl chloride. Stopping the reaction when the product density reaches 1.283 will result in a product that is predominantly benzyl chloride and allowing the reaction to continue until the product density reaches 1.38 will yield benzotrichloride.

The reaction must be carried out in glass or polymer lined reactors since iron catalyses nuclear substitution. The temperature is controlled in this exothermic reaction by the reflux of toluene.

2. Input Materials

Toluene

PCl₃ or PCl₅ (optional)

3. Operating Parameters

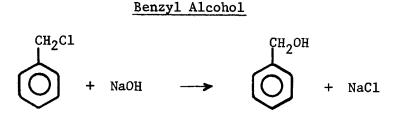
Temperature: 110° C Catalyst: PCl₃ or PCl₅ (optional)

Spec. Eqpt.: Cl₂ resistant container for benzyl - glass for benzotrichloride

- 4. Utilities Not given
- 5. <u>Waste streams</u> HCl is neutralized with a weak base before disposal, so chloride salts will be waste.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 5(1969), p. 281-287.

Austin, G. T., "The Industrially Significant Organic Chemicals-Part 1," "Chemical Engineering," January 21, 1974, p. 132.



 Function - Benzyl alcohol is manufactured in the United States exclusively by hydrolysis of benzyl chloride. Sodium hydroxide or sodium carbonate is usually employed but use of the carbonate minimizes formation of by-products such as dibenzyl ether.

A charge consisting of 1349.4 kg (2,975 lb) of water, 1428.8 kg (3,150 lb) benzyl chloride, and 714.4 kg (1,575 lb) sodium carbonate is put into a 3.785 m^3 (1,000 gal) steel jacketed reactor, agitated, and heated to reflux for 24 hours. The reaction is cooled, sodium chloride added to saturation, and the layers allowed to separate. The lower aqueous layer is drained to the sewer while the upper layer of crude benzyl chloride is purified by vacuum distillation.

2. Input Materials

Benzyl chloride - 1.34 kg/kg alcohol Sodium carbonate - 0.67 kg/kg alcohol Water - 1.27 kg/kg alcohol

3. Operating Parameters

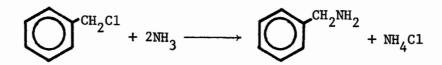
Temperatures: 210°C (410°F) Reaction Time: 24 hours Equipment: 3.75 m³ (1,000 gal) steel-jacketed reactor

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Aqueous layer saturated with sodium chloride and containing sodium carbonate used to be discharged to the sewer but may be disposed of differently now. Waste water may contain traces of benzyl chloride.

6. EPA Source Classificiation Code - None

- 7. References
 - Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 3 (1964), p. 443-444.

Benzyl Amine



- 1. <u>Function</u> Benzylamine is produced commercially by the ammonolysis of benzyl chloride. The reaction is carried out at elevated temperatures (100-200° C) and pressure (100 KPa-2.76 MPa) and a 4 to 10 X excess of aqueous ammonia. The major product under these conditions of excess ammonia is the primary amine, although some secondary, tertiary and quaternary salts are formed. The water and ammonia are separated and recycled and the amines separated and purified by distillation.
- 2. Input Materials

Benzyl chloride

65% aqueous ammonia

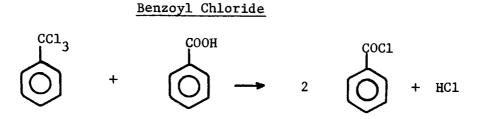
3. Operating Parameters

Temperature: 150-200° C (302-392°F) Pressure: 100 kPa-2.76 MPa (1-27 atm)

- 4. Utilities Not given
- 5. <u>Waste streams</u> by-product secondary and tertiary amines quaternary salts are formed. Ammonium chloride sent to other processes.
- 6. EPA Source Classification Code None
- 7. References

Astle, M. J., <u>Industrial Organic Nitrogen Compounds</u>, Reinhold Publishing Corp., New York, N.Y., 1961, p. 6-8. 7. <u>References</u> (continued)

Shreve, R. N., <u>Chemical Process Industries</u>, McGraw Hill Book Company, New York, N.Y., 1967, p. 815-816.



- 1. <u>Function</u> Benzotrichloride and catalyst (zinc chloride impregnated on pumice) are run into a glass-lined steel reactor which has previously been half filled with molten benzoic acid. A glasscoated agitator is used to stirr the mixture and tank temperature is maintained at 122-130°C for about eight hours. A Karbate (impregnated carbon) condenser removes the hydrochloric acid formed in the reaction. The benzoyl chloride is purified by distillation.
- 2. Input Materials

Benzotrichloride Benzoic acid

3. Operating Parameters

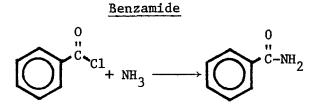
Temperature: 122-130°C (252-266°F)

Pressure: 101 kPa (1 atm)

Catalyst: zinc chloride on pumice

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Waste waters may contain traces of benzoic acid, benzotrichloride, and zinc chloride.
- 6. EPA Source Classification Code None
- Kirk-Othemer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 3 (1964), p. 424.

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- 1. <u>Function</u> Benzamide is produced by the acylation of ammonia with benzoyl chloride. The reaction may be carried out under anhydrous conditions by passing anhydrous ammonia into a solution of benzoyl chloride in an inert solvent such as diethyl ether. In a commercial operation it is more usual to add the benzoyl chloride to a cold (0°C), concentrated aqueous solution of ammonia from which the benzamide percipitates. The crude benzamide is washed with water and purified by recrystallization.
- 2. Input Materials

Benzoyl chloride

Ammonia (anhydrous or concentrated aqueous solution)

3. Operating Parameters

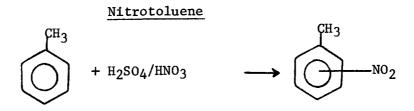
Temperature - $0^{\circ}C$ (32°F)

Pressure - 101 kPa (1 atm)

- 4. Utilities Not given
- <u>Waste Streams</u> Air streams may contain ammonia and some hydrogen chloride. Waste water from product recovery and purification contains ammonia, HC1, NH_AC1 and benzoic acid.
- 6. EPA Source Classification Code None

7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 69-71.



- 1. <u>Function</u> Nitrotoluenes are manufactured by nitration of toluene by a nitrating agent usually consisting of a mixture of sulfuric and nitric acid and recycled fortified acid. The ratio of H_2SO_4 , HNO_3 and H_2O as well as the temperature and rate of agitation has to be controlled to ensure high yield, favorable ratio of desired isomer, and to minimize dangerous side reactions. Nitration is done at relatively low temperatures ($\leq 40^{\circ}C$). The crude product is washed with water, alkali, and water. The isomeric nitrotoluenes are then separated from toluene and other organics by steam distillation and subsequently dried. Separation of the o-, m-, and pisomers is done by a series of vacuum distillations.
- 2. <u>Input Materials</u> basis: 1000 kg yield of nitrotoluene Toluene - 690 kg Nitric acid - 450 kg Sulfuric acid - 810 kg Water - 240 kg 10% NaOH solution - 22 kg
- 3. Operating Parameters

Temperature: 25°C [initially] (77°F)

35-40°C [final] (95-104°F)

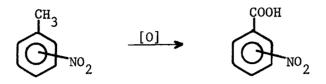
Equipment: Toluene nitration is normally carried out in castiron or stainless-steel nitrators sized for 3,000 gal batches of toluene.

- 4. Utilities None given
- 5. <u>Waste Streams</u> Heavy tar residues from final fractionation stage are disposed of and would contain a complex mixture of organic by-products in the amount of approximately 40 kg/1000 kg nitrotoluene. Waste waters may contain also alkali used in washings, spent acid, and soluble organic by-products.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 13 (1967), p. 844-848.

Albright, L.F. and Hanson, C., "Industrial and Laboratory Nitrations," ACS Symposium Series 22, 1976, p. 190-218.

Nitrobenzoic Acids



- <u>Function</u> m, and p-Nitrotoluene may be oxidized with chromic acid to yield the corresponding m-, and p-nitrobenzoic acids. o-Nitrotoluene is not affected by chromic acid. o-Nitrotoluene is oxidized by potassium permanganate to give o-nitrobenzoic acid.
- 2. Input Materials

Nitrotoluene

Potassium permanganate (to oxidize o-nitrotoluene or p-nitrotoluene)

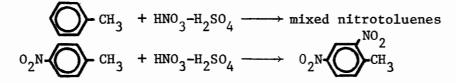
3. Operating Parameters

Temperature: 25-50°C (77-122°F)

Pressure: 101 kPa (1 atm)

- 4. Utilities Not given
- 5. <u>Waste Streams</u> Neutralization of reaction waste liquors would give wastewater streams containing salts of the acid or alkali used.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N. Y., Vol. 13 (1967), p. 848-850. Dinitrotoluene (nitration of toluene)



1. <u>Function</u> - The reaction of nitric acid and toluene to produce dinitrotoluene can be thought of as a two stage reaction. The first stage being the mononitration of toluene. The nitrating agent is the acid mixture 48% sulfuric, 18% nitric, 14% nitrosylsulfuric, 12% water and 8% nitroorganics, which is typical of the fortified spent acid from the dinitration stage. The temperature is initially 25° C raised to 40° C to complete the reaction. The reactor must be vigorously agitated since the toluene is not very soluble in the mixed acids. A typical product mix is 62% ortho, 33% para and 3% meta. The mixture may be separated or used as is in the second nitration step.

The acid mixture used in the second stage contains, for a typical mixture, 50% sulfuric, 20% nitric, 12% nitrosylsulfuric 6% water and 12% nitroorganics. The temperature must be increased to 55 to 85° C at 1 atm pressure. Nitration of the pure p-isomer yields 2,4-dinitrotoluene with no significant amounts of by-product. Nitration of the unresolved product of the mononitration yields an 80-20 mixture of 2,4 and 2,6dinitrotoluene, respectively. The product mixture may be separated into the pure isomers by crystallization or used directly for the manufacture of toluenediisocyanate.

2. Input Materials

Toluene:	506.25 kg/Mg of product
Nitric Acid:	721.25 kg/Mg of product
Sulfuric Acid:	1311 kg/Mg of product
Nitrosyl sulfuric ad	cid: 262 kg/Mg of product

3. Operating Parameters

Temperature:	mononitration	25 - 40° C	(77-104°F)
	dinitration	50-85° C	(122–185°F)
Pressure:	100 KPa		

- 4. Utilities Not available
- 5. Waste Streams

<u>Decantors</u> (water) - Wastewater from the decantors, containing small amounts of nitrated toluene, is discarded and may end up in sewer lines.

<u>Absorber</u> (air) - Reactor vents go to the absorber to oxidize the NO to NO₂ which is absorbed in water to produce nitric acid. Vent from absorber discharges air and unabsorbed oxides of nitrogen. <u>Washer vents</u> (air) - Air saturated with water and some nitrated toluenes will be discharged from the washer vent.

- 6. EPA Source Classification Code None
- 7. References

Austin, G. T., "Industrially Significant Organic Chemicals," "Chemical Engineering," April 15, 1974.

Sittig, M., "Pollution Control in the Organic Chemical Industry," Noyes Data Corporation, Park Ridge, N.J., 1974, p. 126-27.

Brownstein, A. M., "U.S. Petrochemicals - Technologies, Markets and Economics," The Petroleum Publishing Company, Tulsa, Oklahoma, 1972.

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 $\bigotimes_{\text{NO}_2}^{\text{NO}_2} + \text{Fe} \xrightarrow{\text{HCl}} \bigotimes_{\text{CH}_3}^{\text{NH}_2} + \text{FeCl}_3$ $\bigotimes_{\text{NO}_2}^{\text{CH}_3} + 3\text{H}_2 \xrightarrow{\text{cat}} \bigotimes_{\text{NH}_2}^{\text{CH}_3} + 2\text{H}_2^0$

Toluidines

1. <u>Function</u> - The toluidines are made from the nitrotoluenes by reduction. The process most commonly used is the metal-acid process, the most widely utilized combination being iron and hydrochloric acid. Nitrotoluene, powdered iron, and a small amount of water are mixed in a reaction vessel. Hydrochloric acid is added at a rate such that the heat of reaction will maintain a brisk rate of reaction. The converted toluidine is steam distilled, from the reactor, separated, and purified by distillation. Approximately 3.1% of the toluidine remains in the aqueous layer most of which may be recovered by solvent extraction.

Catalytic hydrogenation has been replacing the iron-acid method in recent years yielding a purer product at lower cost. The reduction is done in the vapor phase, passing hydrogen and the nitrotoluene vapor through a fluidized bed of copper clad silica gel.

2. Input Materials

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Iron reduction:
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Nitrotoluene

Hydrochloric acid - iron powder

Catalytic reduction.

Hydrogen

Nitrotoluene

3. Operating Parameters

Iron reduction:	Temperature:	100° C (212°F)
	Pressure:	100 kPa (1 atm)
Catalytic reduction:	Temperature:	250-300° C (482-572°F)
	Pressure:	238 kPa (2.5 atm)
	Catalyst:	Copper on silica

4. Utilities - Not available

5. <u>Waste streams</u> - the major waste water stream is from the steam stripper for the aqueous layer and contains approximately 0.2% toluidine as well as some HC1. Some toluidine hydrochloride is lost in the waste water from the reactor after steam distillation. Air streams contain hydrogen chloride and some particulates.

6. EPA Source Classification Code - None

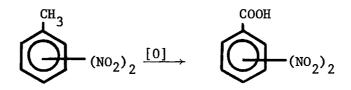
7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 2 (1963), p. 79, 421.

Ibid., Vol. 13 (1967), p. 852.

Kent, J. A., <u>Riegel's Handbook of Industrial Chemistry</u>, 7th Edition, Van Nostrand-Reinhold Company, New York, N.Y., 1974.

Dinitrobenzoic Acids



- 1. <u>Function</u> 2,4-Dinitrotoluene and 2,6-dinitrotoluene are obtained by the dinitration of toluene by conventional nitrating process. The corresponding benzoic acids may be obtained by nitrating in the presence of CrO_3 or $Na_2Cr_2O_7$.
- 2. Input Materials

T**oluen**e

Na2^{Cr20}7 HN03^{-H2}S04

3. Operating Parameters

Temperature: 0°C (32°F) Pressure: 101 kPa (1 atm) Time: 1 to 2 hr

- 4. Utilities not given
- 5. <u>Waste Streams</u> Typical nitration waste streams (NO_x, spent acid) should be present as well as some chromium salts in the sludge.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

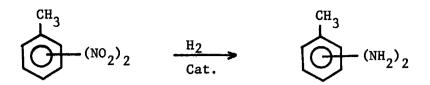
Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 13 (1967), p. 851.

7. References (continued)

Tadeuz, Urbanski, et al., <u>Biul. Wojskowej Akad. Tech.</u> 9, No. 97, 73-83 (1960).

Adolph, E. et al., <u>Tetrahedron</u>, 19(6), 801-7 (1963).

2,4- and 2,6-Diaminotoluenes



- Function The usual industrial dinitration of toluene gives a mixture of 2,4- and 2,6-dinitrotoluenes in a 80:20 ratio. A conventional liquid phase hydrogenation yields the 2,4- and 2,6-diaminotoluenes. The mixture of the diamines is used to manufacture the corresponding diisocyanates used in urethane manufacture.
- 2. Input Materials

Dinitrotoluenes - 1.57 kg/kg Diaminotoluenes Hydrogen - 0.106 kg/kg Diaminotoluenes

3. Operating Parameters

Temperature:	90-190°C (194-374°F)
Pressure:	606 kPa (6 atm)
Catalyst:	palladium on carbon
Phase:	liquid
Reactor type:	jacketed kettle
Solvent:	water

4. <u>Utilities</u> - Basis: 9.41 Gg (20.75 M lb)/yr. capacity (based on

DuPont patents)

Cooling water - 568 m³ (150,000 gal.)/hour Demineralized water - 681 m³ (180,000 gal.)/hour Steam - 5.94 Mg (13,100 lb)/hour Fuel - 5.9 GJ (5.6 M BTU)/hour Electricity - 634 MJ (176 kWh)/hour

5. Waste Streams

Recovery section (water), Toluidine - 11 gm/kg Diaminotoluenes Purification section (water), Toluenediamine - 9.8 gm/kg Diaminotoluenes

- 6. EPA Source Classification Code None
- 7. References

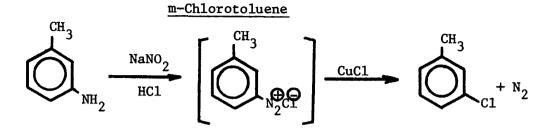
Kirk-Othmer, Encyclopedia of Chemical Technology, Interscience Publishers, New York, N.Y., 2nd Edition, Vol. 20 (1969), p. 562.

Yen, Y. C., <u>Isocyanates - Part I</u>, Report No. 1-A, Stanford Research Institute, Menlo Park, California, June 1968.

Sittig, M., Organic Chemical Process Encyclopedia - 1969, Noyes Development Corp., Park Ridge, N.J., 1969.

Albright, Lyle F., and Hanson, Carl, <u>"Industrial and Laboratory</u> <u>Nitrations"</u>, ACS Symposium Series 22, 1976, p. 314.

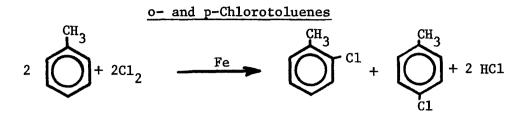
INDUSTRIAL ORGANIC CHEMICALS



- 1. <u>Function</u> m-Chlorotoluene is made by the replacement of the amino group of m-toluidine with a chlorine by formation of a diazonium salt and the reaction of the diazonium salt with cuprous chloride. The reaction is carried out by dissolving the m-toluidine in a 2.5X excess of aqueous hydrochloric acid containing the cuprous chloride. A solution of sodium nitrite is added giving nitrous acid in situ. The product is insoluble in water and separates as a nonaqueous layer. Purification is accomplished by distillation. Urea may be added to remove excess nitrous acid.
- 2. <u>Input Materials</u> Basis: 1 kg m-chlorotoluene meta-Toluidine - 0.85 kg Hydrochloric acid (2.5X excess) Sodium nitrite Cuprous chloride
- <u>Operating Parameters</u>
 Temperature: 0.5°C
 Pressure: 100 kPa (1 atm)
- 4. Utilities Not available
- 5. <u>Waste Streams</u> Air vent streams contain hydrogen chloride, nitrogen, nitric oxide and nitrogen dioxide. Waste water streams contain hydrochloric acid, m-toluidine hydrochloride, some copper salts and small quantities of m-chlorotoluene.

- 6. EPA Source Classification Code None
- 7. <u>References</u>

Astle, M. J., <u>Industrial Organic Nitrogen Compounds</u>, Reinhold Publishing Corp., New York, 1961, p. 198-200.



- 1. <u>Function</u> Ortho- and para-chlorotoluenes are prepared by direct catalytic chlorination of toluene. The reaction is carried out in a liquid phase reactor at a temperature of 110-130°C and 1 atmosphere pressure, in the presence of iron powder to facilitate ring chlorination. By-products of the reaction are dichlorotoluenes and higher chlorinated derivatives. These are separated from the mono-chloro products by distillation. The o- and p- isomers are separated by fractional crystallization.
- 2. <u>Input Materials</u> Basis: 1 Kg chlorotoluene

Toluene - .91 Kg/Kg Chlorine - .70 Kg/Kg Iron Turnings

Sodium hydroxide (10% aqueous to neutralize chlorinated toluenes)

3. Operating Parameters

Temperature - 110-130°C

Pressure - 100 kPa (1 atm)

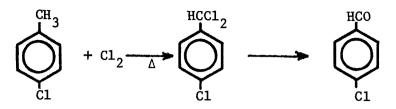
- 4. Utilities Not available
- 5. <u>Waste Streams</u> Air vent streams contain chlorine, hydrogen chloride and some toluene. Vent on absorber emits chlorine, some toluene. Water from decanter contains sodium hydroxide, sodium chloride some dichlorotoluenes. Vent stream from stripping column contains toluene.

6. EPA Source Classification Code - None

7. <u>References</u>

Faith, W.L. et al., <u>Industrial Chemicals</u>, 3rd Edition, John Wiley and Sons, New York, N.Y., 1965, p. 261-263.

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corporation, Park Ridge, N.J., 1974, p. 103. p-Chlorobenzaldehyde



1. <u>Function</u> - p-Chlorobenzaldehyde is produced by hydrolyzing pchlorobenzalchloride, a side chain chlorination product of pchlorotoluene. p-Chlorotoluene is chlorinated at 160°C and l atmosphere pressure in a glass lined reactor, to prevent metal catalyzed ring chlorination. The extent of chlorination is estimated by measuring the density of the reaction product. This method of control results in by-product of chlorobenzylchloride and chlorobenzotrichloride.

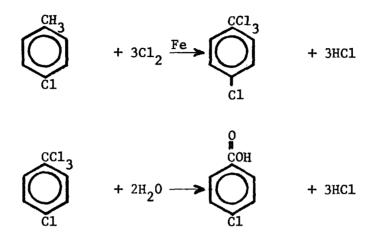
The crude chlorobenzal chloride is hydrolyzed by boiling water yielding chlorobenzaldehyde and by-products of chlorobenzylalcohol, and chlorobenzoic acid.

- 2. <u>Input Materials</u> Based on 1 Kg chlorobenzaldehyde Chlorotoluene - 0.9 Kg Chlorine - 70.5 Kg Water - 70.13 Kg
- 3. <u>Operating Parameters</u> Temperature - 160°C Pressure - 100 kPa (1 atm)
- 4. <u>Utilities</u> Not given

- 5. <u>Waste Streams</u> Vent on gas absorber emits hydrogen chloride and chlorine. Waste water streams may contain hydrochloric acid, benzoic acid, chlorobenzylalcohol and some chlorobenzaldehyde. Because the heat of reaction for the chlorination is controlled by the reflux of chlorotoluene some chlorotoluene vapors may be emitted.
- 6. EPA Source Classification Code None
- 7. References

Faith, W.L. et al., <u>Industrial Chemicals</u>, 3rd Edition, John Wiley and Sons, New York, N.Y., 1965, p. 120,121.

Chlorobenzoic Acids (o- and p-)



1. <u>Function</u> - Chlorobenzoic acids may be prepared by a variety of methods based on well-known reactions. The ortho and para acids can be made from o-chlorotoluene and p-chlorotoluene, respectively, by chlorinating the substituted toluene in the side chain to the chloro-benzotrichloride stage (indicated by the density of the reaction product), and then hydrolyzing.

Mixed o, p-acids are manufactured by reacting mixtures of o, p-chlorotoluenes. The <u>meta</u> acid can be made by direct chlorination of benzoic acid.

2. <u>Input materials</u> - Basis: 1 kg p-chlorobenzoic acid p-chlorotoluene - 0.81 kg Chlorine - >1.3 kg Water - >0.23 kg

Catalyst - quantity not given

3. Operating parameters

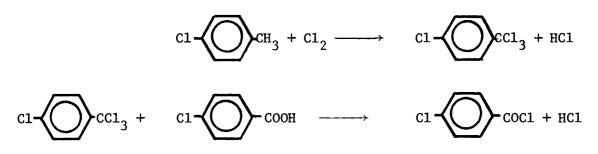
Temperatures: 160°C chlorination; 100°C hydrolysis Pressure: 100 kPa (1 atm) Catalyst: zinc chloride

- 4. Utilities none available
- 5. <u>Waste Streams</u> Hydrogen chloride is emitted from the vent in the gas absorber, possibly some chlorine is also emitted. Waste water streams may contain sodium hydroxide, sodium chloride, sodium chlorobenzoate, zinc chloride and by-products of chlorobenzaldehyde and chlorobenzylalcohol depending upon the purity of the chlorobenzotrichloride hydrolyzed.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishers, New York, Vol. 3 (1967), pp. 436-437.

Faith, W. L., D. B. Keyes and R. L. Clark, <u>Industrial Chemicals</u>, 3rd Edition, John Wiley and Sons Inc., New York, 1965, pp. 141-142.

Chlorobenzoyl Chlorides (o- and p-)



- Function Chlorobenzoyl chloride is made by the reaction of chlorobenzoic acid and chlorobenzotrichloride. This may be operated as part of the process for producing benzoic acid. The product, benzoic acid, is mixed with unhydrolyzed benzoic acid precursor, chlorobenzotrichloride and heated.
- 2. Input Materials

Chlorobenzoic acid

Chlorobenzotrichloride

3. Operating Parameters

Temperature: 150-250°C (302-482°F)

Pressure: 100 kPa (1 atm)

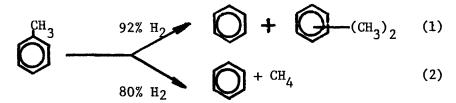
- 4. Utilities Not available
- 5. <u>Waste Streams</u> Vent from gas absorber emits some hydrogen chloride and chlorine. Bottoms from the distillation column contain unreacted chlorobenzoic acid and chlorobenzochloride.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Staff, <u>Chemical Origins and Markets</u>, Chemical Information Services, Stanford Research Institute, Menlo Park, California (1967), p. 21. 7. <u>References</u> (continued)

Hahn, A. V., <u>The Petrochemical Industry</u>, McGraw-Hill Book Co., New York, (1970), p. 518.

INDUSTRIAL ORGANIC CHEMICALS

Benzene and Xylenes (disproportionation; hydrodealkylation)



1. <u>Function</u> - Benzene and xylene are formed by the disproportionation of toluene. Benzene can be produced by the hydrodealkylation (2) of toluene. Both of these processes are becoming increasingly important because of the rising demand for benzene in industry. Petroleum stocks have been the principal sources of benzene in recent times; but the ratio of benzene/toluene/xylenes produced by the catalytic reformer processes is almost exactly opposite to the demand for these products. It was necessary therefore to develop process to produce benzene from toluene and xylene. Both catalytic and thermal processes are employed.

There are four major processes used to convert alkyl benzenes to benzene: Howdry (a fixed bed catalytic process), Hydeal (catalytic dealkylation), Hydrodealkylation, and the Thermal Hydrodealkylation (a non-catalytic, elevated temperature and pressure).

2. Input Materials

Hydrogen

Toluene

C₈ Aromatics

Alkylbenzenes

- 3. Operating Parameters
 - Detol: temperature 538-649° C (1000-1200° F) pressure - 3.5-8.3 MPa (34-82 atm) catalyst - poison resistant, non-noble metal compound pellets Hydeal: Not given

Hydrodealkylation: temperature - 593-760° C (110-1400° F)

pressure - 3.5-7.0 MPa (34-68 atm)

THD: Not given

- <u>Utilities</u> disproportionation of toluene Electric power - 263 MJ (73 kWh) Steam - 1.2 Mg (1.5 short tons) Cooling water (ΔT 10° C) - 2.1 Mg (3.6 short tons) Fuel - 2.0 GJ (0.7 x 10⁶ kcal)
- 5. <u>Waste streams</u> C₉ aromatic hydrocarbon plus diphenyl and higher condensed aromatics as bottoms. Lighter paraffins and olefins as overhead or raffinate. By-product formation 29 kg (64 lb)/ 1000 kg (metric ton) product.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Anon., "Detol," "Hydeal," "Hydrodealkylation," and "Thermal Hydrodealkylation," Pet. Refiner, <u>40</u>(11), 236, 251, 252, 298 (1961).

Mager, E. M., "Aromatics Production," <u>U.S. Petrochemicals,</u> <u>Technologies, Markets, and Economics</u>, Brownstein, A. M., Ed., The Petroleum Publishing Company, Tulsa, Okla., 1972, pp. 123-125.

Methylcyclohexane + H₂ catalyst

- 1. <u>Function</u> Methylcyclohexane is produced commercially by the catalytic reduction of toluene. Since the reaction is catalyzed by Raney nickel, a catalyst which is severly poisoned by sulfur compounds, it is necessary to desulfurize the toluene or to use sulfur-free toluene as the starting material. The reaction is carried out in the liquid phase at 220° C and pressures of 25-34 atm. It is usually carried out in a series of reactors to reduce the amount of recycle, cooling methylcyclohexane in order to avoid excessive catalyst bed temperatures which can lead to isomerization.
- 2. Input Materials

Toluene

Hydrogen

3. Operating Parameters

Temperature: 220° C to 270° C (428-518° F); average conditions 220° C (428° F) Pressure: 2.5-3.6 MPa (25-34 atm) Catalyst: Supported nickel or platinum catalyst

- 4. Utilities Not given
- 5. <u>Waste Streams</u> rearrangement by-products such as dimethylcyclopentanes, ethylcyclopentanes, and paraffinic residues as still bottoms or overheads.

- 6. EPA Source Classification Code None
- 7. <u>Reference</u>

Hydrocarbon Processing and Petroleum Refiner 40(11), 234, 1961.

 $\begin{array}{c}
\underbrace{\overset{\text{Methylcyclohexanol}}{\underbrace{}^{\text{CH}_{3}}} \\
+ 1/2 & 0_{2} & \underbrace{\overset{\text{HBO}_{2}}{\underbrace{}^{\text{NaOH}}} & \underbrace{\overset{\text{CH}_{3}}{\underbrace{}^{\text{CH}_{3}}} \\
\underbrace{\overset{\text{HBO}_{2}}{\underbrace{}^{\text{OH}_{3}}} \\
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- 1. Function Large scale manufacture of methylcyclohexanol employs the oxidation of methylcyclohexane. The process can start by the direct oxidation of methylcyclohexane. The oxidation is most preferably carried out in the presence of metaboric acid, although other special boron compounds can be used. Oxygen reacts with methylcyclohexane to form methylcyclohexyl hydroperoxide, which on reaction with metaboric acid is believed to form a peroxyborate. This peroxyborate is thought to react subsequently to make cyclohexyl borate esters. Caustic may be used in neutralization of product. The water of reaction must be maintained at very low levels or product yield is decreased. The process for producing methylcyclohexanol is similar, if not identical, in some cases to that used to produce cyclohexanol. Methylcyclohexanol is also produced by the hydrogenation of o, p-cresols.
- 2. <u>Input Materials</u> Basis: 1 kg methylcyclohexanol Methylcyclohexane - 0.98 kg Oxygen - 0.16 kg Metaboric acid - quantity not given Caustic - quantity not given
- 3. Operating Parameters

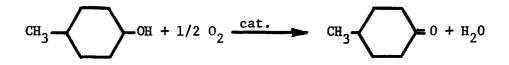
Temperature: 185 - 200°C (365-392°F) Pressure: 2040 - 4800 (20 - 47 atm) Catalyst: boric acid or none (5% of Hydrocarbon)

- 4. Utilities Quantities not given
- 5. <u>Waste Streams</u> The principal source of air pollution occurs during the removal of the water of reaction by azeotropic distillation of cyclohexane-water. Boric acid is recovered and cyclohexane is recycled. Some cyclohexane may be present in the air vent streams. Spent caustic from hydrolysis of borate esters as well as small quantities of cyclohexanol will be present in the waste process water.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Considine, D.M., <u>Chemical and Process Technology</u>, McGraw-Hill Book Company, New York, 1974, pp. 337-338.

Sittig, M., Organic Chemical Process Encyclopedia 1969, 2nd Edition, Noyes Development Corporation, Park Ridge, New Jersey, 1969, p. 203.

Waddams, A.L., <u>Chemicals from Petroleum</u>, 3rd Edition, John Murray, London, 1973, p. 240-241. Methylcyclohexanone



 <u>Function</u> - Commercial processes employ air oxidation of methylcyclohexanol to produce methylcyclohexanone.

The reaction occurs in a fixed bed multitubular reactor in the vapor phase. A silver or copper catalyst is used.

- 2. <u>Input Materials</u> Basis 1 kg methylcyclohexanone Methylcyclohexanol - 1 kg Air - >0.14 kg Catalyst - quantity not given
- 3. <u>Operating Parameters</u> Temperature: ~630°C (1166°F) Pressure: atmospheric

Catalyst: silver or copper

- 4. Utilities Not given
- 5. <u>Waste Streams</u> No specific information was found. Gaseous emissions would include methylcyclohexanol, methylcyclohexanone, and a host of by-products from side reactions depending on catalyst efficiency. The condensed water which is separated and disposed of may contain methylcyclohexanone as well as other organic impurities from the high temperature oxidation.

6. EPA Source Classification Code - None

7. <u>References</u>

Sittig, M., Organic Chemical Process Encyclopedia, 2nd Edition, Noyes Development Corporation, Park Ridge, N.J., (1969), p. 433.

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U.S. Patent 2,930,679 (March 29, 1960).

Benzaldehyde

$$\bigcup^{CH_3} + O_2(air) \xrightarrow{Cat.} \bigcup^{CHO} + H_2O$$

 Function - Toluene can be directly oxidized in the vapor phase to benzaldehyde by using a mixture of air and toluene vapors (14:1 weight ratios) in the presence of a 93% uranium oxide, 7% molybdenum oxide catalyst. Small amounts of CuO are added to minimize oxidation to maleic anhydride.

Direct oxidation of toluene is not the only process used. Some quantities are manufactured by hydrolyzing benzal chloride.

<u>Input Materials</u> - Basis: 1 kg Benzaldehyde (direct oxidation route)

Toluene - 2.2 kg

Air - 30.2 kg

Catalyst - quantity not given

3. Operating Parameters

Temperature: 500°C (932°F)

Pressure: 101 kPa (1 atm)

Catalyst: molybdenum oxide - 7%/uranium oxide - 93% with cuprous oxide

- 4. Utilities quantities not given
- <u>Waste Streams</u> By-products such as benzoic acid, maleic anhydride,
 CO, CO₂, anthraquinone, and high boiling oils; scrubber wastes.
- 6. EPA Source Classification Code None

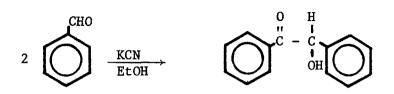
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7. <u>References</u>

Faith, W. L., et al., <u>Industrial Chemicals</u>, John Wiley and Sons, Inc., New York, N.Y., 3rd Edition, 1965, p. 120-124.

Hahn, A. V., <u>The Petrochemical Industry: Market and Economics</u>, McGraw-Hill Book Co., New York, N.Y., 1970, p. 519-518.

Benzoin



- Function Benzoin is manufactured by the reductive condensation of benzaldehyde in an alkaline cyanide solution. The reaction occurs in the liquid phase in alcohol (commonly ethyl alcohol) which will solubilize benzaldehyde, cyanide, and benzoin. The reaction is carried out at reflux conditions.
- 2. <u>Input Materials</u> Basis 1 kg benzoin Benzaldehyde - 1 kg Potassium cyanide catalyst - quantity unknown
- 3. Operating Parameters

Temperature - 80°C (reflux temperature of ethyl alcohol) (176°F)

Pressure - 101 kPa (1 atm)

Time for reaction - 1-3 hours

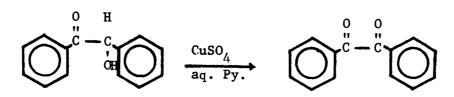
Catalyst - potassium cyanide

- 4. Utilities Not given
- 5. <u>Waste Streams</u> The reflux of ethyl alcohol to control the heat of reaction may cause the presence of ethanol and HCN in the vent streams. Potassium cyanide, ethanol, and benzaldehyde will be found in the waste water streams.
- 6. EPA Source Classification Code None

7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 3 (1967), p. 365.

Benzil



- 1. <u>Function</u> The α -diketone benzil is obtained in high yield by oxidation of benzoin with nitric acid in acetic acid solution or with copper sulfate in aqueous pyridine. Reaction occurs at reflux conditions.
- 2. Input Materials Basis: 1 kg benzil

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Benzoin - 1 kg
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CuSO₄, pyridine - quantities not given

Water or HNO3

Acetic acid

3. Operating Parameters

Temperature - 230°C (reflux condition) (446°F)

Pressure - 101 kPa (1 atm)

Catalyst - CuSO,

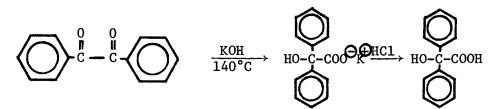
- 4. Utilities Not given
- 5. <u>Waste Streams</u> Pyridine, acetic acid, HNO₃, as well as products and reactants may be present in wastewater. The reaction occurs at reflux. Thus, pyridine, acetic acid, and nitric acid may be present in vent gas.
- 6. EPA Source Classification Code None

7. References

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition, Interscience Publishing Co., New York, N.Y., Vol. 12 (1967), p. 146-147.

U. S. Pat. 2,377,749 (June 5, 1945).

Benzilic Acid



1. <u>Function</u> - Benzilic acid is produced from benzil by a base catalyzed rearrangement. The reaction is run in water at slightly elevated pressure and a temperature of 140°C (melting point of benzil = 137°C). Alternately a sodium hydroxide-sodium bromate catalyst mixture is employed at a temperature of 85-90°C and ambient pressure.

At the conclusion of the reaction (4-5 hours) the sodium salt of benzilic acid is neutralized with hydrochloric acid and crystallized from the solution as it cools to room temperature. The product separated after washing, is of sufficient purity for use in most applications. Crystallization from benzene can be employed to produce a benzilic acid of superior purity.

2. Input Materials

Potassium hydroxide - 0.2 kg Benzil - 1 kg Hydrochloric acid - 0.16 kg

3. Operating Parameters

Temperature - 140°C

Pressure - Not given

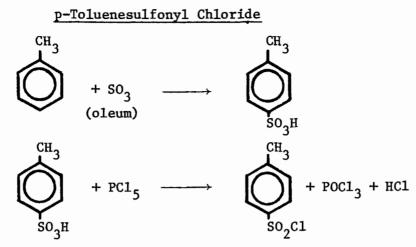
4. Utilities - Not given

- <u>Waste Streams</u> Air vent streams may contain some hydrogen chloride.
 Waste water contain potassium chloride, potassium hydroxide, sodium benzilate, minor amounts of benzilic acid.
- 6. EPA Source Classification Code None

7. References

Doering and Urgan, J. Am. Chem. Soc., <u>78</u>, 5938 (1956).

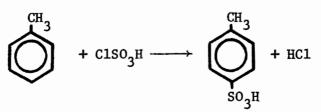
Ballard, D. A., and Dehn, W. M., Org. Syn. Coll., Vol. 1, 89 (1941).



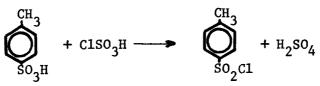
1. <u>Function</u> - p-Toluenesulfonyl chloride is produced, industrially from toluene, oleum and phosphorus pentachloride. The first stage produces p-toluenesulfonic acid. Toluene and oleum are combined to give o- and p-toluene sulfonic acid. The p-isomer is favored at higher temperatures, however the o-isomer can be isomerized to the p- by heating to 140°C. The solution is neutralized with Ba(OH)₂ or BaCO₃, percipitating BaSO₄ and leaving the sulfonic acids in solution from which they are recovered by crystallization.

The sulfonic acids are converted to the sulfonyl chlorides through the action of phosphorous pentachloride. The use of PCl_5 instead of Cl_2 obviates the need for non-ferrous reaction vessels and reaction in the absence of light.

An alternate route to p-toluenesulfonyl chloride is also a two step process using chlorosulfonic acid as both the sulfonating and the chlorinating reagent.



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An excess of chlorosulfonic acid is used to drive the reaction to completion.

 <u>Input Materials</u> - Basis - 1 kg p-toluenesulfonyl chloride (SO₃, PCl₅ route)

Toluene - 0.48 kg

01eum - 2.1 kg

 $PC1_5 - .31 \text{ kg}$

3. Operating Parameters

Temperature: sulfonation - 30-40°C (86-104°F)

chlorination - 80°C (176°F)

Pressure: 100 kPa (1 atm)

- 4. <u>Utilities</u> Not given
- 5. <u>Waste Streams</u> The air vent stream from the gas absorber will contain hydrogen chloride. Barium sulfate and phosphate will precipitate on neutralization of the sulfonating solution. Waste wash water streams may contain small amounts of sulfuric and phosphoric acids and their salts as well as p-toluenesulfonic acids.
- 6. EPA Source Classification Code None
- 7. <u>References</u>

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 19 (1969), p. 298-99.

Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 595, 612.

p-Toluenesulfonamide

$$clo_2s$$
 $ch_3 + 2NH_3$ h_3c $so_2NH_2 + NH_4cl$

- Function Toluenesulfonamide is prepared by reacting toluenesulfonyl chloride with ammonia.
- 2. Input Materials Basis: 1 kg toluenesulfonamide

Ammonia - 0.1 kg

Toluenesulfonyl chloride - 1.1 kg

Catalyst - quantity not given

3. Operating Parameters

Temperature: room temperature or lower Pressure: atmospheric

4. Utilities

Quantities not given

- 5. <u>Waste Streams</u> Hydrogen chloride may appear in the air vent streams as well as ammonia although most of the HCl, reacts with the excess ammonia gas used, to form ammonium chloride. The NH₄Cl will be present in the waste water streams as well as small amounts of toluenesulfonamide.
- 6. EPA Source Classification Code

None

7. Reference

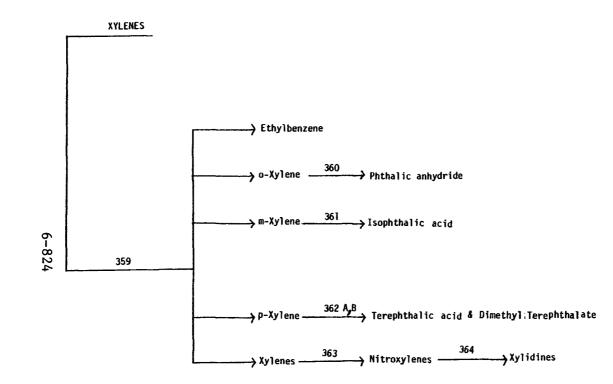
Chemical Technology, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 611-613.

Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd Edition,

Interscience Publishers, New York, N.Y., Vol. 19 (1969), p. 255-260.

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SECTION X XYLENES



XYLENES

Figure 19. Xylenes Section Chemical Tree

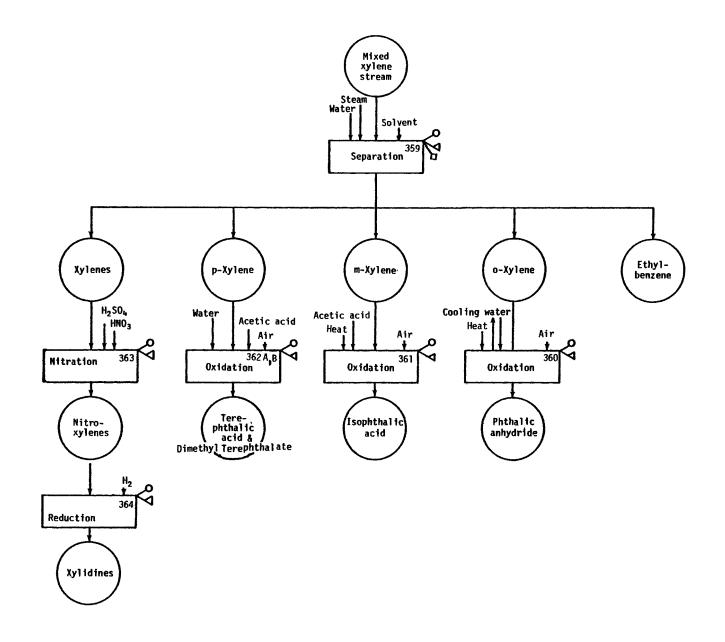


Figure 20. Xylenes Section Process Flow Sheet

o-, m-, and p-Xylenes and Ethyl Benzene

 <u>Function</u> - Over 90% of the domestic production of xylenes is the result of catalytic reforming or hydroforming of certain petroleum fractions. Disproportionation and transalkylation of toluene is a minor source of xylenes. A typical cut of C₈ stock has the following composition:

	Wt. % in distillate	M.P., °C	B.P., °C
ethyl benzene	9–13%	-95.0	136.2
p-xylene	17-20%	13.2	138.4
m-xylene	45-53%	-47.9	139.1
o-xylene	18-24%	-25.2	144.4

By a process termed super-fractionation, ethyl benzene (99.7% purity) can be separated from the xylenes. In addition, o-xylene can be separated from the other xylenes by fractional distillation.

The differences in melting points allow for practical separation of the m- and p-isomers.

The dried feedstock (\sim 10 P.P.M. H₂O) is cooled to -40°C and passed to a crystallizer at -62°C to -66°C. Crystals of p-xylene formed are centrifuged, partially melted and recrystallized at -31°C. The mother liquor (rich in m-xylene) can be recycled or isomerized to yield more p-xylene.

Isomerization processes may employ a platinum on a silicaalumina support as a catalyst. Isomerization occurs in the vapor

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phase in the presence of hydrogen at temperatures around 450°C and pressures in the 10-25 atm range. The product of isomerization is recycled to the crystallization unit.

Other processes of interest in the isolation of xylenes include:

1. Preferential adsorption of p-xylene on a solid absorbent from a mixture of C_8 aromatics (Parex process).

2. Separation of pure m-xylene <u>via</u> sulphonation, formation of clathrates, or formation of an $HF \cdot BF_3$ complex.

3. Separation of m- and p-isomers by formation of Wernertype complexes.

2. Input Materials

C_o aromatics

3. Operating Parameters

Separation of ethyl benzene

(Three 200 ft column in series containing 350 plates. Reflux ratio

25:1 to 50:1.)

Crystallization (p-xylenes)

1st - Temperature: -62°C-66°C (144-151°F)
Pressure: not given

2nd - Temperature: -31°C (88°F) Pressure: not given

Isomerization

Temperature: -450°C (842°F) Pressure: 1.01-2.53 MPa (10-25 atm) Catalyst: Platinum on a silica-alumina support

4. Utilities

Distillation of ethylbenzene and o-xylene: Not given Crystallization of p-xylene (Chevron Process, Crude Feed)

Isomerization of m-xylene (alumina-silica catalyst, Crude Feed)

5. Waste Streams

Distillation - Not given.

2

<u>Isomerization</u> - Separator has an off-gas vent that would expel organic vapors.

- 6. EPA Source Classification Code None.
- 7. <u>References</u>

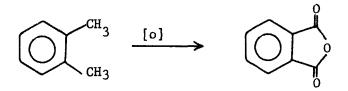
Brownstein, A. M., <u>U. S. Petrochemicals</u>, The Petroleum Publishing Company, Tulsa, Oklahoma, 1972.

Gloyna, E. F., and Ford, D. L., "The Characteristics and Pollution Problems Associated with Petrochemical Wastes", for TWPCA, Contract No. 14-12-461, February, 1970. Ries, H. C., "Xylenes Separation", Report No. 25, Stanford Research Institute, Menlo Park, California, 1967.

Anon., "Development Document for Effluent Limitations Guidelines and Standards of Performance", prepared for Environmental Protection Agency, Contract No. 68-01-1509, June, 1973.

Austin, G. T., "The Industrially Significant Organic Chemicals -Part 9", "Chemical Engineering, "August 5, 1974, p. 99.

Waddams, A. L., <u>Chemicals From Petroleum</u>, 3rd Edition, John Wiley and Sons, New York, N. Y., 1973, p. 209-221. Phthalic Anhydride (from o-xylene)



1. <u>Function</u> - Phthalic anhydride (PAN) is manufactured by air oxidation of o-xylene in a fixed catalyst bed reactor. Oxidation is achieved by feeding the mixture of vaporized o-xylene and preheated air (1:10) to a reactor containing a V_2O_5 based propietary catalyst. The reaction takes place at a temperature of \sim 550°C with a contact time of the order of .10 to .15 seconds. Heat is removed by circulating molten salts across the reactor. Many plants can operate at will on o-xylene or naphthalene feedstock.

The vapors leaving the reactor are condensed, then melted and fed into a pre-decomposer. In the pre-decomposer maleic and benzoic acid are removed and any phthalic acid present is dehydrated. Final purification is done by distillation in vacuum.

2. Input Materials

o-xylene	975 kg/metric ton product
air	25,000 m ³ at 15°C/metric ton product

3. Operating Parameters

Temperature:	550°C (1022°F)
Pressure:	not given
Catalyst:	propietary catalyst based on V_2^{0} 5
Contact Time:	0.10 to 0.15 sec
Av. Plant Capacity:	18 to 45 million kg/yr

6-830

4. Utilities - not given

5. <u>Waste Streams</u> - Waste gas - Most waste gas is scrubbed with water. Removal rates have been shown to be in excess of 99% of all organic acids, however total aldehydes removal is poor with concentrations in the effluent varying between 8 and 26 ppm as formaldehyde. The scrubbing water discharges at 115 - 130°F with 1.7 - 2.5% total acidity as maleic acid.

A phthalic anhydride plant producing 100 million pounds of PAN a year could have a scrubber effluent with an ultimate oxygen demand of from 400 to in excess of 1200 lbs/hr.

6. EPA Source Classification Code - None

7. References

Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>, Noyes Data Corp., Park Ridge, N. J., 1974, p. 186-188.

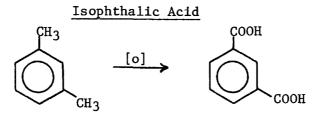
Fawcett, R. L., "Air Pollution Potential of Phthalic Anhydride Manufacture," Journal of the Air Pollution Control Association, 20 (7): 461-465, 1970.

Austin, G. T., "Industrially Significant Organic Chemicals - Part 8," "Chemical Engineering", July 22, 1974, p. 109-110.

"1973 Petrochemicals Handbook", "Hydrocarbon Processing", November, 1973, p. 159-160.

Waddams, A. L., <u>Chemicals from Pétroleum</u>, 3rd Edition, John Wiley and Sons, New York, N. Y., 1973, p. 228-230.

Lowenheim, F. A. and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, New York, N. Y., 1975, p. 661-664. Hedley, W. H. et al., "Potential Pollutants from Petrochemical Processes", Prepared for Control Systems Laboratory, NERC, Environmental Protection Agency, Contract No. 68-02-0226, Task No. 9, 1973, p. 95-96.



- 1. <u>Function</u> As of 1971 Amoco and Arco were the only two producers of isophthalic acid in the U.S. In the Amoco process m-xylene is oxidized in the liquid phase at 150-250°C and a pressure of 15-30 atm. Air is used as the oxidizing agent and the reaction is carried out in acetic acid as solvent, in the presence of a bromine-promoted cobalt salt as catalyst. The isophthalic acid produced will contain varying amounts of terephthalic acid depending on the purity of the m-xylene feedstock.
- 2. Input Materials

m-xylene

Acetic acid

Catalyst

3. Operating Parameters

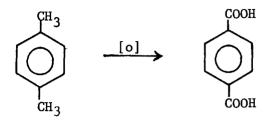
Temperature:	150-250°C (301-481°F)
Pressure:	1.52-3.04 MPa (15-30 atm)
Catalyst:	cobalt salt activated by bromine

- 4. Utilities not given
- <u>Waste Streams</u> Potential water wastes are IPA, terephthalic acid, and acetic acid.
- 6. EPA Source Classification Code None

7. <u>References</u>

Hedley, W. H., et. al., <u>Potential Pollutants from Petrochemical</u> <u>Processes</u>, Prepared for Control Systems Laboratory, NERC, Environmental Protection Agency, Contract No. 68-02-0226, Task No. 9, 1973.

Waddams, A. L., <u>Chemicals From Petroleum</u>, 3rd Edition, John Wiley and Sons, New York, N. Y., 1973, p. 232-235. Terephthalic Acid and Dimethyl Terephthalate



 <u>Function</u> - Terephthalic acid (TPA) is produced by the air oxidation of p-xylene in the liquid phase.

p-Xylene dissolved in acetic acid reacts with air in the presence of a cobalt proprietary catalyst in a reactor at 200°C and 400 p.s.i. The hot slurry from the reactor effluents is fed into a crystallizer. Acetic acid, unreacted p-xylene and water are removed at this step and by further centrifugation. Acetic acid and pxylene are recycled. The crude TPA is leached with acetic acid at high temperature. The resulting TPA of better than 99% purity is washed with hot water to remove traces of catalyst and acetic acid. Subsequent hydrogenation in fixed-bed reactors, crystallization and drying yield fiber grade TPA. A new route to TPA involves the ammoxidation of p-xylene and the subsequent hydrolysis of terephthalonitrile to terephthalic acid. The Hercules-Witten process produces dimethyl terephthalate from p-xylene without isolation of TPA.

2. Input Materials

p-xylene - 680 kg/metric ton polymer grade TPA air - not given acetic acid - not given

6-835

3. Operating Parameters

Temperature:	200°C (392°F)
Pressure:	2.76 MPa (27.2 atm)
Catalyst:	Bromine promoted cobalt catalyst

- 4. Utilities not given
- <u>Waste Streams</u> Off-gas from scrubber contain some organic vapors; wastewaters contain acetic acid, traces of catalyst, and terephthalic acid.

Water flow rate - 3.62×10^{-4} - 9.09×10^{-3} m/kg (86.8 - 2180 gal/ton) COD 5,400 - 24,950 g/m³ (1.95 - 227 lb/1000 lb) BOD₅ 3,600 - 7,500 g/m³ (1.30 - 68.3 lb/1000 lb) TOC 4,200 - 3,730 g/m³ (1.52 - 34 lb/1000 lb)

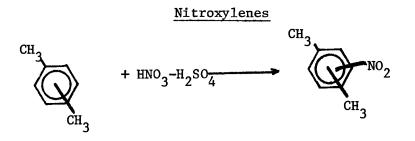
- 6. EPA Source Classification Code None
- 7. <u>References</u>

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Sittig, M., <u>Pollution Control in the Organic Chemical Industry</u>
Noyes Data, Park Ridge, N.J., 1974, p. 198-203.
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"1973 Petrochemical Handbook", "Hydrocarbon Processing", November, 1973, p. 183-185.

Hedley, W. H., et. al., <u>Potential Pollutants in the Petrochemical</u> <u>Processes</u>, Prepared for Control Systems Labotatory, NERC, Environmental Protection Agency, Contract No. 68-02-0226, Task No. 9, 1973.

Waddams, A. L., <u>Chemicals from Petroleum</u>, 3rd Edition, John Wiley and Sons, 1973, p. 232-237. Lowenheim, F. A., and Moran, M. K., <u>Industrial Chemicals</u>, 4th Edition, John Wiley and Sons, 1975, p. 807-813.



 Function - Xylenes, o-, m- or p-isomers, can be nitrated to place nitro groups on the benzene ring. Ortho-xylene gives the 4-nitro and the 4,6-dinitro isomers; meta-xylene gives the 4-nitro isomer, and paraxylene the 2,3-dinitro-or 2,6-dinitro-p-xylene, or the 2-nitro-p-xylene.

The extent of nitration, the number of nitro groups placed in the ring, is a function of acid strength and temperature. The extent of side chain oxidation is dependent on the same two factors; therefore, with polynitrated products a compromise must be reached.

Mononitration of xylenes is carried out near room temperature, 25°C (77°F) with a mixture of nitric 30% and sulfuric (55%) acids and at atmospheric pressure.

2. Input Materials

Xylenes

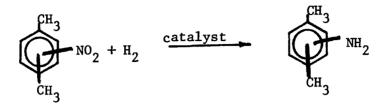
Nitric-sulfuric acid mixture

- 3. <u>Operating Parameters</u> Temperature - 25-40°C (77-104°F) Pressure - 100 kPa (1 atm)
- 4. Utilities Not given

- 5. <u>Waste Streams</u> Spent acid is recovered and recycled to the system. Air emissions from the reactor may contain oxides of nitrogen. Waste water from the product washing procedure contains sodium carbonate, some nitroxylenes and nitrate salts.
- 6. EPA Source Classification Code None
- 7. References

Kirk-Othmer, <u>Encyclopedia of Chemical Technology</u>, 2nd Edition, Interscience Publishers, New York, N.Y., Vol. 22 (1970), p. 484. <u>Chemical Technology</u>, Barnes and Noble Books, New York, N.Y., Vol. 4 (1972), p. 172-174.

Xylidines (reduction of nitroxylenes)



- <u>Function</u> The xylidines are made by the reduction of nitroxylenes. The only technical process used at present is hydrogen reduction. A molybdenum sulfide catalyst is used for this reaction.
- 2. Input Materials

Nitroxylenes

Hydrogen

 MoS_3 on an inert support

3. Operating Parameters

Temperature - 165-170°C (330-340°F)

Pressure - 20.7 MPa (205 atm)

Catalyst - MoS₂

Nitroxylene feed - 0.44 vols/vol catalyst/hr.

Recycle feed - 1.2-1.6 vols/vol

Recycle gas - 80-85% H₂ and 0.6% H₂S

- 4. Utilities Not given
- <u>Waste Streams</u> Waste water from product wash contains sodium carbonate.
 Vents emit some hydrogen.
- 6. EPA Source Classification Code None

7. Reference

Brown, C. L., and Smith, W. W., "Production of Xylidines by High Pressure Hydrogenation," <u>Ind. Eng. Chem.</u>, Vol. 40, (1948), pp. 1538-42.

APPENDIX A

INDUSTRIAL CHEMICALS AND SOLVENTS GLOSSARY

Table A-1 lists specific industrial compounds and their uses. Also included are the major producers listed in alphabetical order for each compound, the plant locations, plant capacities, and total annual production where available. Capacities given are for 1975 and total chemical production is for the specific year noted. Capacity and production estimates are given in millions of kilograms per year (MM kg) and millions of pounds per year (MM lbs).

References

- 1. Hawley, G. G. (ed.). <u>The Condensed Chemical Dictionary</u>. 8th Edition, Van Nostrand Reinhold Company, 1971.
- 2. Staff. <u>Directory of Chemical Producers</u> U.S.A. Chemical Information Services, Stanford Research Institute, Menlo Park (California), 1975.
- 3. Staff. <u>Chem. Sources</u>. Directories Publishing Co., Flemington, New Jersey, 13th Edition, 1972.
- 4. Staff. "Recession Stifles Output of Top 50 Chemicals." <u>Chemical and</u> Engineering News, American Chemical Society, May 5, 1975, p. 31.
- 5. Staff. "Facts and Figures The U.S. Chemical Industry." <u>Chemical</u> and Engineering News, American Chemical Society, June 2, 1975, p. 33.

Table A-1. INDUSTRIAL CHEMICALS AND SOLVENTS.

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 Capac MM kg (1	lty ²	pr MM	tal ^{4,5} oduction kg (MM lb) ar of estimate
Acenaphthene	Dye intermediate; pharmaceuticals; insecticide; fungi- cide; plastics	Hoffmann - La Roche, Inc., Burdick & Jackson Labs., Inc., subsid.	Muskegon, Mich.	-			-
Acetal	Solvent; cosmetics; organic synthesis; perfumes; flavors	Fritzche Dodge & Olcott Inc.	East Hanover, N.J.	-			-
Acetalde- hyde	Acetic acid; acetic anhydride; n-butanol; 2-ethylhexanol; per-	Celanese Corp Celanese Chem. Co., div.	Bay City, Tex. Clear Lake, Tex. Pampa, Tex.	90.8	(200)	731.6	(1611.4)-1970
	acetic acid; pentaery- thritol; pyridines; chloral; l,3-butylene glycol; trimethyl- propane manufacturing	Eastman Kodak Co Eastman Chem. Products, Inc., subsid. Texas Eastman Co., div.	Longview, Tex.	227	(500)		
	intermediate	Monsanto Co Monsanto Polymer & Petrochems. Co.	Texas City, Tex.	2.3	(5)		
		Publicker Indust. Inc.	Philadelphia, Pa.	2.3	(5)		
		Shell Chem. Co Base Chems.	Norco, La.	2.3	(5)		
		Union Carbide Corp Chems. & Plastics Div.	Institute & South	90.9	(200)		
					al = (1485)		
				0/4.2	(1405)		
Acetaldol	Rubber accelerators; age resistors; synthesis; perfumery; engraving; ore flotation; solvent; sol- vent mixture for cellu- lose acetate; fungicides; organic synthesis; printer's rollers; cad- mium plating; dyes; drugs; dyeing assis- tant; synthetic polymers	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-			

		Table A-1. (Continued)		1975 Capacity ²	Total ^{4,5} production MM kg (MM lb)
<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	$Location(s)^{2,3}$	MM kg (MM 1b)	for year of estimate
Acetamide	Organic synthesis (reactant, solvent,	Heico, Inc.	Delaware Water Gap, Pa.	-	-
genera quers; solder hygros wettir	peroxide stabilizer); general solvent; lac- quers; explosives; soldering flux; hygroscopic agent; wetting agent; penetrating agent	Mallinckrodt, Inc Indust. Chems. Div.	St. Louis, Mo.	-	
Acetanilide	Rubber accelerator; inhibitor in hydro- gen peroxide; stabilizer for cellulose ester	Eastman Kodak Co Eastman Chem. Products, Inc., subsid. Tennessee Eastman Co., div.	Kingsport, Tenn.	-	-
	coatings; manufacture of intermediate (paranitro- aniline, paranitroace-	Merck & Co. Inc Merck Chem. Div.	Albany, Ga.	-	
	tanilide, parahexylene-	Salsbury Labs	Charles City, Iowa	-	
	diamine); synthetic cam- phor; pharmaceutical chemicals; dyestuffs; precursor in penicillin manufacture; medicine (antiseptic)	Syntex Corp Arapahoe Chems. Div.	Newport, Tenn.	-	
Acetic acid	Acetic anhydride, cellu- lose acetate, and vinyl	Borden Inc Borden Chem. Div. Petrochems.	Geismar, La.	52.2 (115)	930.7 (2050)-1971
	acetate monomer; acetic esters; chloroacetic production of plastics; pharmaceuticals, dyes; insecticides, photo-	Celanese Corp Cela- nese Chem. Co., div.	Bay City, Texas Bishop, Tex. Clear Lake, Tex. Pampa, Tex.	- (110) 181.6 (400) 250 (550)	
graphic chemicals, e	graphic chemicals, etc.; food additive (as vine- gar); natural latex	Eastman Kodak Co Eastman Chem. Prod. Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	181.6 (400)	
		FMC Corp Chem. Group Indust. Chem. Div.	Bayport, Tex.	18.2 (40)	
		Monsanto Co Monsanto Polymers & Petrochems. Co.	Texas City, Tex.	181.6 (400)	
		Publicker Indust. Co.	Philadelphia, Pa.	36.3 (80)	
		Union Carbide Corp Chems. & Plastics Div.	Brownsville, Tex. Taft, La. Texas City, Tex.	268 (590) 41 (90) 45.4 (100) Total = 1305 (2875)	

,

<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 Capacity ² MM kg (MM 15	Total ^{4,5;} Production MM kg (MM lb) <u>for year of estimate</u>
Acetic anhydride	Cellulose acetate fi- bers and plastics; vinyl acetate; dehydrating and acetylating agent in production of pharma-	Celanese Corp Cela- nese Chem. Co., div. Celanese Fibers Co., div.	Pampa, Tex. Cumberland, Md. Narrows, Va. Rock Hill, S.C. Rome, Ga.	386 (850) -	708.5 (1560.6)-1972
	ceuticals, dyes, per- fumes, explosives, etc.; aspirin	Eastman Kodak Co Eastman Chem. Products. Inc., subsid. ~ Ten- nessee Lastman Co., div. FMC Corp Chem. Group	Kingsport, Tenn. Meadville, Pa.	272.4 (600) 27.2 (60)	
		Indust. Chem. Div. Union Carbide Corp Chem. & Plastics Div.	Brownsville, Tex. Texas City, Tex.	102 (225)	
		onem. a liabolob biv.	Texas or by, Texa J	Total = 787.7 (1735)
Acetone	Chemicals (methyl iso- butyl ketone, methyl	Allied Chem. Corp Specialty Chems. Div.	Frankford, Pa.	143 (315)	902.2 (1987.2)-1973
	<pre>isobutyl carbinol methyl methacrylate bisphenol-A); paint; varnish; lacquer sol-</pre>	Clark Oil & Refining Corp Clark Chem. Corp., subsid.	Blue Island, Ill.	24 (53)	
	vent; to clean & dry	Dixie Chem. Co.	Bayport, Tex.	11 (24)	
	parts of precision equipment; solvent for	Dow Chem. U.S.A.	Oyster Creek, Tex.	109 (240)	
	equipment, solven for potassium iolide & permanganate; deluste- rant for cellulose acetate fibers; speci- fication testing of vulcanized rubber products	Eastman Kodak Co Eastman Chem. Products., Inc., subsid Tennes- see Eastman Co., div.	Kingsport, Tenn.	36 (80)	
		Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Bayway, N.J.	63.6 (140)	
		Georgia-Pacific Corp Chem. Div.	Plaquemine, Lá.	78.1 (172)	
		The Goodyear Tire & Rub- ber Co Chem. Div.	Bayport, Tex.	-	

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 Capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Acetone (continued)	(see previous page)	Monsanto Co Monsanto Polymers & Petrochems. Co	Chocolate Bayou, Tex.	122.6 (270)	(see previous page)
		Oxirane Chem. Co.	Bayport, Tex.	18.2 (40)	
		Publicker Indust. Inc.	Philadelphia, Pa.	15.9 (35)	
		Shell Chem. Co Base Chems.	Deer Park, Tex. Dominquez, Calif. Norco, La.	181.6 (400) 45.4 (100) 45.4 (100)	
		Skelly C11 Co.	El Dorado, Kans.	25.9 (57)	
		Standard Oil of Calif, - Chevron Chem. Co., sub- sid., Oronite Additives & Indust. Chems. Div Indust. Chems.	Richmond, Calif.	15 (33)	
		Union Carbide Corp Chems, & Plastics Div.	Bound Brook, N.J. Institute & South Charleston, W. Va. Texas City, Tex.	41 (90) 68.1 (150) 50 (110)	
		Union Carbide Caribe, Ing., subsid.	Penuelas, P.R.	54.5 (120)	
		United States Steel Corp. USS Chems., div.	Haverhill, Ohio	76.3 (168) Total = 1224.4 (2697)	
Acetone Cyanoh y drin	Insecticides; inter- mediate for organic synthesis, especially	E. I. du Pont de Nemours & Co. Inc Industrial Chems. Dept.	Belle, W. Va.	-	245.2 (540)-1969
methyl methacrylate		Rohm & Haas Co Rohm & Haas Texas Inc., subsid.	Deer Park, Texas	-	
Acetonitrile	Solvent in hydro- carbon processes, especially for buta- diene; specialty sol-	Eastman Kodak Co East- man Chem. Products, Inc., subsid., Texas Eastman Co., div.	Longview, Tex. Mapleton, Ill.	:	-
	vent; intermediate; separation of fatty acids from vegetable oils; manufacture of synthetic pharma- ceuticals	The Standard Oil Co. (Ohlo) - Vistron Corp., subsid., Chems. Dept.	Lima, Ohio	-	

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<u>Chemical</u>	<u>Usage 1</u>	Manufacture(s) ^{2,3}	Location(s) ^{2,3}	Total Capacity ² MM_kg (MM_lb)	Total4,5 production MM kg (MM lb) <u>for year of estimate</u>
Aceto- phenone	Perfumery; solvent; intermediate for	Allied Chem. Corp. Speciality Chems	Frankfort, Pa.	-	-
	pharmaceuticals, resins, etc.;	Skelly Oil Co.	El Dorado, Kans.	-	
	flavoring	Universal Oil Pro- ducts Co Chems. & Plastics Group - Chem. Div. Chemical Use	East Rutherford N.J.	-	
Acetylene	Vinyl chloride & vinylidene chloride;	Airco, Inc.	Calvert City, Ky. Louisville, Ky.	36.3 (80) 109 (240)	230.2 (507) -1974
	<pre>vinyl acetate; welding & cutting metals; neo- prene; acrylonitrile; acrylates; per- & tri-</pre>	Air Products & Chems., Inc., Specialty Gas Dept.	Hometown, Pa.	-	(chemical and non- chemical use)
	chloro-ethylene; cyclo- octatetraene; tetra-	Chemetron Corp Indust. Gases Div.	Pryor, Okla	0.5 (1)	
	hydrofuran; carbon black	Dow Chem. U.S.A.	Freeport, Tex.	6.8 (15)	
		Gaspro Inc.	Honolulu, Hawaii	<0.5 (<1)	
		Liquid Air Corp. of North America - South western Region	Houston, Tex.	-	
		Monochem., Inc.	Geismar, La.	81.7 (180)	
		Northern Gases, Inc.	Waukesha, Wisc.	-	
		Occidental Petroleum Corp Hocker Chem. Corp. subsid., Hocker Chems. & Plastics Corp., subsid. Electrochemical & Speci- alty Chems. Div.	Tacoma, Wash.	4.5 (10)	
		Rohm & Haas Co Rohm & Haas Texas Inc., subsid.	Deer Park, Tex.	15.9 (35)	
		Solox, Inc.	Chattanooga, Tenn.	-	
		Tenneco Inc Tenneco Chems., Organics & Polymers Div.	Houston, Texas	45.4 (100)	

Chemical	<u>Usage 1</u>	Manufacturer(s) ^{2,3}	$Location(s)^{2,3}$	Total Capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Acetylene (continued)	(see previous page)	Union Carbide Corp Chems. & Plastics Div.	Ashtabula, Ohio Institute & South Charlester W	34 (75) 15.9 (35)	(see previous page)
		D14 .	Charleston, W. Va. Seadrift, Tex. Taft, La. Texas City, Tex.	3.6 (8) 9.1 (20) 6.8 (15) 8.2 (18) 36.3 (80)	
		Union Carbide Caribe, Inc., subsid.	Penuelas, P.R.	n.a. Total (Chem. use) = <402 (<885)	
Acetylene (continued)		Non-Chemical Us'age Airco, Inc Arco Indust. Gases Div.	Houston, Tex.	-	
		Air Products & Chems., Inc.	Albany, Ga. Bladensburg, Md.	-	
			Creighton, Pa. Dallas, Tex.	-	
			Granite City, Ill.	-	
			Greensboro, N.C. Hampton, Va. Iselin, N.J. Kingsport, Tenn.	-	
				-	
			Memphis, Tenn.	-	
			Omaha, Neb. Parkersburg, W. Va.	-	
			Rapid City, S.D.	-	
		American Cyanamid Co Specialty Gas Dept Indust. Chems. & Plastics Div.	New Orleans, La.	-	
		Burdett Oxygen Co.	Norristown, Pa.	-	
		Paul Carroll Oxygen Co.	Abilene, Tex.	-	
		Chemetron Corp Indust. Gases Div.	Belton, Tex. Cleveland, Ohio	-	
			Columbus, Ohio	-	
			Conshohocken, Pa. Dallas, Tex.	-	
			Denver, Colo. Detroit, Mich.	=	

			CTHREO)		
Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 Capacity ² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Acetylene (continued)	(see previous page)	Chemetion Corp. (cont'd)	Evansville, Ind. Hodgkins, Ill. Jackson, Miss. Jacksonville, Fla. Knozville, Tenn. McKees Rocks, Pa. Memphis, Tenn. Miami, Fla. New Orleans, La. North Grafton, Mass. Peoria, Ill. Pryor, Okla. St, Paul, Minn. Southaven, Miss. Tampa, Fla.		(see previous page)
		Welding & Indust. Products, Ltd subsid.	Ewa.(Oahu), Hawail	-	
		East Texas Öxygen Co.	Tyler, Tex.	-	
		Kansas Oxygen, Inc.	Hutchinson, Kans.	-	
		Liquid Air Corp. of North America - Northwestern Region	Anchorage, Alas. Boise, Idaho Fairbanks, Alas. Medford, Ore. Missoula, Mont. Portland, Ore. Spokane, Wash.		
		÷ Southeastern Region	Augusta, Ga. Decautur, Ala. Lake Charles, La. Orlando, Fla.	-	
		- Southwestern Region	Abilene, Tex. Lubbock, Tex. Odessa, Tex. Phoenix, Ariz. Tucson, Ariz.	-	
		- Western Region	Las Vegas, Nev. Reno, Nev. Sacramento, Calif. San Bernardino, Calif. Santa Fe Springs, Calif. Union City, Calif.	-	
		Manitowoc Gases, Inc.	Manitowoc, Wisc.	-	

.

<u>Chemical</u>	<u>Usage 1</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 Capacity ² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Acetylene	(see previous page)	Northern Gases, Inc.	Waukesha, Wisc.	-	(see previous page)
(Continued)		Pacific Oxygen Co.	Oakland, Calif.	-	
		Selox, Inc.	Greenville, S.C.	-	
		Union Carbide Corp Ferroalloys Div. Linde Div.	Ashtabula, Ohio Albany, N.Y. Albuquerque, N.M. Altoona, Pa. Amarillo, Tex. Baltimore, Md. Billings, Mont. Birmingham, Ala. Boise, Idaho Butte, Mont. Carter Lake, Iowa Casper, Wyo. Charlotte, N.C. Columbus, Ohio Dallas, Tex. Denver, Colo. Des Moines, Iowa Duluth, Minn. East Buffalo, N.Y. East Chicago, Ind.		
Acrolein	Intermediate for synthetic glycerol,	Shell Chem, Co Base Chems,	Norco, La.	-	27.7 (61) -1974
	polyurethane, poly- ester resins, methionine, - pharmaceuticals; herbicide; tear gas	Union Carbide Corp Chems. & Plastics Div.	Taft, La.	-	
Acrylamide	Synthesis of dyes, etc.; polymers or copolymers as plastics, adhesives,	American Cyanamid Co Indust. Chems. & plastics Div.	Linden, N.J. New Orleans, La.	-	18.2 (40) -1973
	paper & textile sizes, soil conditioning	Bio-Red Labs	Richmond, Calif.	-	
	agents; flocculants;	Dow Chem. U.S.A.	Midland, Mich.	-	
sewage ment;	sewage & waste treat- ment; ore processing; permanent press fabrics	The Standard Oil Co. (Ohio) - Vistron Corp., subsid Chems. Dept.	Lima, Ohio	-	

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 Capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Acrylic acid	Monomer for polyacrylic & polymethacrylic acids	American Aniline & Ex- tract Co., Inc.	Philadelphia, Pa.	-	37.5 (82.5) -1968
	& other acrylic polymers	Celanese Corp Cela- nese Chem. Co., div.	Clear Lake, Tex. Pampa, Tex.	100 (220) 36.3 (80)	
		Dow Badische Co.	Freeport, Tex.	18.2 (40)	
		Rohm & Haas Co., Rohm & Haas Texas Inc., subsid.	Deer Park, Tex.	181.6 (400)	
		Union Carbide Corp Chems. & Plastics Div.	Taft, La.	90.8 (200) Total = 431.3 (950)	
Acry⊥o- nitrile		American Cyanamid Co Indust. Chems. & Plastics Div.	New Orleans, La.	90.8 (200)	614.2 (1352.9)-1973
	nitrile-styrene copoly- mers; nitrile rubber; cyanoethylation of cot- ton; synthetic soil blocks (acrylonitrile	E. I. du Pont de Nemours & Co., Inc Elastomer Chems. Dept. Indust. Chems. Dept.	Beaumont, Tex. Memphis, Tenn.	136.2 (300) 113.5 (250)	
	polymerized in wood pulp); organic synthesis; grain	Monsanto Co Monsanto Folymers & Petrochems. Co.	Chocolate Bayou, La.	208.8 (460)	
fumigant	fumigant	The Standard 011 Co. (Oh1o) - Vistron Corp., subsid Chems. Dept.	Lima, Ohio	177 (390) Total = 7 26.4 (1600)	
Adipic	Manufacture of nylon &	Allied Chem. Corp.	Hopewell, Va.	11.3 (25)	626.5 (1380) -1972
acid	of polyurethane foams; preparation of esters for use as plasticizers	Celanese Corp Cela- nese Chem. Co., div.	Bay City, Tex.	56.7 (125)	
	& lubricants; ingredient of foods, as acidulant; insecticides; adhesives	E. I. du Pont de Nemours & Co., Inc Plastics Dept.	Orange, Tex. Victoria, Tex.	136.2 (300) 136.2 (300)	
		El Paso Natural Gas Co El Paso Products Co., subsid.	Odessa, Tex.	36.3 (80)	

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Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 Capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Adipic acid (continued)	(see previous page)	Monsanto Co Monsanto Indust. Chems. Co Monsanto Textiles Co.	Luling, La. Pensacola, Fla.	27.2 (60) 255 (562) Total = 659.2 (1452)	(see previous page)
Alkylnaph- thalenes (methyl)	Organic synthesis; insecticides	Crowley Hydrocarbon Chems., Inc. Koppers Co., Inc Organic Materials Div.	Houston, Tex. Kent, Ohio Oklahoma City, Okla. Paulsboro, N.J. Follansbee, W. Va.	- 、	-
		Marathon Oil Co.	Robinson, Ill.	-	
Allyl alcohol	Esters for use in resins & plastici-	FMC Corp Chem. Group - Indust. Chem. Div.	Bayport, Tex.	-	-
	zers; intermediate for pharmaceuticals & other organic chemi- cals; manufacture of glycerol & acrolein; military poison gas; herbicide	Shell Chem. Co Base Chems.	Deer Park, Tex.	-	
Allyl	Preparation of allyl	Dow Chem. U.S.A.	Freeport, Tex.	-	-
chloride	alcohol & other de- rivatives; thermo- setting resins for var- nishes, plastics, ad- hesives; synthesis of pharmaceuticals, glycerol & insecticides	Shell Chem, Co Base Chems.	Deer Park, Tex. Norco, La.	-	
Amino- benzoic	Dyes; drugs; perfumes & pharmaceuticals; dye	m Bofors Indust., Inc.	Linden, N.J.	_	_
acid (m,o,p)	intermediates	Salsbury Labs.	Charles City, Iowa	-	
(,0,,p)		<u>,</u>	Wilmington, N.C.	-	
		o Salsbury Labs.	Wilmington, N.C.	-	
		The Sherwin-Williams Co Sherwin-Williams Chems. Div.	St. Bernard, Calif.	-	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	$Location(s)^{2,3}$	1975 capacity ² <u>MM kg (MM lb)</u>	Total ^{4,5.} production MM kg (MM lb) <u>for year of estimate</u>
Amino- benzoic		Bofors Indust., Inc.	Linden, N.J.	_	-
acid (m.o.p)		Northern Fine Chems., Inc.	Franklin, N.J.	_	
(continued)		Salsbury Labs.	Wilmington, N.C.	_	
		Warner-Lambert Co Parke, Davis & Co., subsid.	Holland, Mich.	-	
Amino-	Textile finishing	Dow Chem. U.S.A.	Freeport, Tex.	-	-
ethyl- ethanol-	compounds (antifuming agents, dyestuffs,	Hodag Chem. Corp.	Skokie, Ill.	-	
amine	cationic surfactants); resins, rubber products,	Texaco Inc Jefferson Chem. Co., Inc., subsid.	Conroe, Tex.	-	
	insecticides, & certain medicinals	Union Carbide Corp	Institute & South	-	
		Chems. & Plastics Div.	Charleston, W. Va. Texas City, Tex.	-	
Amyl	Solvent for lacquers &	Commercial Solvents Corp.	Terre Haute, Inc.	-	5,4 (12) -1973
acetates	paints; extraction of penicillin; photographic	Publicker Indust. Inc.	Philadelphia, Pa.	-	
	film; leather polishes; nail polish; warning odor; flavoring agent; printing & finishing fabrics; solvent for phosphors in fluorescent lamps.	Institute & South Charleston, W.Va.			
Amyl alcohols	Solvent; raw material for pharmaceutical prepara-	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	-
(8 1somers)	tions; organic synthesis; lubricants; plasticizers; additives for oils; &	Eastman Kodak Co Eastman Organic Chems.	Texas City, Tex. Rochester, N.Y.	-	
	paints; flotation agent; medicine	Pennwalt Corp., Chem. Div.	Wyandotte, Mich.	-	
Amy 1-	Chemical intermediate;	The Ames Labs., Inc.	Milford, Conn.	_	_
amine	dyestuffs; rubber chemi-	Pennwalt Corp Chem.	Wyandotte, Mich.	_	
	cals; insecticides; synthetic detergents;	Div.	.,		
	synthetic detergents; flotation agents; corro- sion inhibitors; solvent; gasoline additive; pharmaceuticals	Virginia Chems. Inc Indust, Chems. Dept.	Portsmouth, Va.	-	

<u>Çhemical</u>	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Amyl chloride	Synthesis of other amyl compounds; solvent;	Columbia Organic Chem. Co.	Columbia, S. C.	-	-
	rotogravure ink vehicles; soil fumigation	Eastman Kodak - East- man Organic Chems.	Rochester, N. Y.	-	
Amyl mercaptans	Synthesis of organic sul- fur compounds; chief constituent of odorant used in gas lines to locate leaks	Pennwalt Corp.	Greens Bayou, Tex.	-	
Amyl phenol	Dispersing & mixing agent for paint pastes;	Pennwalt Corp Chem. Div.	Wyandotte, Mich	-	
	antiskinning agent for paint, varnish, & oleo- resinous enamels; organic synthesis; Manufacture of oil-soluble resins; plasticizer; germicide; fumigant	Productol Chem. Co.	Santa Fe Springs, Calif.	-	
Aniline	Rubber accelerators & antioxidants ; dyes &	American Cyanamid Co. — Organic Chems. Div.	Bound Brook, N. J. Willow Island, W.Va.	27.2 (60) 22.7 (50)	207.3 (456.6) -1973
	intermediates; photo- graphic chemicals (hydroquinone); iso- cyanates for urethane fogms; pharmaceuticals;	E. I. du Pont de Nemours & Co., Inc. Elastomer Chems. Dept. Indust. Chems. Dept.	Beaumont, Tex. Gibbstown, N. J.	90.8 (200) 59 (130)	
	explosives; petroleum refining; diphenylamine;	First Mississippi Corp. First Chem. Corp., subsid.	Pascagoula, Miss.	45.4 (100)	
	phenolics; herbicides, fungicides	Mobay Chem. Corp Indust. Chems. Div.	New Martinsville, W. Va.	45.4 (100)	
		Rubicon Chems. Inc.	Geismar, La.	25 (55) Total = 315 (695)	
Aniline hydro- chloride	Dyes; intermediates; dyeing & printing; aniline black	American Cyanamid Co Organic Chems. Div.	Bound Brook, N. J.	-	-

<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	$Location(s)^2$,3	1975 Capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Anisidine	Intermediate for azo dyes	Aldrich Chem. Co., Inc.	Milwaukee, Wisc.	-	-
	& for quaiacol; azo dyestuffs	Eastman Kodak Co Eastman Organic Chems.	Rochester, N. Y.	-	
		American Color & Chem. Corp.	Lock Haven, Pa.	-	
		E. I. du Pont de Ne- mours & Co., Inc Organic Chems. Dept Dyes & Chems. Div.	Deepwater, N. J.	_	
		Monsanto Co Monsanto Indust. Chems. Co.	St. Louis, Mo.	-	
		Salsbury Labs.	Wilmington, N. C.	-	
Anisole	Solvent; perfumery; vermicide; intermediate	Chem. Formulators, Inc., Chem. Div.	Nitro, W. Va.	-	-
		Continental Oil Co. ~ Conoco Chems Pitt- Consol Chems.	Newark, N. J.	-	
		Eli Lilly & Co Tippecanoe Labs.	Lafayette, Inc.	-	
		Givaudan Corp Chems. Div.	Clifton, N. J.	-	
Anthranilic	Dyes; drugs; perfumes	Salsbury Labs.	Wilmington, N. C.	~	-
acid	<pre>& pharmaceuticals</pre>	The Sherwin-Williams Co. – Sherwin-Williams Chems. Div.	St. Bernard, Ohio	-	
Anthraqui- none	Intermediate for dyes; & organics; organic inhibitor; bird repel- lent for seeds.	American Cyanamid Co Organic Chems. Div.	Boundbrook, N. Y.	-	-
		E. I. du Pont de Ne- mours & Co Organic Chems. Dept.	Wilmington, Del.	-	
		GAF Corporation	Linden, N. J.	-	
		Sterling Drug Inc	Rensselaer, N. Y.	-	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Benzalde- hyde	Organic synthesis (es- pecially of dyes & dye	Alco Standard Corp Monroe Chem. Co., div.	Eddystone, Pa.	-	-
	intermediates); sol- vent for oils, resins,	Kalama Chem. Inc.	Kalama, Wash.	-	
	some cellulose ethers, cellulose acetate & nitrate flavoring com-	Northwest Indust., Inc Velsicol Chem. Corp., subsid.	Chattanooga, Tenn.	-	
	pounds; synthetic per- fumes; manufacture of cinnamic acid, ben-	Stauffer Chem. Co Specialty Chem. Div.	Edison, N. J.	-	
	zoic acid; phármaceu- ticals & soaps; photo-	Tenneco Inc Organics & Polymers Div.	Fords, N. J.	-	
graphic chemicals; baking chemicals; medicine	baking chemicals;	Universal Oil Products Co Chems. & Plastics Group, Chem. Div.	East Rutherford, N. J.	-	
Benzamide Organic :	Organic synthesis	Aceto Chem. Co., Inc Arsynco, Inc., subsid.	Carlstadt, N. J.	-	-
		Guardian Chem. Corp Eastern Chem. Div.	Hauppauge, N. Y.	-	
Benzene	Styrene; phenol; syn- thetic detergents; cyclohexane for nylon;	Allied Chem. Corp Union Texas Petroleum Div.	Winnie, Tex.	10 (22)	3694 (8136)- 1971
	aniline; DDT; maleic anhydride; dichloro- benzene; benzene hexa- chloride; nitrobenzene;	Amerada Hess Corp Hess Oil Virgin Islands Corp., subsid.	St. Croix, Virgin Islands	50 .(110.2)	
	diphenyl; insecticides; fumigants; solvent; paint removers; rubber	American Petrofina,Inc American Petrofina Co. of Texas, subsid.	Port Arthur, Tex.	50 (110.2)	
cement; antiknock gasoline		Cosden Oil & Chems. Co., subsid.	Big Spring, Tex.	100 (220.5)	
		Armco Steel Corp.	Houston, Tex. Middletown, Ohio	3 (6.6) 6.7(14.7)	
		Ashland Oil, Inc Ashland Chem. Co., div. Petrochems. Div.	Ashland, Ky. North Tonawanda, N. Y.	166.8(367.5) 50 (110.2)	
		Atlantic Richfield Co ARCO Chem. Co., div.	Houston, Tex. Wilmington, Del. Bethlehem, Pa. Lackawanna, N. Y. Sparrows Point, Md.	146.8(323.4) 53.4(117.6) 13.3(19.4) 25 (55.1) 50 (110.2)	

<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg_(MM lb)	Total4,5 production MM kg (MM lb) for year of estimate
Benzene	(see previous page)	CF&I Steel Corp.	Pueblo, Colo.	10 (22)	(see previous page)
(cont'd)		The Charter Co., Char- ter Oil Co., subsid.	Houston, Tex.	16.7(36.7)	
		Cities Service Co., Inc North American Petroleum Group	Lake Charles, La.	83.4(183.7)	
		Coastal States Gas Corp. Coastal States Market- ing, Inc., subsid.	Corpus Christi, Tex.	233.6(514.5)	
		Commonwealth Oil Re- fining Co., Inc Commonwealth Petro- chems., Inc., subsid.	Penuelas, P. R.	617 (1359.7)	
		Crown Central Petro- leum Corp.	Pasadena, Tex.	66.7(147)	
		Dow Chem. U.S.A.	Bay City, Mich. Freeport, Tex.	100.1(220.5) 133.5(294)	
		Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Baton Rouge, La. Baytown, Tex.	240.2(529.2) 206.9(455.7)	
		Gulf Oil Corp Gulf Oil Chems. Co., div Petrochems. Div.	Alliance, La. Philadelphia, Pa. Port Arthur, Tex. Toledo, Ohio	233.6(514.5) 110 (242.5) 126.8(279.3) 3.3(7.3)	
	Interlake, Inc Jones & Laughlin In- dust., Inc Jones & Laughlin Steel Corp., subsid.	Aliqu ippa, Pa.	33.4(73.5)		
		Kerr-McGee Corp South- western Refining Co., Inc., subsid.	Corpus Christi, Tex.	26.7(58.8)	
		Marathon 011 Co.	Texas City, Tex.	20 (44.1)	
		The Mead Corp Metals & Minerals Div.	Woodward, Ala.	4.7(10.3)	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM_kg (MM_lb)	Total ^{4,5} . production MM kg (MM lb) <u>for year of estimate</u>
Benzene (continued)	(see 2nd prev. page)	Mobil Oil Corp Mobil Chem. Co., div Petrochems. Div.	Beaumont, Tex.	200 (441)	(see 2nd previous page)
		Monsanto Co Monsanto Polymers & Petrochems. Co.	Chocolate Bayou, Tex.	250.2(55 1.2)	
		Northwest Indust., Inc. Lone Star Steel Co., subsid.	Lone Star, Tex.	4 (8.8)	
		Penzoil Co Atlas Processing Co., subsid.	Shreveport, La.	40 (88.2)	
		Phillips Petroleum Co.	Sweeny, Tex.	73.4(161.7)	
		Phillips Puerto Rico Core Inc., subsid.	Guayama, P. R.	367 (808.5)	
		Republic Steel Corp Iron & Chem. Div,	Youngstown, Ohio	13.3(29.4)	
		Shell Chem. Co Base Chems.	Deer Park, Tex. Odessa, Tex. Wilmington, Calif. Wood River, Ill.	250.2(551.2) 16.7(36.7) 66.7(147) 133.5(294)	
		Skelly Oil Co.	El Dorado, Kans.	46.7(102.9)	
		Standard Oil Co. of California	El Segundo, Calif.	50 (110.2)	
		Standard Oil Co. (Ind.) Amoco Oil Co., subsid.	Texas City, Tex.	283.6(624.7)	
		Sun Oil Co Sun Oil Co. of Pa., . Suntide Refining Co., subsid.	Marcus Hook, Pa. Tulsa, Okla Corpus Christi, Tex.	50 (110.2) 80 (176.4) 100 (220.5)	
		Tenneco Inc Tenneco Oil Co., div.	Chalmette, La. Port Arthur, Tex. Westville, N. J.	33.4(73.5) 150.1(330.7) 116.8(257.2)	
		Union Carbide Corp Chems. & Plastics Div.	Taft, La.	166.8(367.5)	
		Union Oil Co. of Calif.	Beaumont, Tex. Lemont, Ill.	40 (88.2) 110.1(242.5)	
		Union Pacific Corp Champlin Petroleum Co., subsid.	Corpus Christi, Tex.	33.3(73.5)	
		United States Steel Corp USS Chems., div.	Clairton, Pa. Geneva, Utah	133.5(294) 13.3(29.4)	
				Total = 5816.2(12811)	

Chemical	Usage ¹	Manufacturer(s) ² , ³	Location(s) ^{2,3}	1975 capacity ² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Benzene-	Phenol; resorcinol;	Nease Chem. Co., Inc.	State College, Pa.	-	-
sulfonic acid	organic synthesis; catalyst	Stauffer Chem. Co., Agricultural Chem. div.	Henderson, Nev.	-	
		Jim Walter Corp U.S. Pipe & Foundry Co., subsid., Chem. Div.	Birmingham, Ala.	-	
Benzenedi- sulfonic	-	Koppers Co., Inc Organic Materials Div.	Petrolia, Pa.	-	-
acid		Jim Walter Corp U.S. Pipe & Foundry Co., subsid., Chem. Div.	Birmingham, Ala.	-	
Benzil	Organic synthesis; insecticide	Napp Chems. Inc.	Lod1, N. J.	-	-
Benzilic acid	Chemical intermediate	Stauffer Chem. Co Specialty Chem, Div,	Edison, N. J.	-	-
Benzoic	Sodium &benzyl ben-	Kalama Chem., Inc.	Kalama, Wash.	54.5 (120	36.8 (81) -1974
acid	zoates; plasticizers; alkyd resins; vulcaniza- tion retarder; food	Monsanto Co Monsanto Indust. Chems. Co.	St. Louis, Mo.	4.5 (10)	
	preservative; season- ing tobacco; flavors, perfumes; dentifrices;	Northwest Indust., Inc Velsicol Chem. Corp., subsid.	Beaumont, Tex. Chattanooga, Tenn.	22.7 (50)	
	medicine (germicide)	Pfizer Inc Chems. Div.	Terre Haute, Ind.	2.7 (6)	
		Tenneco Inc Tenneco	Garfield, N. J.	5.4 (12)	
		Chems., Inc., Organics & Polymers Div.		Total =	
Deventer	Openanda, annehanda.		Lodi, N. J.	117.1 (258)	
Benzoin	Organic synthesis; intermediate; photo-	Napp Chems., Inc. Stauffer Chem. Co	Edison, N. J.	-	-
	polymerization catalyst	Specialty Chem. Div.	Edişon, N. D.	-	
Benzo- nitrile	Manufacture of benzo- guanamine; intermediate for rubber chemicals; solvent for nitrile rubber, specialty lac- quers, and many resins & polymers, & for many anhydrous metallic salts	Northwest Indust. Inc Velsicol Chem. Corp., gubsid.	Chattanooga, Tenn.	-	-

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Benzo- phenone	Organic synthesis; perfumery; odor fixa-	Aceto Chem. Co., Inc Arsynco, Inc., subsid.	Carlstadt, N. J.	-	-
	tive; derivatives are used as ultravio-	GAF Corp Chem. Div.	Rensselaer, N. Y.	-	
	let absorbers; flavor- ing; polymerization	Norda Inc.	Boonton, N. J. East Hanover, N. J.	-	
	inhibitor for styrene	Orbis Products Corp.	Newark, N. J.	-	
		Universal Oil Products Co Chems. & plastics Group - Chem. Div.	East Rutherford, N. J	. –	
		Warner-Lambert Co Parke, Davis & Co., subsid.	Holland, Michigan	-	-
Benzo- quinone	Manufacture of dyes & hydroquinone	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	-	-
		Frank Enterprises	Columbus, Ohio	-	
Benzo- trichlo- ride	Synthetic dyes; organic synthesis	Northwest Indust., Inc. Velsicol Chem. Corp., subsid.	Chattanooga, Tenn.	-	-
		Occidental Petroleum Corp., Hooker Chem. Corp., subsid - Hooker Chems. & Plastics Corp., subsid Electrochemi- cal & Specialty Chems. Div.	Niagara Falls, N. Y.	-	
		Tenneco Inc Tenneco Chems., Inc Organics & Polymers Div.	Fords, N. J.	-	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM_kg (MM_1b)	Total ^{4,55} production MM kg (MM lb) for year of estimate
Benzoyl chloride	Medicine; intermediate for production of ben- zoyl groups; inter-	Northwest Indust., Inc Velsicol Chem. Corp., subsid.	Chattanooga, Tenn.	-	-
	mediate for other organics	Occidental Petroleum Corp., Hooker Chem., Hooker Chems. & Plastics Corp., subsid Electro- chemical & Specialty Chems. Div.	Niagara Falls,	-	
		Stauffer Chem. Co Specialty Chem. Div.	Edison, N. J.	-	
		Tenneco Chems., Inc Tenneco Chems., Inc., Organics & Polymers Div.	Fords, N. J.	-	
Benzyl alcohol	Perfumes & flavors; photographic developer	Alco Standard Corp Monroe Chem. Co., div.	Eddystone, Pa.	-	-
	for color movie films;	Cloray NJ Corp.	Newark, N. J.	-	
	dyeing nylon filament, textiles and sheet plastics; solvent for	Givaudan Corp Chems. Div.	Clifton, N. J.	-	
	dyestuffs, cellulose esters, casein, waxes, etc.; heat-sealing poly- ethylene films; inter-	Northwest Indust., Inc Velsicol Chem. Corp., subsid.	Chattanooga, Tenn.	-	
	mediate for benzyl	Orbis Products Corp.	Newark, N. J.	-	
	esters & ethers; local anesthetic; cosmetics, cintments, emulsions;	Stauffer Chem. Co Specialty Chem. Div.	Edison, N. J.	-	
	ball point pen inks; stencil inks.	Tenneco Inc Tenneco Chems., Inc Organics & Polymers Div.	Fords, N. J.	-	
		Universal Oil Products Co. – Chems. & Plastics Group – Chem. Div.	East Rutherford, N. J.	-	
Benzl- amine	Chemical intermediate for dyes, pharmaceuti- cals, & polymers	Aceto Chem. Co., Inc Arsynco, Inc., subsid.	Carlstadt, N. J.	-	-
		Miles Labs., Inc Sumner Div.	Zeeland, Mich.	-	
		Uniroyal, Inc Uni- royal Chem., div.	Naugatuck, Conn.	-	

<u>Chemical</u>	<u>Usage 1</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5.} production MM kg (MM lb) <u>for year of estimate</u>
Benzyl benzoate	Fixative & solvent for musk in perfumes & flavors; medicine (external); plasticizer;	Monsanto Co Monsanto Flavor/Essence, Inc. Monsanto Indust. Chems. Co.	St. Louis, Mo. St. Louis, Mo.	Ξ	-
	miticide	Northwest Indust., Inc Velsicol Chem. Corp., subsid.	Chattanooga, Tenn.	-	
		Pfizer Inc Chems. Div.	Greensboro, N. C.	-	
		Universal Oil Products Co Chems. & Plastics Group - Chem. Div.	East Rutherford, N. J.	-	
Benzyl chloride	Dyes; intermediates; benzyl compounds; syn- thetic tannins; per-	W, R. Grace & Co Hatco Group - Ratco Chem. Div.	Fords, N. J.	6.8 (15)	40 .9 (90) - 197a
	fumery; pharmaceuticals; manufacture of photo- graphic developer; gasoline gum inhibi- tors; penicillin precursors; quaternary	Monsanto Co Monsanto Indust. Chems. Co.	Bridgeport, N. J.	34 (75)	
		Northwest Indust., Inc. Velsicol Chem. Corp., subsid.	Chattanooga, Tenn.	4.5 (10)	
	ammonium compounds	Stauffer Chem. Co Specialty Chem. Div.	Edison, N. J.	5 (11)	
		Tenneco Inc Tenneco Chems., Inc Organics	Fords, N. J.	3.2 (7)	
		& Polymers Div.		Total ≠ 536 (118)	
Benzy1	Dyes	GAF Corp Chem. Div.	Rensselear, N. Y.		-
dichloride		Tenneco Inc Tenneco Chems., Inc Organics & Polymers Div.	Great Meadows, N. J.	-	
Biphenyl	Organic synthesis; heat	Bethlehem Steel Corp.	Sparrows Point, Md.	-	2.3 (5) -1971
	transfer agent; fungi- cides; dyeing assistant	Chemol, Inc.	Greensboro, N. C.	-	
	for polyester	Dow Chem. U.S.A.	Bay City, Mich. Freeport, Tex.	٦	
		Monsanto Co Monsanto Indust, Chems. Co.	Anniston, Ala.	-	
		Pilot Chem. Co Pilot Indust. of Texas, subsid.	Houston, Tex.	-	
		Sybron Corp The Tanatex Chem. Co., div.	Lyndhurst, N. J.	-	
		Woonsocket Color & Chem. Co.	Woonsocket, R. I.	-	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Bisphenol	Epoxy, polycarbonate,	Dow Chem. U.S.A.	Freeport, Tex.	45.4 (100)	145.1 (319.7)-1973
A	phenoxy, & polysul- fone resins	Gen. Electric Co Plastics Business Div Engineering Plastics Product Dept.	Mount Vernon, Ind.	32.7 (72)	
		Shell Chem. Co Polymers & Detergent Products	Deer Park, Tex.	68 (150)	
		Union Carbide Corp Chems. & Plastics Div.	Marietta, Ohio	18.2 (40)	
	,	Union Carbide Caribe, Inc., subsid.	Penuelas, P. R.	31.8 (70)	
				Total = 196.1 (432)	
Bromo- benzene	Solvent; motor fuels; top-cylinder com- pounds; crystallizing solvent; organic synthesis	Dow Chem. U.S.A.	Midland, Mich.	-	-
Bromo- naphtha-	Organic synthesis; microscopy;	Eastman Kodak Co Eastman Organic Chems.	Rochester, N. Y.	-	-
lene	refractometry	Guardian Chem. Corp Eastern Chem. Div.	Hauppauge, N. Y.	-	
		R.S.A. Corp.	Ardsley, N. Y.	-	
Butadiene	Principally in sty- rene-butadiene rubber,	Atlantic Richfield Co ARCO Chem. Co., div.	Channelview, Tex.	127 (280)	1663 (3662.8)-1973
	& to a lesser degree in polybutadiene and nitrile elastomers;	Copolymer Rubber & Chem. Corp.	Baton Rouge, La.	58.1 (128)	
	as the starting material for adiponitrile (nylon	Dow Chem. U.S.A.	Bay City, Mich. Freeport, Tex.	10.9 (24) 39 (86)	
	66); in latex paints; resins; organic intermediate	El Paso Natural Gas Co El Paso Products Co., subsid.	Odessa, Tex.	90.8 (200)	
		Exxon Corp Exxon Chem. Co. U.S.A Exxon Chem. Co., div.	Baton Rouge, La.	154.4 (340)	
		The Firestone Tire & Rub- ber Co., Firestone Synthetic Rubber & Latex Co., div.	Orange, Tex.	99.9 (220)	

<u>Chemical</u>	<u>Usage l</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM_lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Butadiene (continued)	(see previous page)	Getty Oil Co.	Delaware City, Del.	9.1 (20)	(see previous page)
(,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		Mobil Oil Corp Mobil Chem. Co., div Petrochems. Div.	Beaumont, Tex.	36.3 (80)	
		Monsanto Co Monsanto Polymers & Petrochems. Co.	Chocolate Bayou	54.5 (120)	
		Neches Butane Products Co.	Port Neches, Tex.	290.6 (640)	
		Northern Natural Gas Co. Northern Petrochem. Co., subsid., Polymers Div.	Morris, Ill.	29.5 (65)	
		Petro-Tex Chem. Corp Petro-Tex Chem. Co., subsid.	Houston, Tex.	449.5 (990)	
		Phillips Petroleum Co Petrochem, & Supply Div.	Phillips, Tex.	131.7 (290)	
		Puerto Rico Olefins Co.	Penuelas, P. R.	90.8 (200)	
		Shell Chem. Co Base Chems,	Deer Park, Tex.	120.3 (265)	
		Standard Oll Co. (Ind.) - Amoco Chems. Corp., sub- sid.	Chocolate Bayou, La.	40.9 (90)	
		Union Carbide Corp Chems. & Plastics Div.	Seadrift, Tex. Taft, La. Texas City, Tex.	20.4 (45) 40.9 (90) 20.4 (45)	
		Union Carbide Carbide, Inc. Subsid.	Penuelas, P. R.	70.4 (155)	
				Total = 1,985.3 (4,373)	

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<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Locațion(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} . production MM kg (MM lb) <u>for year of estimate</u>
n-Butyl acetate	Solvent in production of lacquers, lacquer enamels;	Celanese Corp Cela- nese Chem. Cor., div.	Bishop, Tex.	6.8 (15)	43.4 (95.7) -1972
;	pyroxylin solutions; leather dressings; per- fumes, flavoring extracts; solvent for natural gums & synthesic resins; dehy-	Eastman Kodak Co Eastman Chem. Products, Inc., subsid - Tenn. Eastman Co., div.	Kingsport) Tenn.	6.8 (15)	
	drating agent	Publicker Indust. Inc.	Philadelphia, Pa.	6.8 (15)	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va. Texas City, Tex.	22.7 (50)	
			10000 010 0 , 1000	Total = 43.1 (95)	
sec-Butyl acetate		Exxon Corp Exxon Chem. Co.	Baton Rouge, La.	÷	<24.9 (<54.9) →1967
	th inn ers; nail enamels; celluloid products;	Hercules, Inc.	Hattlesburg, Miss.	-	
	artificial leather; leather finishes; plastic wood; washable wallpaper	Shell Chem, Co Indust. Chems./Petro- chems. (See also - n-Butyl acetate)	Deer Park, Tex.	-	
tert- Butyl acetate	Possible antiknock agent in gasoline	Exxon Corp Exxon Chem. Co. (See also - n-Butyl acetate)	Baton Rouge, La.	-	-
n-Butyl- acrylate	Intermediate in organic synthesis; polymers &	Celanese Corp Cela- nese Chem. Co., div.	Clear Lake, Tex. Pampa, Tex.	-	-
	copolymers for solvent coatings, adhesives,	Dow Badische Co.	Freeport, Tex.	-	
	paints, binders; emulsifier	Rohm & Haas Co Rohm & Haas Texas Inc., subsid.	Deer Park, Tex.	-	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va. Taft, La.	- -	

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	$Location(s)^2, 3$	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
n-Butyl alcohol	Preparation of esters, especially butyl ace- tate; solvent for	Celanese Corp Cela- nese Chem. Co., div.	Bay City, Tex. Bishop, Tex. Clear Lake, Tex.	68.1 (150) 20.4 (45)	235.4 (518.6) -1973
	resins & coatings; plasticizers; dyeing assistant; hydraulic	Continental Oil Co Conoco Chems.	Westlake, La.	2.3 (5)	
	fluids; detergent	Dow Badische Co.	Freeport, Tex.	43.1 (95)	
	formulations; dehydrat- ing agent (by azeo- tropic distillation); intermediate; "butyl- ated" melamine	Eastman Kodak Co Eastman Chem. Products Inc., subsid Texas Eastman Co., div.	Longview, Tex.	31.8 (70)	
	resins	W. R. Grace & Co Hatco Group - Hatco Chem. Div.	Fords, N. J.	-	
		Oxochem Enterprise	Penuelas, P. R.	36.3 (80)	
		Publicker Indust. Inc.	Philadelphia, Pa.	15.9 (35)	
		Shell Chem. Co Base Chems.	Deer Park, Tex.	36.3 (80)	
		Union Carbide Corp Chems. & Plastics Div.	Seadrift, Tex.	27.2 (60)	
		Union Carbide Caribe,	Penuelas, P. R.	18.2 (40)	
		Inc., subsid.		Total = 299.6 (660)	
sec- Butyl alcohol	Preparation of methyl ethyl ketone; solvent; organic synthesis	Celanese Chem, Co.	Bay City, Tex. Bishop, Tex. Clear Lake, Tex.	-	205.6 (453) -1973
		Exxon Corp Exxon Chem. Co.	Baton Rouge, La.	-	
		Shell Chem. Co Indust, Chems./Petro- chems.	Deer Park, Tex.	-	
tert- Butyl alcohol	Alcohol denaturant	Shell Chem. Co Indust. Chems./ Petrochems.	Martinez, Calif.	-	508.5 (1120) -1973
		Oxirane Chem. Co.	Bayport, Tex.	-	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
tert-	Chemical intermediate	Dow Chem. U.S.A.	Midland, Mich.	-	-
Butyl- phenol	for synthetic resins, plasticizers, surface-	Ethyl Corp.	Orangeburg, S. C.	-	
phonol	active agents, perfumes, & other products; a	Productol Chem. Co.	Santa Fe Springs, Calif.	-	
	permissible antioxi- dant for aviation gasoline: plasticizer	Schenectady Chem., Inc.	Rotterdam Junction, N. Y.	-	
	gasoline; plasticizer for cellulose acetate intermediate for anti- oxidants, special starches, oil soluble phenolic resins; pour- point depressors & emulsion breakers for petroleum oils & some plastics; synthetic lubricants; insec- ticides; industrial odorants	Union Carbide Corp Chems. & Plastics Div.	Bound Brook, N. J.	-	
tert- Butyl- toluene	Solvent; intermediate	Shell Chem. Co Base Chems.	Martinez, Calif.	-	-
n-Butyr- aldehyd e	Polyvinyl butyral; butyrate plastics	Celanese Corp Celanese Chem. Co., div.	Bay City, Tex. Bishop, Tex. Freeport, Tex.	 136.2 (300)	-
		Eastman Kodak Co Eastman Chem. Pro- ducts, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	227 (500)	
		Oxochem Enterprise	Penuelas, P. R.	158.9 (350)	
		Shell Chem. Co Base Chems.	Deer Park, Tex.	111.2 (245)	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va. Seadrift, Tex.	- 68.1 (150)	
		Union Carbide Caribe,	Penuelas, P. R.	136.3 (300) Total = 837.6 (1845)	

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5.} production MM kg (MM lb) <u>for year of estimate</u>
n-Butyric acid	Synthesis of butyrate ester perfume &	Celanese Corp Cela- nese Chem. Co., div.	Pampa, Tex.	-	-
	flavor ingredients; pharmaceuticals; de- liming agent; dis- infectants; emulsi- fying agents;	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Eastman, Tenn.	-	
	sweetening gasolines	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
n-Butyric anhydride	Manufacture of butyrates; drugs; tanning agents	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	-	-
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
n-Butyr- onitrile	Basic material in in- dustrial, chemical & pharmaceutical inter- mediates & products;	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	-	-
	poultry medicines	Lonza Inc.	Mapleton, Ill.	-	
Carbon disul- fide	Viscose rayon; cel- lophane; manufacture of carbon tetrachloride	FMC Corp Chem. Group - Indust. Chem. Div.	South Charleston, W. Va.	81.7 (180)	351.8 (775) - 1972
	& flotation agents; veterinary medicine; sclvent	Pennwalt Corp Chem. Div.	Greens Bayou, Tex.	4.5 (10)	
	SCIVENT	PPG Indust., Inc Chem. Div Indust. Chem. Div.	Natrium, W. Va.	27.2 (60)	
		Stauffer Chem. Co Indust. Chem. Div.	Delaware City, Del. Le Moyne, Ala.	15 8. 9 (350) 113.5 (250)	
				Total = 385.9 (850)	
Carbon	Organic synthesis	Great Lakes Chem. Corp.	El Dorado, Ark.	-	-
tetra- bromide		Olin Corp Designed Products Div.	Rochester, N. Y.	-	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
n-Butyl-	Intermediate for	Air Products & Chems.	Pensacola, Fla.	-	1.82 (4) -1973
amine	emulsifying agents; pharmaceuticals, in- secticides; rubber	Pennwalt Corp Chem. Div.	Wyandotte, Mich.	-	
	chemicals; dyes; tanning agents	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
		Va. Chems. Inc Indust. Chems. Dept.	Portsmouth, Va.	-	
sec-Butyl- amine	-	Pennwalt Corp Chem. Div.	Wyandotte, Mich.	-	-
		Va. Chems. Inc Indust. Chems. Dept.	Portsmouth, Va.	-	
tert-Butyl- amine	Intermediate for rubber accelerators; insec-	Monsanto Co Monsanto Indust. Chem. Co.	Texas City, Tex.	-	-
	ticides; fungicides; dyestuffs; pharmaceu- ticals	Rohm & Haas Co Rohm & Haas Tex Inc., subsid.	Deer Park, Tex.	-	
p-tert- Butyl- benzoic acid	-	Shell Chem. Co Base Chems.	Martinez, Calif.	-	-
l,3 Butylene glycol	Polyesters; polyure- thanes; surface active agents; plasticizers; humectant; coupling agent; solvent; food additive & flavoring	Celanese Corp Celanese Chem. Co., div.	Bishop, Tex.	-	-
Butylenes	Polymer & alkylate gaso- line; polybutenes;	Dow Chem. U.S.A.	Bay City, Mich. Freeport, Tex.	Ξ	10,074 (22,190)-1967
	butadiene; intermediate for C, & C ₅ aldehydes, alcohols, & other	Gulf Oil Corp Gulf Oil Chems. Co., div Petrochems div.	Cedar Bayou, Tex.	-	
	derivatives; Solvent; cross-link- ing agent; butadiene synthesis; synthesis of C ₄ & C ₅ derivatives	Petro-Tex Chem. Corp Petro-Tex Chem. Co., subsid.	Houston, Tex.	-	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM_kg (MM_lb)	Total 4,5 production MM kg (MM lb) for year of estimate
Carbon tetra-	Refrigerants & propel- lants; metal degreasing;	Allied Chem. Corp Specialty Chem. Div.	Moundsville, W. Va.	3.6 (8)	458.3 (1009.4) -1971
chloride	agricultural fumigant; chlorinating organic compounds; production of	Dow Chemical U.S.A.	Freeport, Tex. Pittsburg, Cal.	59 (130) 20 .4 (45)	
	semiconductors	E. I. du Pont de Nemours & Co., Inc Organic Chems Dept. Freon® - Products Div.	Plaquemine, La. Corpus Christi, Tex.	45.4 (100) -	
		FMC Corp Chem. Group - Indust. Chem. Div.	South Charleston, W. Va.	136.2 (300)	
		Inland Chem. Corp.	Manat1, P. R.	-	
		Stauffer Chem. Co Indust. Chem. Div.	Le Moyne, Ala. Louisville, Ky. Niagara Falls, N. Y.	90.8 (200) 31.8 (70) 68.1 (150)	
		Vulcan Materials, Co Chems. Div.	Geismar, La. Wichita, Kans.	15.9 (35) 18.2 (40) Total = 716.4 (1578)	

<u>Chemical</u>	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Cellulose acetate	Acetate fiber; lacquers; protective coating solutions; photographic	Celanese Corp Celanese Fibers Co., div.	Narrows, Va. Rock Hill, S. C. Rome, Ga.	227 (500)	209.8 (462.2) -1973
	film, transparent sheet- ing, thermoplastic mold- ing composition, cigaret- te filters, magnetic	E. I. du Pont de Ne- mours & Co., Inc Textile Fibers Dept.	Waynesboro, Va.	27.2(60)	
	tapes, osmotic cell membrane	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	156.6(345)	
		FMC Corp Chem. Group - Fiber Div.	Meadville, Pa.	11.3(25) Total = 422.2(930)	
Chloranil	Agricultural fungicide; dye intermediate; ele- trodes for pH measure- ments; vulcanizing agent	-	-	-	-
Chloro-	Herbicide; intermediate	Dow Chem. U.S.A.	Midland, Mich.	20.4(45)	29.1 (64.2) -1969
acet1c ac1d	in production of car- boxymethylcellulose, ethyl chloroacetate, glycine, synthetic	Hercules Inc Coating & Specialty Products Dept.	Hopewell, Va.	9.1(20)	
	caffeine, sarcosine,	The Procter & Gamble	Memphis, Tenn.	1.4(3)	
	thioglycolic acid, EDTA, 2,4-D, 2,4,5-T	Co The Buckeye Cellulose Corp., subsid.		Total = 30.9 (68)	
m-chloio- aniline	Intermediate for azo dyes & pigments; phar- maceuticals; insecti- cides; agricultural	E. I. du Pont de Nemours & Co., Inc., Organic Chems. Dept Dyes & Chems: Div.	Deepwater, N. J.	-	-
	chemicals	GAF Corp Chem. Div.	Linden, N. J.	-	
o-chloro- aniline	Dye intermediate; stan- dards for colorimetric apparatus; manufacture of petroleum solvents	E. I. du Pont de Nemours & Co., Inc Organic Chems. Dept Dyes & Chems. Div.	Deepwater, N. J.	-	-
	& fungicides	Monsanto Co Monsanto Indust. Chems. Co.	Luling, La.	-	

<u>Chemical</u>	<u>Usagel</u>	Manufacturer(s) ^{2,3}	Location(s) ² , ³	1975 capacity² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
p-chloro- aniline	Dye intermediate; pharmaceuticals; agri- cultural chemicals	E. I. du Pont de Nemours & Co., Inc., Organic Chems. Dept Dyes & Chems. Div.	Deepwater, N. J.	-	-
		Monsanto Co Monsanto Indust, Chems. Co.	Luling, La.	-	
Chloro- benzalde- hyde	Intermediate in the preparation of tri- phenyl methane & related dyes; organic intermediate	Occidental Petroleum Corp Hooker Chem. Corp., subsid Hooker Chems. & Plastics Corp. subsid - Electrochemi- cal & Specialty Chems. Div.	Niagara Falls, N. Y.	-	-
		Tenneco Inc Tenneco Chems., Inc Organics & Polymers Div.	Fords, N. J.	-	
Chloro- benzene	Phenol; chloronitro- benzene; DDT; aniline;	Allied Chem. Corp Indust. Chems. Div.	Syracuse (Solvay), N. Y.	11.3 (25)	183.2 (403.5) -1972
	solvent carrier for methylene dilsocyanate;	Dow Chem. U.S.A.	Midland, Mich.	136.2 (300)	
	intermediate & solvent	Monsanto Co Monsanto Indust. Chems. Co.	Sauget, Ill.	52.2 (115)	
		Montrose Chem. Corp. of California	Henderson, Nev.	31.8 (70)	
		Occidental Petroleum Corp Hooker Chem. Corp., subsid Hooker Chems. & Plastics Corp., subsid Electrochemi- cal & Specialty Chems. Div.	Niagara Falls, N.Y.	6.8 (15)	
		PPG Indust., Inc Chem. Div Indust. Chem. Div.	Natrium, W. Va.	41.3 (91)	
		Standard Chlorine Chem. Co., Inc.	Delaware City,	34 (75) Total = 313.7 (691)	

<u>Chemical</u>	Usagel	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Chloro- benzoic acid	Intermediate for the preparation of dyes, fungicides, pharma- ceuticals & other organic chemicals	Tenneco Inc Tenneco Chems., Inc Organics & Polymers Div.	Fords, N. J.	-	-
Chloro- benzoyl chloride	Intermediate for pharmaceuticals, dyes & other organic chemicals	Tenneco Inc Tenneco Chems., Inc Organics & Polymers Div.	Fords, N. J.	-	-
Chloro- Refrigerant; solvent; difluoro- aerosol propellant; ethane intermediate	aerosol propellant;	E. I. du Pont de Nemours & Co., Inc., Organic Chems. Dept Freon® Products Div.	Antioch, Calif. Deepwater, N. J. East Chicago, Ind. Louisville, Ky. Montague, Mich.		-
		Pennwalt Corp Chem, Div.	Calvert City, Ky.	-	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
Chloro- form	Fluorocarbon refrig- ants & propellants; fluorocarbon plastics; dyes & drugs; general solvent; analytical	Allied Chem. Corp Specialty Chems. Div.	Moundsville, W. Va.	13.6 (30)	106.8 (235.2) -1972
		Diamond Shamrock Corp Diamond Shamrock Chem. Co Electro Chems. Div.	Belle, W. Va.	8.2 (18)	
	chemistry; fumigant; insecticides	Dow Chem. U.S.A.	Freeport, Tex.	45.4 (100)	
		Stauffer Chem. Co Indust. Chem. Div.	Louisville, Ky.	34.1 (75)	
		Vulcan Materials Co Chems. Div.	Geismar, La. Newark, N. J. Wichita, Kans.	4.5 (10) 13.6 (30) Total = 133 (293)	
Chloro- naphtha-	Wax; condenser impreg- nation; moisture-, flame-	American Color & Chem. Corp.	Lock Haven, Pa.	-	-
lene	acid-, insect-proofing	GAF Corp Chem. Div.	Linden, N. J.	-	
	of wood, fabric & other fibrous bodies; mois- ture-, & flame-proofing covered wire & cable; solvent (for rubber, aniline & other dyes; mineral & vegetable oils, varnish gums & resins, & other waxes when mixed in the molter state	Koppers Co., Inc Organic Materials Div.	Bridgeville, Pa.		
	in the motten state				

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM_kg_(MM_lb)_	Total ^{4,5} production MM kg (MM lb) for year of estimate
o- cresol	See m cresol	Continental Oil Co Conoco Chems Pitt Consol Chems.	Newark, N. J.	-	See m-cresol
		Koppers Co., Inc Organic Materials Div.	Follansbee, W. Va.	-	
		The Merichem Co.	Houston, Tex.	-	
		Productol Chem. Co.	Santa Fe Springs, Calif.	-	
		Stimson Lumber Co Northwest Petrochem. Corp., div.	Anacortes, Wash.	-	
p-cresol	See m-cresol	American Cyanamid Co Organic Chems. Div.	Bound Brook, N. J.	-	See m-cresol
		The Sherwin-Williams Co Sherwin-Williams Chems. Div.	Chicago, Ill.	-	
Cresylic acid	Phosphate esters; phenolic resins; wire enamel solvent; plastici- zers; gasoline additives; laminates coatings for magnet wire for small	Continental Oil Co Conoco Chems Pitt- Consol Chems.	Newark, N. J.	22.7 (50)	31.7 (69.9) -1971
		Crowley Tar Products Co., Inc.	Houston, Tex.	-	
	electric motors; dis- infectants; metal	Koppers Co., Inc Organic Materials Div.	Follansbee, W. Va.	15.9 (35)	
	cleaning compounds; phenolic resins flota-	The Merichem Co.	Houston, Tex.	45.4 (100)	
	tion agents; surfactants; chemical intermediates;	Mobil Oil Corp North American Div.	Beaumont, Tex. Paulsboro, N. J.	1.4 (3)	
	oil additives; solvent refining of lubricating oils; scouring com- pounds; pesticides	Productol Chem. Co.	Santa Fe Springs, Calif.	13.6 (30)	
		Stimson Lumber Co Northwest Petrochem. Corp., div.	Anacortes, Wash.	13.6 (30)	
		U.S. Steel Corp USS Chems., div.	Clairton, Pa.	9.1 (20)	
				Total = 121.7 (268)	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5.} production MM kg (MM lb) for year of estimate
Chloro- nitro- benzene	<pre>Intermediate, especially for dyes; manufacture of p-nitrophenol, from which parathion is made</pre>	E. I. du Pont de Nemours & Co., Inc Organic Chems. Dept Dyes & Chems. Div.	Deepwater, N. J.	20.4 (45)	-
		Monsanto Co Monsanto Indust. Chems. Co.	Sauget, Ill.	43.1 (95)	
				Total = 63.5 (140)	
Chloro-	Intermediate in synthesis	Aldrich Chem, Co., Inc.	Milwaukee, Wisc.	_	-
phenols	of dyes & drugs; denatu-	Dow Chem. U.S.A.	Midland, Mich.	-	
	rant for alcohol; selec- tive solvent in refining mineral oils	Eastman Kodak Co Eastman Organic Chems.	Rochester, N. Y.	-	
		Monsanto Co Monsanto Indust, Chems. Co.	Sauget, Ill.	-	
		Specialty Organics, Inc.	Irwindale, Calif.	-	
m-chloro- toluene	Solvent; intermediate	R.S.A. Corp.	Ardsley, N. Y.	-	-
ochloro- toluene	Solvent & intermediate for organic chemicals & dyes	Occidental Petroleum Corp Hooker Chem. Corp., subsid., Hooker Chems. & Plastics Corp., subsid Electrochemi- cal & Specialty Chems. Div.	Niagara Falls,	-	-
		Tenneco Inc Tenneco Chems., Inc Organics & Polymers Div.	Fords, N. J.	-	
p-chloro- toluene	Solvent & intermediates for organic chemicals & dyes	(See o-chlorotoluene)	-	-	-
m- cresol	Disinfectant; phenolic resins; tricresyl phos- phate; ore flotation; textile scouring agent; organic intermediate; mfg. of salicylaldehyde; coumarin, & herbicides; in food antioxidants; surfactant	Koppers Co., Inc Organic Materials Div.	011 City, Pa.	-	Total m,o,p cresol = 10.5 (23.1) -1970

<u>Chemical</u>	<u>Usage l</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM 1b)	Total*'5. production MM kg (MM lb) for year of estimate
Croton- aldehyde	Intermediate for n- butyl alcohol & 2- ethyl-hexyl alcohol; solvent; preparation of rubber accelerators; purification of lubrica- ting oils; insecticides; tear gas; fuel-gas warn- ing agent; organic synthesis; leather tan- ning; alcohol denaturant	Union Carbide Corp Chems. & Plastics Div.	Institute & Charleston, W. Va.	-	-
Crotonic acid	Synthesis of resins, polymers, plasticizers, drugs	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	-	-
Cumene	Production of phenol, acetone, & alpha- methylstyrene; solvent	Ashland Oil, Inc Ash- land Chem. Co., div Petrochems. Div.	Ashland, Ky.	136,2 (300)	1325.7 (2920) - 1974
		Clark Oil & Refining Corp Clark Chem. Corp., subsid.	Elue Island, Ill.	50 (110)	
		Coastal States Gas Corp. Coastal States Marketing, Inc., subsid.	Corpus Christi,	63.6 (140)	
		Dow Chem. U.S.A.	Midland, Mich.	4.5 (10)	
		Gulf Oil Chems. Co., div Gulf Oil Corp Petrochems. Div.	Philadelphi a, Pa. Port Arthur, Tex.	204.3 (450) 204.3 (450)	
		Marathon Oil Co.	Texas City, Tex.	95.3 (210)	
		Monsanto Co Monsanto Polymers & Petrochems. Co.	Chocolate Bayou,	290.6 (640)	
		Phillips Petroleum Co Petrochem & Supply Div,	Phillips, Tex.	0.5 (1)	
		Skelly Oil Co.	El Dorado, Kans.	63.6 (140)	

Chemical	<u>Usage 1</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² <u>MM kg (MM lb)</u>	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Cumene (con't)	(see previous page)	Standard Oil of Calif Chevron Chem. Co., sub- sid., Oronite Additives & Indust. Chems. Div Indust. Chems.	El Segundo, Calif.	45.4 (100)	(see previous page)
		Standard Oil Co. (Ind.) Amoco Chems. Corp., subsid.	Texas City, Tex.	22.7 (50)	
		Sun Oil Co Sun Oil Co. of Penn., subsid Suntide Refining Co., subsid.	Corpus Christi,	113.5 (250)	
		Texaco Inc.	Westville, N. J.	63.6 (140)	
		Union Carbide Corp	Penuelas, P. R.	290.6 (640)	
		Union Carbide Caribe, Inc., subsid.		Total = 1648 (3631)	
Cumene hydro-	Production of acetone & phenol; polymerization catalyst, particularly in redox systems, used for rapid polymerization	Allied Chem. Corp Specialty Chems. Div.	Frankford, Pa.	-	-
peroxide		Hercules Inc., Organics Dept Synthetics Dept.	Gibbstown, N. J. Gibbstown, N. J.	-	•
	i i i i i i i i i i i i i i i i i i i	Reichhold Chems., Inc Specialty Chems. Div.	Austin, Tex.	-	
Cyano- acetic acid	Organic synthesis	Kay-Fries. Chems., Inc.	Stany Point, N. Y.	-	-
Cyanogen chloride	Organic synthesis; tear gas; warning agent in fumigant gases	Nilok Chems., Inc.	Memphis, Tenn.	-	-
Cyanuric acid	Organic synthesis	FMC Corp Chem. Group- Indust. Chem. Div.	South Charleston,	-	-
		Monsanto Co Monsanto Indust. Chems. Co.	Everett, Mass.	-	
Cyanuric chloride	Chemical synthesis; dyestuffs; pharmaceuti-	Ciba-Geigy Corp Agricultural Div.	McIntosh, Ala. St. Gabriel, La.	-	-
	cals; explosives; surfactants	Nilok Chems., Inc.	Memphis, Tenn.	-	

Total^{4,5}

<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capac1ty ² <u>MM kg (MM 1b)</u>	production MM kg (MM lb) for year of estimate
Cyclo- hexane	Manufacture of nylon; solvent for cellulose ethers, fats, oils,	American Petrofina, Inc. Cosden Oil & Chem. Co., subsid.	Big Spring, Tex.	45.3 (99.8)	1062.4 (2340) -1974
	waxes, bitumens, resins, crude rubber; extracting essential oils; chemical (organic synthesis, re- crystallizing medium);	Commonwealth Oil Refin- Co., Inc Corco Cyclohexane, Inc subsid.	Penuelas, P. R.	117.7 (259.2)	
	paint & varnish remover; glass substitutes; vapor has been used as	Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Baytown, Tex.	117.7 (259.2)	
	lubricant for steel (experimental)	Guif Oil Corp Gulf Oil Chems. Co., div Petrochems. Div.	Port Arthur, Tex.	97.1 (213.8)	
		Phillips Petroleum Co	Borger, Tex. Sweeny, Tex.	117.7 (259.2) 252.8 (556.8)	
		Phillips Puerto Rico Core Inc., subsid.	Guayama, P. R.	214.7 (473)	
		Texaco Inc.	Port Arthur, Tex.	117.7 (259.2)	
		Union Oil Co. of Calif.	Beaumont, Tex.	100 (220.3)	
		Union Pacific Corp Champlin Petroleum Co., subsid.	Corpus Christi,	67 (147.6)	
				Total = 1323.4 (2915.1))
Cyclo- hexanol	Soap making; to in- corporate solvents &	Allied Chem. Corp Fibers Div.	Hopewell, Va.	-	325.5 (716.9) -1968
	phenolic insecticides; source of adipic acid for nylon; textile	Celanese Corp Cela- nese Chem. Co., div.	Bay City, Tex.	-	
	finishing solvent;	Dow Badische Co.	Freeport, Tex.	-	
	<pre>blending agent; lacquers; paints & varnishes; finish removers; dry cleaning; emulsified products; leather degreasing; polishes; plasticizers; plas-</pre>	El Paso Products Co., subsid El Paso Natural Gas Co.	Odessa, Tex.	-	
		Monsanto Co. — Monsanto Indust. Chems. Co. — Monsanto Textiles Co.	Luling, La. Pensacola, Fla.	-	
	tics; germioides	Nípro, Inc.	Augusta, Ga.	• -	
		Rohm & Haas Co Rohm & Haas Ky. Inc., subsid.	Louisville, Ky.	-	

<u>Chemical</u>	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM 1b)	Total ^{4,5} . production MM kg (MM lb) for year of estimate_
Cyclo- hexa	Organic synthesis; particularly of adipic	Allied Chem. Corp Fibers Div.	Hopewell, Va.	157.1 (346)	343.5 (756.5) -1971
	acid & caprolactam (about 95%); polyvinyl chloride & its copolymers, &	Celanese Corp Cela- nese Chem. Co., div.	Bay City, Tex.	45.4 (100)	
	methacrylate ester poly-	Dow Badische Co.	Freeport, Tex.	113.5 (250)	
	mers; solvent for DDT in aerosol bombs; general wood stains; paint & varnish removers; spot	El Paso Natural Gas Co El Paso Products Co., subsid.	Odessa, Tex.	29 (64)	
	& stain removers; de- greasing of metals;	Monsanto Co. — Monsanto Textiles Co.	Pensacola, Fla.	227 (500)	
	in polishes; leveling agent in dyeing & de-	Nipro, Inc.	Augusta, Ga.	68.1 (150)	
	lustering silk; lube oil additive; general	Rohm & Haas Co Rohm & Haas Ky. Inc subsid.	Louisville, Ky.	18.2 (40)	
	solvent	Union Carbide Corp Chems. & Plastics Div.	Taft, La.	31.8 (70)	
				Total = 701.4 (1545)	
Cyclo- hexene	xene catalyst solvent; oil extraction clo- Boiler-water treatment; xyl- corrosion inhibitor	Phillips Petroleum Co Petrochem, & Supply Div.	Phillips, Tex.	-	-
		Uniroyal, Inc Uniroyal Chem., div.	Naugatuck, Conn.	-	
Cyclo- hexyl-		Abbott Labs Chem. D1v.	Wichita, Kans.	4.5 (10)	-
amine		Monsanto Co Monsanto Indust. Chems. Co.	Sauget, Ill.	1 (2)	
		Virginia Chems., Inc Indust. Chems. Dept.	Portsmouth, Va.	3.6 (8)	
				Total = 9.1 (20)	

<u>Chemical</u>	<u>Usage1</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² <u>MM kg (MM 1b)</u>	Total ^{4,5} production MM kg (MM lb) for year of estimate
Decahydro- naphtha- lene	naphtha- waxes, resins, rubber, lene etc.; substitute for turpentine; cleaning	E. I. du Pont de Ne- mours & Co., Inc Organic Chems. Dept Dyes & Chems. Div.	Deepwater, N. J.	-	_
<pre>machinery; stain-re- mover; shoe creams, floor waxes, etc.; cleaning fluids; lubricants</pre>	Lonza Inc.	Mapleton, Ill.	-		
Decanol	Decanol Plasticizers; deter- gents; synthetic lubri- cants; solvents; per- fumes; flavorings	Continental Oil Co Conoco Chems.	Westlake, La.	-	-
		The Proctor & Gamble Co.	Ivorydale, Ohio	-	
Diacetone alcohol	Solvent for nitro- cellulose, cellulose	Celanese Corp Cela- nese Chem. Co., div.	Bishop, Tex.	-	-
	acetate, various oils, resins, waxes, fats, dyes, tars; lacquers;	Shell Chem. Co Base Chems.	Deer Park, Tex. Dominguez, Calif.	-	
	dopes, coating composi- tion; wood preservatives; stains; rayon & artifical leather; imitation gold leaf; dyeing mixtures; extraction of resins & waxes; preservative for animal tissues; metal- cleaning compounds; hydraulic compression fluids; stripping agent (textiles); labora- tory reagent; the techni- cal grade, containing acetone, has greater solvent power	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
Diamino- benzoic	-	Bofors Indust., Inc.	Linden, N. J.	-	-
acid		Salsbury Labs.	Wilmington, N. C.	-	

<u>Chemical</u>	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Dichloro- D	Dye intermediate;	Blue Spruce Co.	Edison, N. J.	-	-
aniline	aniline intermediate for biologically active compounds	Eastman Kodak Co Eastman Organic Chem.	Rochester, N. Y.	-	
		E. I. du Pont de Ne- mours & Co., Inc Organic Chems. Dept Dyes & Chems, Div.	Deepwater, N. J.	-	
		Monsanto Co Monsanto Indust. Chems. Co.	Luling, La.	-	
Dichloro- benzene (m,o,p)	Mfg. of 3,4-dichloro- aniline; solvent for a wide range of organic	Allied Chem. Corp Indust. Chem. Div Chem. Products Corp.	Syracuse (Solvay), Cartersville, Ga.	9 (20) 2.3 (5)	63.4 (139.7) -1972
	materials & for oxides of nonferrous metals;	Dow Chem. U.S.A.	Midland, Mich.	14.1 (31)	
	solvent carrier in production of toluene	Monsanto Co Monsanto Indust. Chems. Co.	Sauget, Ill.	12.7 (28)	
	diisocyanate; dye manu- facturing; fumigant & insecticide; degreasing hides & wool; metal polishes, industrial odor control; moth repellent; germicide	Occidental Petroleum Corp Hooker Chem. Corp., subsid - Hooker Chems. & Plastics Corp subsid Electrochemical & Specialty Chems. Div.	Niagara Falls, N. Y.	-	
	space odorant; manu- facture of 2,5-dich-	PPG Indust., Inc Chem. Div Indust. Chem. Div.	Natrium, W. Va.	21.3 (47)	
	loroaniline; dyes; intermediates; pharmacy; agriculture (fumigat-	Solvent Chem. Co., Inc.	Malden, Mass. Niagara Falls, N. Y.	1.4 (3) 9.1 (20)	
	ing soil)	Specialty Organics Inc.	Irwindale, Calif.	1.4 (3)	
		Standard Chlorine Chem. Co., Inc.	Delaware City, Del. Kearny, N. J.	27.2 (60) 7.3 (16) Total =	
				105.8 (233)	

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Dichloro- ethylene (vinyl- idene chloride)	General solvent for organic materials; dye extraction; perfumes; lacquers; thermoplastics; organic synthesis; medicine; copolymerized with vinyl chloride or acrylonitrile to form various kinds of saran; other copolymers are also made; adhesives; component of synthetic fibers	Dow Chem. U.S.A. PPG Indust., Inc Chem. Div Indust. Chem. Div.	Freeport, Tex. Plaquemine, La. Lake Charles, La.	-	-
Dichloro- ethyl ether	General solvent; selec- tive solvent for produc- tion of high-grade lubri- cating oils; textile scouring & cleansing; fulling compounds; wet- ting & penetrating com- pounds; organic synthe- sis; paints, varnishes, lacquers; finish removers; solting & dry cleaning; solt fumigant	Buckman Labs., Inc. Dow Chem. U.S.A. Union Carbide Corp Chems. & Plastics Div.	Cadet, Mo. Memphis, Tenn. Freeport, Tex. Institute & South Charleston, W. Va.	-	-
Dichloro- hydrin	General solvent; inter- mediate in organic syn- thesis; paints, varnishes, lacquers, celluloid cements; water colors' binder; photographic lacquers	Eastman Kodak Co Eastman Organic Chems.	Rochester, N. Y.	-	-
Dichloro- pentane	Solvent for oils, greases, rubber, resins & bi- tuminous materials; removal of tar; reclaiming rubber; paint & varnish removers; degreasing of metals; insecticide; soil fumi- gant; removal of wax deposits on oil-well equipment	-	-	-	-

<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location $(s)^{2,3}$	1975 capacity ² MM kg (MM lb)	Total*; ⁵ production MM kg (MM lb) <u>for year of estimate</u>
Dichloro- propene	Organic synthesis; soil fumigants	Dow Chemical U.S.A.	Freeport, Tex.	-	-
Dicyclo- hexyl-	Intermediate; insecti- cides; plasticizer; corrosion inhibitors; antioxidants in rubber; lubricating oils, fuels; catalysts for paint, varnishes & inks; detergents; extractant	Abbott Labs Chem. Div.	Wichita, Kans.	-	-
amine		Va. Chems. Inc Indust. Chems. Dept.	Portsmouth, Va.	-	
Diethanol- amine		Allied Chem. Corp Specialty Chems, Div.	Orange, Tex.	9.1 (20)	50.4 (111) -1974
		Dow Chem. U.S.A.	Freeport, Tex. Midland, Mich.	13.6 (30) 15.9 (35)	
		Olin Corp Designed Products Div.	Brandenburg, Ky.	11.3 (25)	
	plasticizers, etc.; solubilizing 2,4-D	Texaco Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	34 (75)	
		Union Carbide Corp Chems. & Plastics Div.	Seadrift, Tex.	113.5 (250)	
				#T otal = 197.5 (435)	
Diethylene glycol	Polyurethane & unsatu- rated polyester resins;	Allied Chem. Corp Specialty Chems. Div.	Orange, Tex.	4.5 (10)	122 (268.7) -1973
	triethylene glycol; tex- tile softener; petroleum solvent extraction; de-	BASF Wyandotte Corp Indust. Chems. Group	Geismar, La.	9.5 (21)	
	solvent extraction; de- hydration of natural gas; plasticizers & surfac- tants; solvent for nitrocellulose, & many dyes & oils; humectant for tobacco, casein, synthetic sponges, paper products; cork composi- tions; book-binding adhesives; dyeing as- sistant; cosmetics	Celanese Corp Celanese Chem. Co., div.	Clear Lake, Tex.	10.9 (24)	
		Dixie Chem. Co.	Bayport, Tex.	-	
		Dow Chem. U.S.A.	Freeport, Tex. Plaquemine, La.	10.9 (24) 21.3 (47)	
		Eastman Kodak Co East- man Chem. Products, Inc., subsid Texas East- man Co., div.	Longview, Tex.	3.6 (8)	

^{*} Includes mono- and tri-ethanol amines

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) <u>for year of production</u>
Diethylene glycol (Con't)	(see previous page)	Northern Natural Gas Co - Northern Petro- chem. Co., subsid Polymers Div.	Morris, Ill.	13.6 (30)	(see previous page)
		Olin Corp Designed Products Div.	Brandenburg, Ky.	2.3 (5)	
		PPG Indust., Inc Chem. Div Houston Chem. Co., div	Beaumont, Tex.	4.5 (10)	
		PPG Indust. (Caribe)	Guayanilla, P. R.	18.2 (40)	
		Shell Chem. Co Base Chems.	Geismar, La.	4.5 (10)	
		Texaco Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	16.3 (36)	
		Union Carbide Corp Chems. & Plastics Div.	Seadrift, Tex. Taft, La.	97.6 (215)	
		Union Carbide Caribe, Inc., subsid.	Penuelas, P. R.		
				Total = 218 (480)	
Diethylene	Solvent for nitro-	Dow Chem. U.S.A.	Midland, Mich.	-	6.8 (15) -1972
glycol mono- butyl ether	cellulose, oils, dyes, gums, soaps, polymers; plasticizer intermediate	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	-	
		Olin Corp Designed Products Div.	Brandenburg, Ky.	-	
		Shell Chem. Co Base Chems.	Geismar, La.	-	
		Texaco Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	~	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
Diethylene glycol mono- butyl	Solvent for oils, resins, gums, also for cellulose nitrate & polymeric coatd ings; plasticizers in lacquers & coatings	Eastman Kodak Co East- man Chem. Products, Inc., subsid Tex. Eastman Co., div.	Longview, Tex.	-	-
ether acetate		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	

<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} . production MM kg (MM lb) <u>for year of estimate</u>
Diethylene	Solvent for dyes, nitro-	Dow Chem. U.S.A.	Midland, Mich.	-	20.4 (45) -1972
glycol mono- ethyl ether	cellulose, & resins, mu- tual solvent for mineral oil-scap & mineral oil- sulfonated oil mixtures; nonaqueous stains for wood; for setting the twist & conditioning	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	-	
		Olin Corp Designed Products Div.	Brandenburg, Ky.	-	
	yarns & cloth; textile printing; textile soaps; lacquers; organic syn-	Shell Chem. Co Base Chems,	Geismar, La.	-	
	thesis; brake fluid diluent	Texaco Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	-	
	Solvent for cellulose esters, gums, resins; coatings & lacquers; printing inks	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
Diethylene glycol mono- ethyl ether acetate		-	-	-	-
Diethylene glycol mono- hexyl ether acetate	-	-	-	-	-
Diethylene	Solvent; brake fluid	Dow Chem. U.S.A.	Midland, Mich.	-	6.8 (15) -1972
glycol mono- methyl ether	component; intermediate	Eastman Kodak Co East- man Chem. Products, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	-	
		Olin Corp Designed Products Div.	Brandenburg, Ky.	-	
		PPG Indust., Inc Chem. Div Houston Chem. Co., div.	Beaumont, Tex.	-	
		Shell Chem. Co Base Chems.	Geismar, La.	-	
		Texaco Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	-	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	

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<u>Chemical</u>	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Diethylene glycol mono- methyl ether acetate	Solvent	-	-	-	-
Diethylene glycol dibutyl ether	High-boiling, inert solvent with applica- tion in extraction pro- cesses & in coatings & inks; diluent in vinyl chloride disper- sions; extractant for uranium ores	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	-
Diethylene glycol diethyl ether	Solvent for nitrocellu- lose; resins, lacquers; high-boiling medium & solvent for organic synthesis	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	-
Diethylene glycol dimethyl ether	Solvent; anhydrous reac- tion media for organo- metallic syntheses	The Ansul Co Chem. Div. Olin Corp Designed Products Div.	Marinette, Wisc. Rochester, N. Y.	-	-
Diethyl- amine	Rubber chemicals; tex- tile specialties;	Air Products & Chems., Inc.	Pensacola, Fla.	-	5 (11.1) -1972
	<pre>selective solvent; dyes; flotation agents; resins;</pre>	Pennwalt Corp Chem. Div.	Wyandotte, Mich.		
	pesticides; polymeriza- tion inhibitors; pharma- ceuticals; petroleum	Union Carbide Corp Chems. & Plastics Div.	Taft, La.	-	
	chemicals; electroplat- ing; corrosion inhibitors	Va. Chems. Inc Indust. Chems. Dept.	Portsmouth, Va.	-	
Diethyl sulfate	Ethylating agent in organic synthesis	Union Carbide Corp Chems, & Plastics Div.	Institute & South Charleston, W. Va.	-	-

Chemical	<u>Usagel</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Difluoro- ethane	Refrigerant; aerosol propellant; intermediate	Allied Chem. Corp Specialty Chems. Div.	Baton Rouge, La.	-	-
		E. I. du Pont de Ne- mours & Co., Inc Organic Chems. Dept Freon® products div.	Louisville, Ky.	-	
Diiso- butylene	Alkylation; intermediates; antioxidants; surfactants; lube additives; plastici-	The B. F. Goodrich Co B. F. Goodrich Chem. Co., div.	Port Neches, Tex.	-	-
	zers; rubber chemicals	Petro-Tex Chem. Corp Petro-Tex Chem. Co., subsid.	Houston, Tex.	-	
		Texaco Inc.	Port Arthur, Tex.	-	
Diketene	Production of aceto- arylamides; pigments & toners; pesticides; food preservatives; pharma-	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	-	-
	ceutical intermediates	FMC Corp Chem. Group - Indust. Chem. Div.	Meadville, Pa.	-	
Dimethyl- amine	Acid gas absorbent; sol- vent; antioxidants; mfg.	Air Products & Chems., Inc.	Pensacola, Fla.	-	55.2 (121.5) -1973
	of dimethylformamide & dimethylacetamide; dyes;	Commercial Solvents Corp.	Terre Haute, Ind.	-	
	flotation agent; gasoline stabilizers; pharmaceuti- cals; textile chemicals;	E. I. du Pont de Ne- mours & Co., Inc., Biochems. Dept.	Belle, W. Va.	-	
	ethyl- solvent; manufacture of	GAF Corp Chem. Div.	Calvert City, Ky.	-	
N,N-di- methyl-		Allied Chem. Corp Specialty Chems. Div.	Buffalo, N. Y.	-	-
aniline		American Cyanamid Co Organic Chems. Div.	Bound Brook, N. J.	-	
		E. I. du Pont de Ne- mours & Co., Inc Organic Chems. Dept Dyes & Chems. Dept.	Deepwater, N. J.	-	
		Dye Specialities, Inc.	Jersey City, N. J.	-	

ChemicalUsage1Manufacturer(s)2.1Location(s)2.13Monufacturer(s)2.13Total 100 (appacity2)DimethylRefrigerant; solvent; estraction agent; propel- lant for sprays (objecture)E. I. du Pont de Ne- mours & Co., Inc mours & Co., Inc polymerizationBelle, W. VaN,N-di- methylSolvent for vinyl resins a cactylene, butadiene, a cactylene, butadiene, 				,	•		
etherextraction agent; propel- lant for sprays; ohemical lyst & stabilizer in polymerizationnours & Co., Inc Institute & South Charleston, W. Va.N.N-di- methyl- formamideSolvent for vinyl resins & kodelylene, buildien, stabilizer in polymerizationAir Products & Chems., Plastics Div.Institute & South Charleston, W. Va.N.N-di- methyl- formamideSolvent for vinyl resins & kodelylene, buildien, stabilizer in carboxylation resc- tions; organic synthesisAir Products & Chems., Plastics Div.Pensacola, FlaDimethyl sulfaceSolvent for vinyl resins tions; organic synthesisAir Products & Chems., Plastics Div.Pensacola, FlaDimethyl sulfaceSolvent for vinyl resins tions; organic synthesisAir Products & Chems., Plastics Div.Pensacola, FlaDimethyl sulfaceMethylating agent for amines & phenolsE. I. du Font de Ne- mours & Co., Inc Biochems. Dept. Lashat Chems. Nept.Belle, W. VaDimethyl sulfaceGas odorant; solvent for many inorganic substances; catalyst impregnatorCrow Zellerbach Corp Penswalt Corp Chem. Div.Beaumont, TexDimethyl sulfoxideSolvent for polymeriza- tions & opanide resctions; analytical resen; spin- tion synthe resctions; analytical resen; spin- to othems pesti- cides, paint stripping; hydraulic fluids; hydraulie fluids; hydraulie fluids; hydraulie patho- medicine, plant patho-Crow Zellerback Corp Chem. Products Div.Bogalusa, La. Camas, MashDimethyl sulfoxideSolvent for		<u>Chemical</u>	Usage 1	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	capacity ²	production MM kg (MM lb)
iyst & stabilizer'in polymerizationUnion Carbide Corp Chems. & Plastics Bluv.Institute & South Charleston, W.Va.N,N-di- 		ether extraction agent; propel- lant for sprays; chemical	mours & Co., Inc	Belle, W. Va.	-	-	
methyl- formamide& acetylene, butadiene, adid gases; catalyst in carboxylation reac- 	lyst & stabilizer in polymerization	lyst & stabilizer in			-		
 in carboxylation reactions; organic synthesis b. 1. du Font de Netions; beile, W. Va. tions; organic synthesis b. 1. du Font de Netions; beile, W. Va. biochems. Dept. Lachat Chems. Inc. Biochems. Dept. Lachat Chems. Inc. Chicago Heights, III. Dimethyl Gas odorant; solvent for many inorganic substances; catalyst impregnator Dimethyl Solvent for polymerizations; analytical reagent; spinning polyacrylonitrile k other synthetic fibers; industrial cleaners pestions; analytical reagent; spinning polyacrylonitrile k other synthetic fibers; industrial cleaners pestions; industrial cleaners pestion; in of drugs, etc., int blood stream by topical application; medicine; plant pathoo- 		methyl-	& acetylene, butadiene,		Pensacola, Fla.	-	-
Dimethyl sulfateMethylating agent for amines & phenolsE. I. du Pont de Ne- mours & Co., Inc Biochems. Dept Indust. Chems. Dept.Belle, W. VaDimethyl sulfideGas odorant; solvent for many inorganic substances; catalyst impregnatorCrown Zellerback Corp Div.Bogalusa, LaDimethyl sulfideSolvent for polymeriza- tion & cyanide reactions; industrial cleaners pesti- cides, paint stripping; hydraulic fluids; preservation of drugs, etc., into blod stream by topicai application; medicine; jeant patho-Solvent for polymeriza- tion & cyanide reactions; common cleaners pesti- cides, paint stripping; hydraulic fluids; preservation of drugs, etc., into blod stream by topicai application; medicine; plant patho-Solvent for polymeriza- tion & cyanide reaction; common cleaners pesti- cides, paint stripping; hydraulic fluids; preservation of cells at low temperatures; diffu- sin of drugs, etc., into blod stream by topicai application; medicine; plant patho-Solvent for polymeriza- topicai application; medicine; plant patho		formamide acid gases; catalyst in carboxylation reac-	mours & Co., Inc	Belle, W. Va.	-		
sulfateamines & phenolsmours & Co., Inc Biochems. Dept.Linden, N. J.Dimethyl sulfideGas odorant; solvent for many inorganic 				Lachat Chems. Inc.		-	
Dimethyl sulfideGas odorant; solvent for many inorganic substances; catalyst impregnatorCrown Zellerbach Corp Chem. Products Div.Bogalusa, LaDimethyl sulfoxideSolvent for polymeriza- tion & cyanide reactions; analytical reager; spin- ning polyacrylonitrile & other synthetic fibers; industrial cleaners pesti- cides, paint stripping; hydraulic fluids; preservation of cells at low temperatures; diffu- sino blood stream by topical application; medicine; plant patho-Crown Zellerback Corp Crown Zellerback Corp Bogalusa, La. Crown Zellerback Corp Bogalusa, La. Camas, Wash				mours & Co., Inc	Belle, W. Va.	-	-
<pre>sulfide for many inorganic substances; catalyst impregnator</pre> Chem. Products Div. Pennwalt Corp Chem. Beaumont, Tex Div. Pennwalt Corp Chem. Beaumont, Tex Div. Phillips, Tex Petrochem. & Supply Div. Dimethyl Solvent for polymeriza- tion & cyanide reactions; analytical reagent; spin- ning polyacrylonitrile & other synthetic fibers; industrial cleaners pesti- cides, paint stripping; hydraulic fluids; preservation of cells at low temperatures; diffu- sion of drugs, etc., into blood stream by topical application; medicine; plant patho-					Linden, N. J.	~	
<pre>impregnator impregnator i</pre>			for many inorganic		Bogalusa, La.	-	
Petrochem. & Supply Div. Dimethyl Solvent for polymeriza- sulfoxide tion & cyanide reactions; analytical reagent; spin- ning polyacrylonitrile & other synthetic fibers; industrial cleaners pesti- cides, paint stripping; hydraulic fluids; preservation of cells at low temperatures; diffu- sion of drugs, etc., into blood stream by topical application; medicine; plant patho-					Beaumont, Tex.		
<pre>sulfoxide tion & cyanide reactions; Chem. Products Div. Camas, Wash. analytical reagent; spin- ning polyacrylonitrile & other synthetic fibers; industrial cleaners pesti- cides, paint stripping; hydraulic fluids; preservation of cells at low temperatures; diffu- sion of drugs, etc., into blood stream by topical application; medicine; plant patho-</pre>					Phillips, Tex.	-	
			tion & cyanide reactions; analytical reagent; spin- ning polyacrylonitrile & other synthetic fibers; industrial cleaners pesti- cides, paint stripping; hydraulic fluids; preservation of cells at low temperatures; diffu- sion of drugs, etc., into blood stream by topical application; medicine; plant patho-	Crown Zellerback Corp Chem. Products Div.		-	-

<u>Chemical</u> Dinitro-	<u>Usagel</u> Organic synthesis;	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb) -	Total ^{4,5} . production MM kg (MM lb) <u>for year of estimate</u>
benzene	dyes; camphor substitute in celluloid production				
Dinitro- benzoic acid	-	Ashland Oil, Inc Ashland Chem. Co., div Chem. Products Div.	Great Meadows,	-	-
		Bofors Indust., Inc.	Linden, N. J.	-	
		Salsbury Labs.	Charles City, Iowa	-	
Dinitro- toluene	Organic synthesis; toluidines; dyes;	Air Products & Chems., Inc.	Pensacola, Fla.	-	-
	explosives	E. I. du Pont de Ne- mours & Co., Inc Organic Chems. Dept Dyes & Chems. Div.	Deepwater, N. J.	-	
		Rubicon Chems. Inc.	Geismar, La.	-	
Dioxane	Solvent for cellulosics	Dow Chem. U.S.A.	Freeport, Tex.	-	-
	& wide range of organic products; lacquers; paints; varnishes;	Ferro Corp Grant Chem. Div.	Baton Rouge, La.	-	
	paint & varnish ré- movers; wetting & dis- persing agent in tex- tile processing, dye baths, stain and print- ing compositions; cleaning & detergent preparations; cements; cosmetics; deodorants; fumigants; emulsions; polishing compositions; stabilizer for chlori- nated solvents; scintil- lation counter	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
Dioxo- lane	Low-boiling solvent & extractant for oils, fats, waxes, dyes, & cellulose derivatives	Ferro Corp Grant Chem. Div.	Baton Rouge, La.	-	-

<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Diphenyl- amine	Rubber antioxidants & accelerators; stabiliz-	American Cyanamid Co Organic Chems. Div.	Bound Brook, N. J.	-	-
	ers for plastics; solid rocket propellants; pesticides; explosives; dyes; pharmaceuticals	E. I. du Pont de Ne- mours & Co., Indust. Chems. Dept.	Gibbstown, N. J.	-	
	ajes, pharmaceutrars	First Mississippi Corp First Chem. Corp., subsid.	Pascagoula, Miss.	-	
		Rubicon Chems. Inc.	Geismar, La.	-	
Diphenyl oxide	Organic synthesis; perfumery, particularly soaps; heat-transfer medium; resins for laminated electrical insulation	Dow Chem. U.S.A.	Midland, Mich.	-	-
Diphenyl- thiourea	Intermediates; dyes (sulfur colors, indigo,	American Cyanamid Co Organic Chems. Div.	Bound Brook, N. J.	-	-
	<pre>methyl indigo); vulcani- zation accelerator; synthetic organic pharmaceuticals; flota- tion agent; acid inhibitor</pre>	Monsanto Co Monsanto Indust. Chems. Co.	Nitro, W. Va.	-	
Dipropy- lene	Solvent for nitrocellulose; shellac; partial solvent	Dow Chem. U.S.A.	Freeport, Tex. Plaquemine, La.	15.9 (35) 5.4 (12)	24.2 (53.3) -1973
glycol	ol for cellulose acetate; solvent mixtures; lacquers; coatings; printing inks	Olin Corp Designed Products Div.	Brandenburg, Ky.	2.3 (5)	
,	convinge, printing like	Oxirane Chem. Co.,	Bayport, Tex.	5.9 (13)	
		Texaco Inc., Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	3.2 (7)	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South	5.4 (12)	
				Total = 38.1 (84)	

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Dodecene	Flavors; perfumes; medicine; oils; dyes;	Atlantic Richfield Co ARCO Chem. Co., div.	Wilmington, Calif.	-	-
	resins	Continental Oil Co Conoco Chems.	Westlake, La.	-	
		Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Baton Rouge, La.	-	
		Gulf Oil Corp Gulf Oil Chems. Co., div. Petrochems. Div.	Cedar Bayou, Tex.	-	
		The Humphrey Chem. Co.	North Haven, Conn.	-	
		Sun Oil Co Sun Oil Co. of Penn., subsid.	Duncan, Okla. Marcus Hook, Pa. Toledo, Ohio	-	
		Texaco Inc.	Port Arthur, Tex.	-	
		Union Oil Co. of Calif.	Beaumont, Tex.	-	
Dodecyl- aniline	Intermediate	Monsanto Co Monsanto Indust. Chems. Co.	Sauget, Ill.	-	-
Dodecy1-	Solvent; intermediate	GAF Corp Chem. Div.	Calvert City, Ky.	-	-
phenol	for surface-active agents; oil additives; resins; fungicides;	Monsanto Co Monsanto Indust. Chems. Co.	Kearny, N. J.	-	
	bactericides; dyes; pharmaceuticals, ad- hesives; rubber	Productol Chem. Co.	Santa Fe Springs, Calif.	-	
	chemicals	Union Carbide Corp Chems. & Plastics Div.	Marietta, Ohio	-	
Epichloro-	Major raw material for	Dow Chem. U.S.A.	Freeport, Tex.	124.8 (275)	81.7 (180) -1973
hydrin	epoxy & phenoxy resins; mfg. of glycerol; cur- ing propylene-based	Shell Chem. Co Base Chems.	Deer Park, Tex. Norco, La.	72.6 (160) 27.2 (60)	
	rubbers; solvent for cellulose esters & ethers; high wet- strength resins for paper industry			Total = 224.7 (495)	

<u>Chemical</u>	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estim
Ethanol	Solvent for resins, fats, oils, fatty acids, hydro-	Commercial Solvents Corp.	Terre Haute,	-	862.6 (1900) -19
	carbons, alkali hydroxi- des; extractive medium; manufacture of inter- mediates, organic deri- vatives (especially ace-	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	74.4 (164)	
	taldehyde), dyes, syn- thetic drugs, elasto-	Georgia-Pacific Corp Chem. Div.	Bellingham, Wash.	11.9 (26.3)	
	mers, detergents, clean- ing solutions, surface	Grain Processing Corp.	Muscatine, Iowa	-	
	coatings, cosmetics,	Inland Chem. Corp.	Juneau, Wisc.	_	
	pharmaceuticals, ex- plosives, anti-freeze; beverages; antisepsis; medicine	National Distillers & Chem. Corp Chems. Div U.S. Indust. Chems. Co., div.	Tuscola, Ill.	196.7 (433.2)	
		Publicker Indust. Inc.	Gretna, La. Philadelphia, Pa.	178.9 (394)	
		Shell Chem. Co Base Chems.	Deer Park, Tex.	119.2 (262.6)	
		Union Carbide Corp Chems. & Plastics Div.	Texas City, Tex.	357.6 (787.7)	
				Total ≠ 938.8 (2067.8)	
Ethyl acetate	General solvent in coatings & plastics; organic synthesis; smokeless powders; pharmaceuticals	Celanese Corp Celanese Chem. Co., div.	Bishop, Tex. Pampa, Tex.	27.2 (60)	-
		Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tex. Longview, Tex.	9 (20) 9 (20)	
		Monsanto Co Monsanto Indust. Chems. Co	Trenton, Mich.	6.8 (15)	
		Monsanto Polymers & Petrochems. Co.	Springfield, Mass.	9 (20)	
		Publicker Indust, Inc. Union Carbide Corp.	Philadelphis, Pa.	9 (20)	
		Chems, and Plastics Div,	Brownsville, Tx. Institute and South Charleston, W.Va. Texas City, Tex.	45.4 (100)	
				Total = 115.8 (255)	
Ethyl aceto- acetate	Organic synthesis; antipyrine; lacquers; dopes; plastics; manufacture of dyes,	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	-	~
	pharmaceuticals, anti- malarials, vitamin B; flavoring	Lonza Inc.	Mapleton, Ill.	-	

<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Ethyl acrylate	Polymers; acrylic paints; intermediates	Celanese Corp Cela- nese Chem. Co., div.	Clear Lake, Tex. Pampa, Tex.	-	75 (165.2) - 1968
		Dow Badische Co.	Freeport, Tex.	-	
		Rohm & Haas Co Rohm & Haas Texas Inc., subsid.	Deer Park, Tex.	-	
		Union Carbide Corp Chems. & Plastics Div.	Taft, La.	-	
Ethyl-	Dye intermediates;	Air Products & Chems.,	Pensacola, Fla.	-	25.2 (55.5) -1972
amine	solvent extraction; petroleum refining; stabilizer for rubber	Pennwalt Corp Chem. Div.	Wyandotte, Mich.	-	
	latex; detergents; organic synthesis	Union Carbide Corp Chems. & Plastics Div.	Taft, La.	-	
		Virginia Chems. Inc Indust. Chems. Dept.	Portsmouth, Va.	-	
Eth y l benzene	Intermediate in produc- tion of styrene; solvent	American Petrofina, Inc Cosden Oil & Chem. Co., subsid.	Big Spring, Tex.	61.3 (135)	2588 (5700) - 1974
		ARCO/Polymers, Inc.	Houston, Tex. Port Arthur, Tex.	45.4 (100) 245.2 (540)	
		The Charter Co Charter Oil Co., subsid., Charter International Cil Co., subsid.	Houston, Tex.	15.9 (35)	
		Commonwealth Oil Refin- ing Co., Inc Styro- chem Corp., subsid.	Penuelas, P. R.	40.9 (90)	
		Cos-Mar, Inc.	Carville, La.	326.9 (720)	
		Dow Chem. U.S.A.	Freeport, Tex. Midland, Mich.	846.7 (1865) 158.9 (350)	
		El Paso Natural Gas Co., El Paso Products Co., subsid.	Odessa, Tex.	124.8 (275)	
		Foster Grant Co., Inc.	Baton, Rouge, La.	440.4 (970)	
		Gulf Oil Corp Gulf Oil Chems. Co., div Petrochems. Div.	Welcome, La.	256.5 (565)	

<u>Chemical</u>	Usage ¹	<u>Manufacturer(s)^{2,3}</u>	Location(s) ^{2,3}	1975 capacity ² MM kg (MM <u>1b)</u>	Total ^{4;5} production MM kg (MM lb) <u>for year of estimate</u>
Ethyl benzene (con't)	(See previous page)	Monsanto Co, - Monsanto Polymers & Petrochems. Co.	Chocolate Bayou, Tex. Texas City, Tex.	667.4 (1470) -	(See previous page)
		Phillips Petroleum Co Petrochem. & Supply Div.	Phillips, Tex.		
		Standard Oil Co. (Ind.) Amoco Chems. Corp., subsid.	Texas City, Ťex.	429.0 (945)	
		Sun Oil Co, - Sun Oil Co. of Pa., subsid Suntide Refining Co., subsid.	Corpus Christi, Tex.	47.7 (106)	
		Tenneco Inc Tenneco Oil Co., div.	Chalmette, La.	11.8 (26)	
		Union Carbide Corp Chems. & Plastics Div.	Seadrift, Tex.	154.4 (340)	
				Total = 3873.1 (8531)	
Ethyl	Organic synthesis;	Dow Chem. U.S.A.	Midland, Mich.	-	-
bromide	medicine (anesthetic); refrigerant; solvent;	Great Lakes Chem. Corp.	El Dorado, Ark.	-	
	grain & fruit fumigant	Northwest Indust., Inc. 4 Michigan Chem. Corp., subsid.	St. Louis, Mich.	٦,	
Ethyl	Hot-melt adhesives &	American Polymers, Inc.	Patterson, N. J.	-	2.9 (6.5) -1973
ce llulose	coatings for cables, paper, textiles, etc.; extrusion wire insula- tion; protective coat- ing's pigment-grind- ing'base; toughening agent for plastics; printing inks; molding powders; proximity fuses; vitamin prepara- tion; casing for rocket propellants; food & feed additive	Nercules Inc Coatings & Specialty Products Dept.	, ,		

Total4,5

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM 1b)	production MM kg (MM lb) for year of estimate
Ethyl	Manufacture of tetra-	Dow Chem. U.S.A.	Freeport, Tex.	34 (75)	299.7 (660.1) -1973
chloride	ethyl lead & ethyl- cellulose; anesthetic; organic synthesis,	Ethyl Corp.	Baton Rougé, La. Pasadena, Tex.	95.3 (210) 68.1 (150)	
	alkylating agent; refrigeration; analy- tical reagent; solvent	PPG Indust., Inc Chem. Div Indust. Chem. Div.	Lake Charles, La.	54.5 (120)	
	for phosphorus, sulfur, fats, oils, resins & waxes; insecticides	Shell Chem. Co Base Chems.	Deer Park, Tex.	38.6 (85)	
		Stauffer Chem. Co Plastics Div Polymers West	Carson, Calif.	50 (110)	
				Total = 340.5 (750)	
Ethyl	Solvent; organic	Dow Chem, U.S.A.	Midland, Mich.	-	-
chloro- acetate	synthesis; military poison gas; vat	Kay-Fries Chems. Inc.	Stony Point, N. Y.	-	
	dyestuffs	Monsanto Co Monsanto Indust. Chems. Co.	St. Louis, Mo.	-	
Ethyl	Organic synthesis;	Kay-Fries Chems. Inc.	Stony Point, N. Y.	-	-
cyano- acetate	pharmaceuticals; dyes	Lonza Inc.	Mapleton, Ill.		
Ethylene	Manufacture of ethyl alcohol, ethylene glycols, ethylene dichloride, aluminum alkyls, vinyl chloride, ethyl chloride, ethy- lene oxide, ethylene	Allied Chem. Corp Union Texas Petroleum Div.	Geismar, La. Houston, Tex.	340.5 (750) 227 (500)	10,710.0 (23,590)-1974
		ARCO/Polymers, Inc Atlantic Richfield Co ARCO Chem. Co., div.	Wilmington, Calif.	45.4 (100)	
	chlorohydrin, acetalde-	Chemplex Co.	Clinton, Iowa	227 (500)	
	hyde, linear alcohols, polystyrene, styrene, polyethylene, poly- vinyl chloride, SBR,	Cities Service Co., Inc North American Petroleum Group	Lake Charles, La.	426.8 (940)	
	polyester resins tri- chloroethylene, etc.;	Continental Oil Co Conoco Chems.	Westlake, La.	295.1 (650)	
	refrigerant; cryogenic research; agricultural chemistry; welding & cutting of metals; anesthetic	Dow Chem. U.S.A.	Bay City, Mich. Freeport, Tex. Plaquemine, La.	77.2 (170) 1135 (2500) 499.4 (1100)	
		E. I. du Pont de Ne- mours & Co., Inc Plastics Dept.	Orange, Tex.	374.5 (825)	
		Eastman Kodak Co Eastman Chem. Products, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	363.2 (800)	

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Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capaci MM_kg (M	.ty²	Total ^{4,5} production MM kg (MM lb) for year of estimate
Ethylene (cont'd)	(See previous page)	El Paso Natural Gas Co El Paso Products Co., subsid.	Odessa, Tex.	234.7	(517)	(See previous page)
		Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Baton Rouge, La. Baytown, Tex.	771.8 31.8	(1700) (70)	
		The B. F. Goodrich Co B. F. Goodrich Chem. Co., div.	Calvert City, Ky.	158.9	(350)	
		Gulf Oil Corp Gulf Oil Chems. Co., div Petrochems. Div.	Cedar Bayou, Tex. Port Arthur, Tex.	190.7 522.1	(420) (1150)	
		Mobil Oil Corp Mobil Chem. Co., div Petrochems. Div.	Beaumont, Tex.	213.4	(470)	
		Monsanto Co Monsanto Polymers & Petrochems. Co.	Chocolate Bayou, Texas City, Tex.	295.1 68.1		
		National Distillers & Chem. Corp Chems. Div U.S. Indust. Chems. Co., div.	Tuscola, Ill.	158.9	(350)	
		Northern Natural Gas Co Northern Petrochem. Co., subsid., Polymers Div.	Morris, Ill.	363.2	(800)	
		Olin Corp Designed Products Div.	Brandenburg, Ky.	54.5	(120)	
		Petro Gas Producing Co.	Groves, Tex.	9	(20)	
		Phillips Petroleum Co.	Sweeny, Tex.	517.6	(1140)	
		Puerto Rico Olefins Co.	Penuelas, P. R.	454	(1000)	
		Shell Chem, Co Base Chems.	Deer Park, Tex. Norco, La.	681 250	(1500) (550)	
		Standard Oil Co. (Ind.) - Amoco Chems. Corp., subsid.	Chocolate Bayou,	454	(1000)	
		SunOlin Chem. Co.	Claymont, Del.	102	(225)	

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Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Ethylene (cont'd)	(See previous page)	Texaco Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	238.3 (525)	(See previous page)
		Union Carbide Corp Chems. & Plastics Div.	Seadrift, Tex. Taft, La. Texas City, Tex. Torrance, Calif. Whiting, Ind.	549.3 (1210) 186.1 (410) 726.4 (1600) 77.2 (170) 68.1 (150)	
		Union Carbide Caribè, Inc., subsid.	Penuelas, P. R,	351.8 (775)	
				Total = 11,285 (24,857)	
Ethylene carbonate	Solvent for many polymers & resins; solvent extraction; synthesis of pharma- ceuticals, rubber chemicals, textile finishing agents	Texaco Inc Jefferson Chem. Co., Inq., subsid.	Conroe, Tex.	-	-
Ethylen g chloro- hydrin	Solvent for cellulose agetate, ethylcellulose; introduction of hydro- ethyl group in organic synthesis; to acti- vate sprouting of dor- mant potatoes; mfg. of ethylene cxide & ethylene glycol	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	-
Ethylene diamine	Solvent for albumin & fibrin; medicine; neutralizing olls; stabilizing rubber latex; corrosion in- hibitor in antifreeze solutions; textile lubricants; dyes; rubber accelerators; making ethylenediamine nitrate, chlorate, and EDTA; de- hairing skins; emulsifier; organic synthesis; poly- amide resin adhesives; heat-sensitive adhesives	Dow Chem. U.S.A. Union Carbide Corp Chems. & Plastics Div.	Freeport, Tex. Taft, La. Texas City, Tex.	13.6 (30) 16.3 (36) 10.9 (24) Total = 40.9 (90)	30 (66) -1974

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Ethylene dibromide	Scavenger for lead in gasoline; grain & fruit	Dow Chem. U.S.A.	Magnolia, Ark. Midland, Mich.	-	152.1 (335) -1973
	fumigant; general sol- vent; waterproofing preparations; organic	Ethyl Corp Brine Products Div.	Magnolia, Ark.	-	
	synthesis; insecticide;	Great Lakes Chem. Corp.	El Dorado, Ark.	-	
	medicine	Northwest Indust., Inc Michigan Chem. Corp., subsid.	El Dorado, Ark.	-	
		PPG Indust., Inc Chem. Div Houston Chem. Co., div.	Beaumont, Tex.	-	
Ethylene dichloride	Vinyl chloride; chlori- nated solvent intermedi- ate; coupling agent in antiknock gasollne; paint, varnish & finish removers; metal degreas- ing; soaps & scouring compounds; wetting & penetrating agents; organic synthesis; ore flotation	Allied Chem. Corp Indust. Chems. Div.	Baton Rouge, La.	295.1 (650)	3505 (7,720)-1974
		Continental Oil Co Conoco Chems.	Westlake, La.	454 (1000)	
		Diamond Shamrock Corp Diamond Shamrock Chem. Co., Electro Chems. Div.	Deer Park, Tex.	118 (260)	
		Dow Chem. U.S.A.	Freeport, Tex. Oyster Creek, Tex. Plaquemine, La.	590.2 (1300) 499.4 (1100) 526.6 (1160)	
		Ethyl Corp.	Baton Rouge, La. Pasadena, Tex.	249.7 (550) 118 (260)	
		The B. F. Goodrich Co B. F. Goodrich Chem. Co., div.	Calvert City, Ky.	408.6 (900)	
		PPG Indust., Inc Chem. Div Indust. Chem. Div PPG	Lake Charles, La.	454 (1000)	
		PPG Indust.,(Caribe)	Guayanilla, P. R.	379.1 (835)	
		Shell Chem. Co Base Chems.	Deer Park, Tex. Norco, La.	544.8 (1200) 528.9 (1165)	
		Stauffer Chem. Co Plastics Div Pol y - mers West	Carson, Calif.	136.2 (300)	

<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s)2,3	1975 capacity² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Ethylene dichloride	(See previous page)	Texaco Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	31.8 (70)	(See previous page)
(cont'd)		Union Carbide Corp Chems. & Plastics Div.	Taft, La. Texas City, Tex.	68.1 (150) 68.1 (150)	
		Vulcan Materials Co. — Chems. Div.	Geismar, La.	109 (240)	
				Total = 5,579.7 (12,290)
Ethylene glycol	Coolant & antifreeze; asphalt-emulsion paints;	Allied Chem. Corp Specialty Chems. Div.	Orange, Tex.	18.2 (40)	1,398 (3,080)-1974
	heat-transfer agent in refrigeration & electron tubes; low-pressure lami- nates; brake fluids; glycol diacetate; poly- ester fibers & films; low-freezing dynamite;	BASF Wyandotte Corp Indust. Chems. Group	Geismar, La.	68.1 (150)	
		Calcasieu Chem. Corp.	Lake Charles, La.	81.7 (180)	
		Celanese Corp Cela- nese Chem. Co., div.	Clear Lake, Tex.	136.2 (300)	
	solvent; extractant for	Dixie Chem. Co.	Bayport, Tex.	-	
	<pre>various purposes; sol- vent mixtures for cel- lulose esters & ethers, especially cellophane; cosmetics (up to 5\$); lacquers; alkyd resins; printing inks; wood</pre>	Dow Chem. U.S.A.	Freeport, Tex. Plaquemine, La.	65.8 (145) 199.8 (440)	
		Eastman Kodak Co. — Eastman Chem. Products, Inc., subsid. — Texas Eastman Co., div.	Longview, Tex.	22.7 (50)	
	stains; adhesives; lesther dyeing; tex- tile processing: tobac+	ICI United States Inc Specialty Chems. Div.	New Castle, Del.	4.5 (10)	
	tile processing; tobac- co; ingredient of deicing fluid for airport runways	Northern Natural Gas Co., Northern Petrochem. Co., subsid Polymers Div.	Morris, Ill.	136.2 (300)	
		Olin Corp Designed Products Div.	Brandenburg, Ky.	22.7	
		PPG Indust., Inc Chem. Div Houston Chem. Co., div	Beaumont, Tex.	45.4 (100)	
		PPG Indust. (Caribe)	Guayanilla, P. R.	181.6 (400)	
		Shell Chem. Co Base Chems.	Geismar, La.	45.4 (100)	

<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Ethylene glycol	(See previous page)	Texaco Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	163.4 (360)	(See previous page)
(cont'd)		Union Camp Corp Chem. Products Div.	Dover, Ohio	-	
		Union Carbide Corp Chems. & Plastics Div.	Seadrift, Tex. Taft, La.	395 (870) 136.2 (300)	
		Union Carbide Caribe, Inc., subsid.	Penuelas, P. R.	286 (630)	
				Total = 2.009 (4425)	
Ethylene glycol diacetate	Solvent for cellulose esters & ethers; resins; lacquers; printing inks; per-	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	-	-
	fume fixative; non- discoloring plastici- zer for ethyl & benzyl cellulose	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
Ethylene glycol dibutyl ether	High-boiling inert solvent; specialized solvent & extraction applications	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	-
Ethylene glycol diethyl ether	Organic synthesis (reac- tion medium); solvent & diluent for detergents	-	-	-	-
Ethylene glycol dimethyl ether	Solvent	The Ansul Co Chem. Div.	Marinette, Wisc.	-	-
Ethylene glycol monoace- tate	Solvent for nitro- cellulose, cellulose acetate, camphor	Glyco Chems., Inc. Scher Brothers, Inc.	Williamsport, Pa. Clifton, N. J.	-	-

Total^{4,5}

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM lb)	production MM kg (MM lb) for year of estimate
Ethylene	Solvent for nitrocellu-	Dow Chem. U.S.A.	Midland, Mich.	-	54.5 (120) -1972
glycol mono- butyl ether	lose resins; spray lac- quers; quick-drying lacquers; varmishes; enamels; dry-cleaning compounds; varnish	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	-	
	removers; textile (preventing spotting in	Olin Corp Designed Products Div.	Brandenburg, Ky.	-	
	printing or dyeing); mutual solvent for "soluble" mineral oils	Shell Chem. Co Base Chems.	Geismar, La.	-	
	to hold soap in solution & to improve the emulsi-	Texaco Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	-	
	fying properties	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
Ethylene glycol mono- butyl	High-boiling solvent for nitrocellulose lacquers, epoxy resins, multicolor lacquers; film coalescing aid for polyvinyl acetate latex	Eastman Kodak Co East- man Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	-	-
ether acetate		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
Ethylene	Solvent for nitrocellulose; natural & synthetic resins; mutual solvent for formula- tion of soluble olls; lac- quers & lacquer thinners; dyeing & printing tex- tiles; varnish removers; cleaning solutions; leather; anti-icing addi- tive for avaition fuels.	Dow Chem. U.S.A.	Midland, Mich.	-	77.2 (170) -1972
glycol mono- ethyl ether		Eastman Kodak Co Eastman Chem. Products, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	-	
		Clin Corp Designed Products Div.	Brandenburg, Ky.		
Ethylene glycol	Solvent for nitrocellu- lose; oils & resins; re-	Shell Chem. Co Base Chems.	Geismar, La.	-	-
mono- ethyl ether	tards "blushing" in lac- quers; varnish removers; wood stains; textiles;	Texaco Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	-	
acetate	leather	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va. Seadrift, Tex.	-	
		Eastman Kodak Co Eastman Chem. Products, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	-	
		Olin Corp Designed Products Div.	Brandenburg, Ky.	-	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	

<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Ethylene glycol mono- hexyl ether	High-boiling solvent	-	-	-	-
Ethylene	Solvent for nitro-	Dow Chem. U.S.A.	Midland, Mich.	-	43 (95) -1972
glycol mono- ethyl ether	cellulose, cellulose acetate, alcohol- soluble dyes, natural & synthetic resins;	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	-	
	solvent mixtures; lacquers; enamels; varnishes; leather; perfume fixative; wood stains; sealing moixture-proof cello- phane; jet fuel deicing additive	Olin Corp Designed Products Div.	Brandenburg, Ky.	-	
		Pierce Chem. Co.	Rockford, Ill.	-	
		PPG Indust., Inc Chem. Div Houston Chem. Co., div.	Beaumont, Tex.	-	
		Shell Chem. Co. Base Chems.	Geismar, La.	-	
		Texaco Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	-	
		Union Carbide Corp	Institute & South	-	
		Chems. & Plastics Div.	Charleston, W. Va. Taft, La.	-	
Ethylene glycol mono- methyl	Solvent for nitrocellu- lose, cellulose acetate, various gums, resins, waxes, oils; textile	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	-	-
	printing; photographic film; lacquers; dopes	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
Ethylene glycol mono- octyl ether	Solvent for cellulose esters; plasticizer	-	-	-	-

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Ethylene glycol mono- phenyl ether	Solvent for cellulose acetate, dyes inks, re- sins; perfume & soap fixative; bacterial agent; organic synthesis of plasticizers, germi- cides, perfume materials & pharmaceuticals	Dow Chem. U.S.A.	Midland, Mich.	-	-
Ethylene glycol mono- propyl ether	-	Olin Corp Designed Products Inc.	Brandenburg, Ky.	-	-
Ethylene oxide	Manufacture of ethy- lene glycol & higher	Allied Chem. Corp Specialty Chems. Div.	Orange, Tex.	22.7 (50)	1,798 (3,960) -1974
	glycols; polyester fi- ber & film; surfactants; acrylonitrile; ethanol-	BASF Wyandotte Corp Indust. Chems. Group	Geismar, La.	100 (220)	
	amines; petroleum demulsi-	Calcasieu Chem. Corp.	Lake Charles, La.	74.9 (165)	
	fier; fumigant; rocket propellant	Celanese Corp Celanese Chem. Co., div.	Clear Lake, Tex.	136.2 (300)	
		Dow Chem. U.S.A.	Freeport, Tex. Plaquemine, La.	90.8 (200) 181.6 (400)	
		Eastman Kodak Co Eastman Chem. Products, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	18.2 (40)	
		Northern Natural Gas - Co - Northern Petrochem. Co., subsid Poly- mers Div.	Morris, Ill.	90.8 (200)	
		Olin Corp Designed Products Div.	Brandenburg, Ky.	50 (110)	
		PPG Indust., Inc Chem. Div Houston Chem. Co., div.	Beaumont, Tex.	38.6 (85)	
		PPG Indust. (Caribe)	Guayanilla, P. R	136.2 (300)	
		Shell Chem. Co Base Chems.	Geismar, La.	136.2 (300)	
		SunOlin Chem. Co.	Claymont, Del.	43.1 (95)	
		Texaco Inc Jefferson Chem. Co., Inc., subsid.	Fort Neches, Tex.	227 (500)	
		Union Carbide Corp Chems. & Plastics Div.	Seadrift, Tex. Taft, La.	367.7 (810) 204.3 (450)	
		Union Carbide Caribe, Inc., subsid.	Penuelas, P. R.	277 (610)	
				Total =	

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Total = 2,195.1 (4,835) .

Chemical	<u>Usage1</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM lb)	Total4'' ⁵ production MM kg (MM lb) <u>for year of estimate</u>
Ethyl ether	Manufacture of ethylene & other chemical syn- thesis; industrial sol-	Hercules Inc Coatings & Specialty Products Dept.	Hopewell, Va.	1 (2)	27.2 (60) -1974
	vent (smokeless powder); analytical chemistry; anesthetic; perfumery;	Mallinckrodt, Inc Medicinal Div.	St. Louis, Mo.	1 (2)	
	extractant; alcohol denaturant	National Distillers & Chem. Corp Chems. Div.	Tuscola, Ill.	18.2 (40)	
		Publicker Indust., Inc.	Philadelphia, Pa.	4.5 (10)	
		Squibb Corp E. R. Squibb & Sons, Inc., subsid U.S. Pharma- ceutical Co Operations	New Brunswick,	1 (2)	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va. Texas City, Texas	6.8 (15) Total = 32.2 (71)	
Ethyl resins; defoam hexanol wetting agent; synthesis; solv mixtures for n	Plasticizer for PVC	Dow Badische Co.	Freeport, Tex.	-	-
	wetting agent; organic synthesis; solvent mixtures for nitrocel- lulose, paints, lac- quers, baking finishes; penetrant for merceriz- ing cotton; textile	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	-	
		W. R. Grace & Co Hatco Group - Hatco Chem. Div.	Fords, N. J.	-	
	finishing compounds; plasticizers; inks;	Oxochem Enterprise	Penuelas, P. R.	-	
	rubber; paper; lubri- cants; photography;	Shell Chem. Co Base Chems.	Deer Park, Tex.	-	
	dry cleaning	Union Carbide Corp Chems. & Plastics Div.	Seadrift, Tex.	-	
		Union Carbide Caribe, Inc., subsid.	Penuelas, P. R.	-	
Ethyl ortho- formate	Intermediate	Kay-Fries Chems., Inc.	Stony Point, N. Y.	-	-
Ethyl oxalate	Solvent for cellulose & ethers, many natural & synthetic resins; radio tube cathode fixing lac- quers; dye intermediate; pharmaceuticals; perfume preparations; organic synthesis	FMC Corp. Chem. Group - Indust. Chem. Div.	Baltimore, Md.	-	-
Ethyl sodium oxalacetate	dyes; synthesis	FMC Corp. Chem. Group - indust. Chem. Div.	Baltimore, Md.	-	-

Chemical	Usage 1	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,55} production MM kg (MM lb) <u>for year of estimate</u>
Formalde- hyde (contid)	(See previous page)	Occidental Petroleum Corp Hooker Chem. Corp., subsid Hooker Chems. & Plastics Corp., subsid Durez Div.	North Tonawanda, N. Y.	61.3 (135)	(See previous page)
		Reichhold Chems., Inc.	Hampton, S. C. Houston, Tex. Kansas City, Kans. Malvern, Ark. Moncure, N. C. Tacoma, Wash. Tuscaloosa, Ala. White City, Ore.	22.7 (50) 54.5 (120) 22.7 (50) 50 (110) 54.5 (120) 21.8 (48) 32.7 (72) 113.5 (250)	
		Rohm & Haas Co.	Philadelphia, Pa.	11.3 (25)	
		Skelly Oil Co Chembond Corp., subsid.	Springfield, Ore. Winnfield, La.	31.8 (70) 31.8 (70)	
		Tenneco Inc Tenneco Chems., Inc Organics & Polymers Div.	Fords, N. J. Garfield, N. J.	84 (185) 45.4 (100)	
		Union Carbide Corp Chems. & Plastics Div.	Bound Brook, N. J.	54.5 (120)	
		Univar Corp Pacific Resins & Chems., Inc., subsid.	Eugene, Ore.	43.1 (95)	
		Wright Chem. Corp.	Acme, N. C.	36.3 (80)	
				Total = 3,808.0 (8,389)	
Forma- mide	Solvent, softener, intermediate in or- ganic synthesis	E. I. du Pont de Ne- mours & Co., Inc Biochems. Dept.	Belle, W. Va.	-	-

Chemical Usage ¹	Manus	facturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacit MM kg (MM			uction (MM 1	.b)
Formalde- Urea & Melami hyde phenolic resi		ed Chem. Corp ialty Chems. Div.	South Point, Ohio	140.7 (310)	976 (2,	150)	-1974
chemicals; d (disinfectan	etetramine; Chem	en Inc Borden 1. Div Adhesives 1ems., Div., East	Demopolis, Ala. Diboll, Tex. Fayetteville, N. C. Louisville, Ky. Sheboygan, Wisc.	45.4 (36.3 (106.7 (36.3 (59 (80) 235)			
vative; hard reducing age recovery of ver; corrosi tor in oil we	ening agent; Adhe: nt, as in West gold & sil- on inhibi- ells; durable-	sives & Chems., Div.,	Fremont, Calif. Kent, Wash. La Grande, Ore. Missoula, Mont. Springfield, Ore.	102.1 (36.3 (29.5 (40.9 (109 (80) 65)			
press treatm tile fabrics condensation & other carb	to sugars cerai	nese Corp Cela- : Chem. Co., div.	Bishop, Tex. Newark, N. J. Rock Hill, S. C.	681 (53.1 (53.1 (
for food use perimental)		mercial Solvents	Seiple, Pa.	29.5 (65)			
	mour	. du Pont de Ne- s & Co., Inc chems. Dept.	Belle, W. Va. La Porte, Tex.	222.5 (136.2 (
		st. Chems. Dept.	Healing Springs, N. C.	90.8 (
			Linden, N. J. Toledo, Ohio	68.1 (118 (150) 260)			
	GAF	Corp Chem. Div.	Calvert City, Ky.	45.4 (100)			
		gia-Pacific Corp n. Div.	Albany, Ore. Columbus, Ohio Coos Bay, Ore. Crossett, Ark. Taylorsville, Miss. Vienna, Ga.	54.5 (54.5 (45.4 (72.6 (54.5 (45.4 (120) 100) 160) 130)			
	Oil Indu	COIL Corp Gulf Chems. Co., div ust. & Specialty ns. Div.	Vicksburg, Miss.	20.4 (45)			
		cules Inc chetics Dept.	Louisiana, Mo. Wilmington, N. C.	77.2 (45.4 (
	Poly	anto Co Monsanto ymers & Petrochems.	Addyston, Ohio Chocolate Bayou,	45.4 (88.5 (
	Co.		Tex. Eugene, Ore. Springfield, Mass.	45.4 (133.9 (

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Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM lb)	Total ^{4,5;} production MM kg (MM lb) <u>for year of estimate</u>
Formic acid	Dyeing & finishing of textiles & paper; leather treatment; chemi-	Celanese Corp Celanese Chem. Co., div.	Pampa, Tex.	4.5 (10)	-
	cals (formates, oxalic acid, organic esters); manufacture of fumigants,	Middleboro Indust., Inc.	Middleboro, Mass.	3.2 (7)	
	insecticides, refriger-	Sonoco Products Co.	Hartsville, S. C.	.5 (1)	
	ants; solvents for perfumes, lacquers; electroplating: medi-	Union Carbide Corp Chems. & Plastics Div.	Brownsville, Tex.	22.7 (50)	
	electroplating; medi- cine; brewing (anti- septic); silvering glass; cellulose for- mate; natural latex coagulant; ore flota- tion; vinyl resin plasticizers; animal feed additive			Total = 30.9 (68)	
Tumaric Loid	Modifier for polyester, alkyd, & phenolic res- ins; paper-size resins; plasticizers; rosin es- ters & adducts; upgrading natural drying oils (es- pecially tall oil) to improve drying character- istics; in foods, to re- place citric & tartaric acids as acidulant & flavoring agent (FDA approved); mordant; organic synthesis	Allied Chem. Corp Specialty Chems. Div.	Moundsville, W. Va.	6.8 (15)	19.1 (42) -1974
		Monsanto Co Monsanto Indust. Chems. Co.	St. Louis, Mo.	13.6 (30)	
		Occidental Petroleum Corp Hocker Chem. Corp., subsid Hocker Chem. Corp., subsid Hocker Chems. & Flastics Corp., subsid Puerto Rico Chem. Co., subsid.	Arecibo, P. R.	-	
		Petro-Tex Chem. Corp Petro-Tex Chem. Co., Subsid.	Houston, Tex.	3.6 (8)	
		Pfizer Inc Chems, Div.	Terre Haute, Ind.	11.3 (25)	
		Tenneco Inc Tenneco Chems., Inc Organics & Polymers Div.	Garfield, N. J.	4.5 (10)	
		U.S. Steel Corp USS Chems., div.	Neville Island, Pa.	4.5 (10)	
				Total ≈ 44.5 (98)	

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<u>Chemical</u>	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM_kg (MM_lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Glycer- alde- hyde	Biochemical research; intermediate; nutrition; preparation of polyes- ters, adhesives; cellu- lose modifier; leather tanning	-	-	-	-
Glycerol (natural	Alkyd resins; cello- phane; explosives;	Natural: Acme-Hardesty Co., Inc.	Jenkintown, Pa.	_	158.1 (348.2) -1969
guacarar	ester gums; pharmaceu-	Alba Mfg. Co.	Aurora, Ill.	-	190.1 (940.2) -1909
synthetic)	ticals; perfumery;		-	-	
	plasticizer for regenerated cellulose; cosmetics; foodstuffs;	Ashland Oil, Inc Ashland Chem. Co., div., Chem. Products Div.	Hammond, Ind. Mapleton, Ill.	-	
	conditioning tobacco; liqueurs; solvent; printer's ink rolls;	Chicago Sanitary Pro- ducts Co.	Chicago, Ill.	-	
	polyurethane poly- ols; emulsifying agent; rubber stamp & copying inks; binder for cements & mixes; paper coatings & finishes; special soaps; lubricant & softener; bacteriostat; penetrant; hydraulic fluid; humectant	Colgate-Palmolive Co.	Berkeley, Calif. Jeffersonville, Ind. Jersey City, N. J.	-	
			Kansas City, Kans.	-	
		Darling & Co.	Chicago, Ill.	-	
		Dow Chem. Co.	Anchorage, Alas.	-	
		Emery Indust., Inc Western Operations	Cincinnati, Ohio Santa Fe Springs, Calif.	-	
		The Greyhound Corp Armour & Co., subsid Armour-Dial, Inc., div.	Montgomery, Ill.	-	
		The Andrew Jergens Co.	Cincinnati, Ohio	-	
		H. Kohnstamm & Co., Inc.	Clearing, Ill.	-	
		Kraftco Corp Humko Sheffield Chem.	Memphis, Tenn.	-	
		Lever Brothers Co.	Baltimore, Md. Edgewater, N. J. Hammond, Ind. Los Angeles, Calif. St. Louis, Mo.	-	
		Millmaster Onyx Corp A. Gross & Co., div.	Newark, N. J.	-	
		Murro Chem. Co.	Portsmouth, Va.	-	
		Pacific Soap Co.	Vernon, Calif.	-	
		Pioneer Soap Co., Inc.	San Francisco, Calif.	-	

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Total4,5

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Glycerol (cont'd)	(See previous page)	The Procter & Gamble Co.	Baltimore, Md. Chicago, Ill. Dallas, Tex. Ivorydale, Ohio Kansas City, Kans. Long Beach, Calif. Port Ivory, N. Y. Quincy, Mass. Sacramento, Calif. St. Louis, Mo.		(See previous page)
		The Hewitt Soap Co., Inc., subsid.	Dayton, Ohio	-	
		Purex Corp., Ltd.	Bristol, Pa. Omaha, Neb. Philadelphia, Pa.	-	
		PVO Internat'l. Inc.	Boonton, N. J.	-	
		Safeway Stores, Inc Newport Products Co., div.	Oakland, Calif.	-	
		Stepan Chem. Co Surfactant Dept.	Anaheim, Calif. Elwood, Ill. Fieldsboro, N. J.	-	
		Union Camp Corp Chem. Products Div.	Dover, Ohio	-	
		Woburn Chem. Corp.	Kearny, N. J.	-	
		Synthetic: Dow Chem. U.S.A.	Freeport, Tex.	50 (110)	
		FMC Corp Chem. Group - Indust. Chem. Div.	Bayport, Tex.	18.2 (40)	
		Shell Chem. Co Base Chems.	Deer Park, Tex. Norco, La.	54.5 (120) 22.7 (50)	
				Synthetic Total 145.3 (320)	=
Glycerol tr1(poly-	-	ICI U.S. Inc Specialty Chems. Div.	New Castle, Del.	-	-
oxypropy- lene)		Olin Corp Designed Products Div.	Brandenburg, Ky.	-	
ether		Pelron Corp.	Lyons, Ill.	-	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
		Witco Chem. Corp O rg anics Div.	Clearing, Ill.	-	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM Ib) <u>for year of estimate</u>
Glycine	Organic synthesis; medicine; biochemical research; buffering agent; chicken feed additive; reduces bitter taste of saccharin	Chattem Drug & Chem. Co Chattem Chems. Div.	Chattancoga, Tenn.	-	-
Glyoxal	Mfg. of textile resins for permanent press process; dimensional	American Cyanamid Co Organic Chems. Div (Captive Use)	Charlotte, N. C.	-	-
	stabilization of rayon & other fibers; insolu- bilizing agent for com-	Union Carbide Corp Chems. & Plastics Div.	Taft, La.	-	
	pounds containing poly- hydroxyl groups (poly- vinyl alcohol, starch, & cellulosic materials); insolubilizing of pro- teins (casein, gelatin & animal glue); embalm- ing fluids; leather tanning; paper coatings with hydroxyethylcellu- lose; reducing agent in dyeing textiles	Witco Chem, Corp Organics Div.	Clearing, Ill.	-	
Guanidine	Organic synthesis	-	-	-	-
Heptene	Organic synthesis; plant growth retardant; lubri- cant additive; catalyst	American Petrofina Inc. Cosden Oil & Chem. Co., subsid.	Big Spring, Tex.	-	204 (450) -1967
	surfactants	Getty Oil Co.	Delaware City, Del.	-	
		The Humphrey Chem. Co.	North Haven, Conn.	-	
		Phillips Petroleum Co Petrochem. & Supply Div.	Phillips, Tex.	-	
		Standard Oil Co. (Ind.) - Amoco Chems. Corp., subsid.	Yorktown, Va.	-	

Chemical	Usage 1	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb for year of esti
Hexa∽ chloro- ethane	Organic synthesis; re- tarding agent in fer- mentation; camphor sub- stitute in nitrocellu- lose; rubber accelera- tor; pyrotechnics & smoke devices; solvent; explosives; medicine	Kummel Chem. Co., Inc.	South Plainfield, N. J.	-	-
Hexa- decyl alcohol	Perfumery; emulsifier; emollient; foam stabili- zer in detergent; face creams; lotions, lip-	Ashland Oil, Inc Ashland Chem. Co., div Chem. Products Div.	Mapleton, Ill.	-	2.72 (6.0) -1
	sticks; toilet prepara- tions; chemical inter- mediate; detergents;	Continental Oil Co Conoco Chems.	Westlake, La.	-	
	pharmaceuticals; cosme- tics; base for making	Givaudan Corp Chems. Div.	Clifton, N. J.	-	
	sulfonated fatty alco- hols; to retard evapor- ation of water, when	The Procter & Gamble Co.	Ivorydale, Ohio Sacramento, Calif.	-	
	spread as a film on reservoirs, or sprayed on growing plants	Robinson-Wagner Co., Inc.	Mamaroneck, N. Y.	-	
Hexa- methy- lene glyccl	Solvent; resin inter- mediate; coupling agent	Guardian Chem. Corp Eastern Chem. Div.	Hauppauge, N. Y.	-	-
Hexa- methy- lene	Catalyst in phenol- formaldehyde & resorcinol- formaldehyde resins; in-	Borden Inc Borden Chem. Div. ~ Adhesives & Chems. Div East	Demopolis, Ala. Fayetteville, N. C.	5.4 (12) 10.9 (24)	45.7 (100.7) -1
tetra- mine	gredient in rubber-to- textile adhesives; pro- tein modifier; organic synthesis; pharmaceuti-	W. R. Grace & Co Indust, Chems. Group - Dewey & Almy Chem. Div.	Nashua, N. H.	-	
	cals; ingredient of high explosive cyclonite (q.v.); fuel tablets	Occidental Petroleum Corp Kooker Chem. Corp., subsid Hooker Chems. & Flastics Corp subsid Durez Div.	North Tonawanda,	12.7 (28)	
		Plastics Engineering Co.	Sheboygan, Wisc.	3.6	
		Tenneco Inc Tenneco Chems., Inc Organics Polymers Div.	Fords, N. J.	10 (22)	
		Union Carbide Corp Chems. & Plastics Div.	Bound Brook, N. J.	4.5 (10)	
		Wright Chem. Corp.	Acme, N. C.	14.1 (31) Total =	
				61.3 (135)	

Chemical	Usage 1	<u>Manufacturer(s)^{2,3}</u>	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Hydrogen cyanide	Manufacture of acrylo- nitrile, acrylates, adiponitrile, cyanide	American Cyanamid Co Indust. Chems. & Plastics Div.	New Orleans, La.	12.2 (27)	138.1 (304.3) -1973
	salts, dyes; fumigant for orchards & tree crops; chelates	Dow Chem. U.S.A. E. I. du Pont de Ne- mours & Co., Inc	Freeport, Tex. Beaumont, Tex. Laplace, La.	2.3 (5) 13.6 (30) 9.1 (20)	
		Elastomer Chems, Dept, Indust, Chems, Dept, Plastics Dept,	Memphis, Tenn. Victoria, Tex.	57.6 (127) 18.2 (40)	
		Hercules Inc Coat- ings & Specialty Products Dept.	Glens Falls, N. Y.	1.1 (2.4)	
		Monsanto Co Monsanto Polymers & Petrochems. Co.	Chocolate Bayou, Tex Texas City, Tex.	• 25.4 (56) 34.1 (75)	
		Rohm & Haas Co Rohm & Haas Texas Inc., subsid.	Deer Park, Tex.	81.7 (180)	
	_	The Standard Oil Co. (Ohio) - Vistron Corp., subsid Chems. Dept.	Lima, Ohio	13.6 (30)	
·				Total = 269 (592.4)	
Hydro- quinone	Photographic deve- loper (except color	Carus Corp Carus Chem. Co., div.	La Salle, Ill.	3.5 (7.7)	-
	film); dye intermediate; medicine; antioxidant; inhibitor; stabilizer in paints & varnishes,	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	7.3 (16.0)	
	motor fuels & oils; anticxidant for fats & oils; inhibitor of	The Goodyear Tire & Rubber Co Chem. Div.	Bayport, Tex.	2.7 (6.0)	
m- hydroxy-	polymerization Intermediate for plas- ticizers; resins; light	Mallinckrodt, Inc Washine Div.	Lodi, N. J.	Total = 13.5 (29.7)	-
benzoic acid	stabilizers; petroleum; additives; pharmaceuti- cals; intermediates; synthetic drugs	Tenneco Inc Tenneco Chems., Inc Organics & Polymers Div.	Garfield, N. J.	-	

Chemical	<u>Usage¹</u>	Manufacturer(s) ²⁺³	Location(s)2,3	1975 capacity ² MM kg (MM lb)	Total ^{*,,5} production MN kg (NM lb) <u>for year of estimate</u>
Iso amy l alcohol		Publicker Indust. Inc.	Gretna, La. Philadelphia, Pa.	-	-
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
Isoa my l chloride	(Mixtures, usually also containing normal amyl chloride); solvent (nitrocellulose, var- nishes, lacquers, neo- prene); rotogravure inks; soil fumigation; organic compounds	-	-	-	-
Iso <u>amy</u> lene	Organic synthesis; dental & surgical anesthetic; high octane fuel manufacture	Phillips Petroleum Co Fetrochem & Supply Div.	Phillips, Tex.	-	-
Isobutanol	Organic synthesis; la-	Dow Badische Co.	Freeport, Tex.	-	<u> </u>
	tent solvent in paints & lacquers; intermediate for amino coating re- sins; substitute for n-	W. R. Grace & Co Hatco Group - Hatco Chem. Div.	Fords, N. J.	-	
	butyl alcohoi, paint re- movers; fluorometric determinations; liquid chromatography	Oxochem Enterprise	Penuelas, P. R.	-	
Isobutyl acetate	Solvent for nitrocellu- lose in thinners, seal- ants, & topcoat lacquers; perfumery; flavoring	Eastman Kodak Co Eastman Chem. Products Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	-	5.3 (11.75) -1972
	agent	Fritzche Dodge & Olcott Inc.	East Hanover, N. J.	-	
		Union Carbide Corp	Institute & South	-	
		Chems. & Plastics Div.	Charleston, W. Va. Texas City, Tex.	-	
Isobutyral- dehyde	Intermediate for rubber antioxidants & accelera-	Celanese Corp Celanese Chem. Co., div.	Bishop, Tex.	-	-
	tors, for neopentyl glycol; organic	Dow Badische Co.	Freeport, Tex.	-	
	synthesis	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	-	
		Oxochem Enterprise	Penuelas, P. R.	-	
		Union Carbide Corp Chems. & Plastics Div Union Coribdo Coribo	Texas City, Tex.	-	
		Union Caribde Caribe, Inc., subsid.	Penuelas, P. R.	-	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Iso- butyric acid	Manufacture of esters for solvents, flavors, & perfume båses; dis- infecting agent; deliming hides; varnish; tanning agent	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	-	-
Iso- decanoic acid	Intermediate for metal salts, ester type lubricants, plasticizers	Union Carbide Corp Chems. & Plastics Div.	Texas City, Tex.	-	-
Iso~ decanol	Antifoaming agent in textile processing	Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Baton Rouge, La.	-	81.7 (180) -1974
		Getty Oil Co.	Delaware City, Del.	-	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
		U.S. Steel Corp USS Chems., div.	Haverhill, Ohio	-	
Iso- decyl chloride	Solvent for oils, fats, greases, resins, gums, extractants, cleaning compounds; intermediate for insecticides, phar- maceuticals, plasticizers, polysulfide rubbers, resins, & cationic sur- factants	-	-	-	-
Iso- octyl alcohol	Ingredient of plastici- zers; intermediate for non-ionic detergents &	Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Baton Rouge, La.	-	55.4 (122) -1967
	surfactants; synthetic drying oils. cutting &	Getty Oil Co.	Delaware City, Del.	-	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	$Location(s)^{2,3}$	1975 capacity ² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Ico- octyl alcohol (cont'd)	(See previous page) lubricating oils, hydrau- lic fluids; resin sol- vent; emulsifier; anti- foaming agent; intermed- iate for insecticides, pharmaceuticals, plas- ticizers, polysulfide rubbers, resins, & cationic surfactants	U.S. Steel Corp USS Chems., div.	Delaware City, Del.	-	
Isophorone	In solvent mixtures for finishes; for poly- vinyl & nitrocellulose resins; pesticides; stoving lacquers	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	-
Isophthalic acid	Polyester, alkyd, poly- urethane, & other high polymers; plasticizers	Standard Oil Co. (Ind.) - Amoco Chems. Corp., subsid.	Joliet, Ill.	40.9 (90) Total = 40.9 (90)	53.6 (118) -1974
Isoprene	Monomer for manufacture of polyisoprene; chemical intermediate	Caribe Isoprene Corp. Exxon Corp Exxon Chem. Co., div Exxon Chem. Co., U.S.A.	Ponce, P. R. Baton Rouge, La.	30 (66) 4.5 (10)	151.8 (334.3) -1971
		The Goodyear Tire & Rubber Co. ~ Chem. Div.	Beaumont, Tex.	76.3 (168)	
		Neches Butane Products Co.	Port Neches, Tex.	45.4 (100)	
		Shell Chem. Co Base Chems.	Deer Park, Tex. Wood River, Ill.	55.8 (123) Total = 182 (401)	
Isopropanol	Manufacture of acetone & its derivatives; manu-	Atlantic Richfield Co ARCO Chem. Co., div.	Channelview, Tex.	15.9 (35)	-
	facture of glycerol & isopropyl acetate; sol- vent for essential & other oils, alkaloids,	Eastman Kodak Co East- man Chem. Products, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	-	
	gums, resins, etc.; latent solvent for cel- lulose derivatives; coatings solvent;	Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Baton Rouge, La.	279.2 (615)	
	deicing agent for li- quid fuels; pharmaceu-	Shell Chem. Co Base Chems.	Deer Park, Tex. Dominguez, Calif.	276.9 (610) 94 (207)	
	ticals; perfumes; lacquers; extraction pro- cesses; dehydrating agent; preservative	Union Carbide Corp Chems. & Plastics Div.	Texas City, Tex. Whiting, Ind.	85 (187) 85 (187)	

<u>Chemical</u>	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Iso- propyl acetate	Solvent for nitrocellu- lose, resin gums, etc.; paints, lacquers, & printing inks, organic	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	4.5 (10)	-
	synthes1s	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va. Texas City, Tex.	13.6 (30)	
				Total = 18.1 (40)	
Iso- propyl-	Solvent; intermediate in synthesis of rubber ac-	Air Products & Chems., Inc.	Pensacola, Fla.	-	-
amine	celerator, pharmaceuti- cals, dyes, insecticides; bactericides, textile	Pennwalt Corp Chem. Div.	Wyandotte, Mich.	-	
	specialties, & surface- active agents; dehairing	Union Carbide Corp Chems. & Plastics Div.	Taft, La.	-	
	agent; solubilizer for 2,4-D acid	Va. Chems. Inc Indust. Chems. Dept.	Portsmouth, Va.	-	
Iso- propyl chloride	Solvent; intermediate; isopropylamine	Occidental Petroleum Corp Hooker Chem. Corp., subsid Hooker Chems. & Plastics Corp., sub- sid., Electrochemical & Specialty Chems. Div.	Niagara Falls, N. Y.	-	-
Isopropyl- phenol	Intermediate for syn- thetic resins, plasti- cizers, surface active agents, perfumes	Ethyl Corp Productol Chem. Co.	Orangeburg, S. C. Santa Fe Springs, Calif.	-	-
Ketene	Acetylating agent, gen- erglly reacting with com- pounds having an active hydrogen atom; reacts with ammonia to give acetamide; starting point for making var- ious commercially im- portant products, espe- cially acetic anhydride & acetate esters	Monsanto Co Monsanto Indust. Chems. Co.	Muscatine, Iowa	-	-

<u>Chemical</u>	<u>Usage 1</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² <u>MM kg (MM 1b)</u>	Total ^{4,5} production MM kg (MM lb) <u>for year of</u> estimate
Maleic acid	Organic synthesis (malic, succinic, aspartic, tartaric, propionic, lac- tic, malonic, acrylic, hydracrylic acids); dyeing & finishing of cotton, wool & silk; preservative for oils & fats	Pfanstiehl Labs., Inc.	Waukegan, Ill.	-	-
Maleic anhydride	Polyester resins; alkyd coating resins; fumaric	Allied Chem, Corp Specialty Chems, Div,	Moundsville, W. Va.	9.1 (20)	128.5 (283) -1974
	acid manufacture; pesti- cides; preservative for oils & fats; paper;	Koppers Co., Inc Organic Materials Div.	Bridgeville, Pa.	15.4 (34)	
	permanent-press resins (textiles)	Monsanto Co Monsanto Indust. Chems. Co.	St. Louis, Mo.	47.7 (105)	
		Petro-Tex Chem. Corp Petro-Tex. Chem. Co., subsid.	Houston, Tex.	22.7 (50)	
		Reichhold Chems., Inc.	Elizabeth, N. J. Morris, Ill.	13.6 (30) 27.2 (60)	
		Tenneco Inc Tenneco Chems., Inc Organics & Polymers Div.	Fords, N. J.	10 (22)	
		U.S. Steel Corp USS Chems., div.	Neville Island,	18.2 (40)	
				Total = 163.9 (361)	
Malic acid	Medicine; manufacture of various esters &	Allied Chem. Corp Specialty Chems. Div.	Moundsville, W. Va.	-	-
	salts; wine manufacture; chelating agent; food acidulant; flavoring	Norse Labs. Inc.	Santa Barbara, Calif		
Mesityl oxide	Solvent for cellulose esters & ethers, oils,	Shell Chem. Co Base Chems.	Deer Park, Tex. Dominguez, Calif.	-	-
	gums, resins, lacquers, roll-coating inks, stains, ore flotation; paint & varnish-removers; insect repellent	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	

<u>Chemical</u>	Usage 1	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Meth- acrylic acid	Monomer for large-vol- ume resins & polymers; organic synthesis; many	E. I. du Pont de Ne- mours & Co., Inc Biochems. Dept.	Belle, W. Va.	-	30.9 (68) -1968
	of the polymers are based on esters of the acid, as the methyl, butyl, or iosbutyl esters (see acrylic resin)	Rohm & Haas Co.	Bristol, Pa.	-	
Meth- acrylo- nitrile	Vinyl nitrile monomer; copolymer with styrene, butadiene, etc.; elasto- mers, coatings, plastics	The Standard Oil Co. (Ohio); Vistron Corp., subsid Chems. Dept.	Lima, Ohio	-	-
Meth- allyl alcohol	Intermediate	-	-	-	-
Meth- allyl	Intermediate for pro- duction of insecticides,	FMC Corp Chem. Group Indust. Chem. Div.	Baltimore, Md.	-	-
chloride	plastics, pharmaceuticals, other organic chemicals; fumigant for grains, tobacco, & soil	Stauffer Chem, Co Specialty Chem, Div.	Edison, N. J.	-	
Methanol	Manufacture of formalde~ hyde & dimethyl terephtha+	Air Products & Chems., Inc.	Pensacola, Fla.	149.8 (330)	3,082 (6,790) -1974
	late; chemical synthesis (methyl amines, methyl chloride, methyl meth-	Borden Inc Borden Chem. Div Petrochems.	Geismar, La.	479.4 (1,056)	
	acrylate, etc.); avia- tion fuel (for water	Celanese Corp Celanese Chem. Co., div.	Bishop, Tex. Clear Lake, Tex.	179.8 (396) 689.2 (1,518)	
	injection); automotive antifreeze; solvent for nitrocellulose, ethylcel-	Commercial Solvents Corp.	Sterlington, La.	149.8 (330)	
	lulose, polyvinyl butyral, shellac, rosin, manila	mours & Co., Inc			
	resin, dyes; denaturant for ethyl alcohol; de-	Elastomer Chems. Dept. Plastics Dept.	Beaumont, Tex. Orange, Tex.	599.3 (1,320) 344.6 (759)	
-	hydrator for natural gas	GaPacific Corp Chem. Div.	Plaquemine, La.	299.6 (660)	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Methanol (cont'd)	(See previous page)	Hercules Inc Synthetics Dept.	Hercules, Calif. Plaquemine, La.	299.6 (660)	(See previous page)
		Monsanto Co Monsanto Polymers & Petrochems. Co.	Texas City, Tex.	299.6 (660)	
		Rohm & Haas Co Rohm & Haas Texas Inc., subsid.	Deer Pa r k, Tex.	65.9 (1,452)	
		Tenneco Inc Tenneco Chems., Inc Organics & Polymers Div.	Houston, Tex.	239.7 (528)	
				Total = 3,796.3 (8,362)	
Methyl acetate	Paint remover com- pounds; lacquer solvent; intermediate	Borden Inc Borden Chem, Div Thermo- plastic Products	Bainbridge, N. Y. Compton, Calif. Demopolis, Ala. Illiopolis, Ill. Leominster, Mass.	-	-
		Eastman Kodak Co Eastman Organic Chems.	Rochester, N. Y.	-	
		Monsanto Co Monsanto Polymers & Petrochems. Co.	Springfield, Mass.	-	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
Methyl aceto- acetate	Solvent for cellulose ethers; ingredient of solvent mixtures for cellulose esters;	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	-	-
	organic synthesis	Lonza Inc.	Mapleton, Ill.	-	
Methyl- amine	Intermediate for acceler- ators, dyes, pharmaceuti-	Air Products & Chems., Inc.	Pensacola, Fla.	22.7 (50)	85.1 (187.4) -1973
	cals; insecticides; fun- gicides; surface active agents; tanning; dyeing	Commercial Solvents Corp.	Terre Haute, Ind.	8.2 (18)	
	of acetate textiles; fuel additive; polymeri- zation inhibitor; com-	E. I. du Pont de Ne- mours & Co., Inc Biochems. Dept.	Belle, W. Va. La Porte, Tex.	74.9 (165) 11.8 (26)	
	ponent of paint remov- ers; solvent; photo- graphic developer; rocket propellant	GAF Corp Chem. Div. Rohm and Haas Co.	Calvert City, Ky. Philadelphia, Pa.	4.5 (10) 6.3 (14) Total =	
	iocket propertant			128.5 (283)	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
N-methyl- aniline	Organic synthesis; solvent; acid ac-	Allied Chem. Corp Specialty Chems. Div.	Buffalo, N. Y.	-	-
	ceptor	American Cyanamid Co Organic Chems, Div.	Bound Brook, N. J.	-	
Methy l butynol	Stabilizer in chlori- nated solvents; vis- cosity reducer & stab-	Air Products & Chems., Acetylenic Chems. Div.	Calvert City, Ky.	-	-
	ilizer; electroplating brightener; inter- mediate	Hoffmann-La Roche Inc.	Nutley, N. J.	-	
Methyl chloride	Catalyst carrier in low- temperature polymeriza-	Allied Chem. Corp Specialty Chems. Div.	Moundsville, W. Va.	11.3 (25)	201.8 (444.5) -1973
	<pre>tion (butyl rubber); tetramethyl lead; sili- cones; refrigerant; medi- cine; fluid for thermo- metric & thermostatic equipment; methylating</pre>	Continental Oil Co Conoco Chems.	Westlake, La.	45.4 (100)	
		Diamond Shamrock Corp Diamond Shamrock Chem. Co Electro Chems. Div.	Belle, W. Va.	11.3 (25)	
	agent in organic syn- thesis, such as methyl-	Dow Chem. U.S.A.	Plaquemine, La.	68 .1 (150)	
	cellulose; extractant & low-temperature solvent;	Dow Corning Corp.	Carrollton, Ky. Midland, Mich.	9.1 (20) 6.8 (15)	
	propellant in high- pressure aerosols; herbicide	E. I. du Pont de Ne- mours & Co., Inc Indust. Chems. Dept.	Niagara Falls, N. Y.	36.3 (80)	
		Ethyl Corp.	Baton Rouge, La.	45.4 (100)	
		Gen. Electric Co Chem. & Metallurgical Div Silicone Pro- ducts Dept.	Waterford, N. Y.	22.7'(50)	
		Stauffer Chem. Co Indust. Chem. Div.	Louisville, Ky.	6.8 (15)	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	22.7 (50)	
		Vulcan Materials Co Chems. Div.	Geismar, La. Newark, N. J. Wichita, Kans.	- - Total = 286 (630)	

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ² ,3	1975 capacity ² MM_kg (MM_1b)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Methyl- cyclo- hexane	Solvent for cellulose ethers; organic synthesis	Phillips Petroleum Co Petrochem. & Supply Div.	Phillips, Tex.	-	-
Methyl- cyclo- hexanol	-	Lonza Inc	Mapleton, Ill.	-	-
Methyl- cyclo- hexanone	Solvent; lacquers; solvent for cellulose esters & ethers for lac- quers; antioxidant for lubricants; blending agent for special textile soaps & detergents	Frank Enterprises	Columbus, Ohio	-	-
Methyl- dioxo- lane	Extractant & solvent for oils, fats, waxes, dye- stuffs, & cellulose derivatives	-	-	-	-
Methyl formate	Organic synthesis; cellulose acetate sol- vent; military poison gases; fumigant; lar- vicides	Celanese Corp Celanese Chem. Co., d1v.	Pampa, Tex.	-	-
		E. I. du Pont de Ne- mours & Co., Inc Biochems, Dept.	Belle, W. Va.	-	
Methylene chloride	Paint removers; special photographic film; fumi-	Allied Chem. Corp Specialty Chems. Div.	Moundsville, W. Va.	22.7 (50)	214 (471.3) -1973
	<pre>gant; solvent degreasing; solvent mixtures for cellulose esters & ethers; textile & leather coat-</pre>	Diamond Shamrock Corp Diamond Shamrock Chem. Co Electro Chems. Div.	Belle, W. Va.	27.2 (60)	
	ings; refrigeration; local anesthetic; pharmaceutical	Dow Chem. U.S.A.	Freeport, Tex. Plaquemine, La.	68.1 (150) 40.9 (90)	
	& food extraction; plas- tics processing; spotting agent; dewaxing; chemical	E. I. du Pont de Ne- mours & Co., Inc Indust. Chems. Dept.	Niagara Falls,	18.2 (40)	
	(organic synthesis); as a propellant for aerosols; blowing agent in foams	Stauffer Chem. Co Indust. Chem. Div.	Louisville, Ky.	27.2 (60)	

<u>Chemical</u>	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Methylene chloride (cont'd)	(See previous page)	Vulcan Materials Co Chems, Div.	Geismar, La. Newark, N. J. Wichita, Kans.	18.2 (40) 13.6 (30)	(See previous page)
				Total = 236.1 (520)	
Methylene dianiline	Determination of tungs- ten & sulfates; polymer	Allied Chem. Corp Specialty Chems. Div.	Moundsville, W. Va.	-	-
	& dye intermediate; corrosion inhibitor;	Dow Chem. U.S.A.	Midland, Mich.	-	
	epoxy resin hardening agent	Mobay Chem. Corp Indust, Chems. Div.	New Martinsville, W. Va.	-	
		Rubicon Chems. Inc.	Geismar, La.	-	
Methyl ethyl ketone	thyl lose coatings & vinyl	Atlantic Richfield Co ARCO Chem. Co., div.	Channelview, Tex.	29 (64)	229.6 (505.8) - 1974
		Celanese Corp Celanese Chem. Co., div.	Pampa, Tex.	52,2 (115)	
	less powder; cleaning fluids; printing; catalyst carrier; Note: does not dis-	Dart Indust., Inc Chem. Group - Chem. Specialties Sector - Aztec Chems.	Elyria, Ohio	-	
	solve cellulose ace- tate and most waxes	Dixie Chem. Co.	Bayport, Tex.	1.4 (3)	
	tabe and most waxes	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tex.	-	
		Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Bayway, N. J.	90.8 (200)	
		Shell Chem. Co Base Chems.	Deer Park, Tex. Martinez, Calif.	45.4 (100)	
		oneno.	Norco, La.	22.7 (50)	
		Union Carbide Corp Chems. & Plastics Div.	Brownsville, Tex.	27.2 (60)	
				Total = 268.8 (592)	

<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capac1ty² MM kg (MM lb)	Total ^{4,35} production MM kg (MM lb) <u>for year of estimate</u>
Methyl- isobutyl	Solvent for dyestuffs; oils, gums, resins,	Shell Chem. Co Base Chems.	Deer Park, Tex. Dominguez, Calif.	Ξ	15.9 (35) -1973
carbinol	waxes, nitrocellulose & ethylcellulose; or- ganic synthesis; froth flotation; brake fluids	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
Methyl isobutyl ketone	isobutyl nishes, nitrocellulose	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	13.6 (30)	70.3 (154.8)-1973
		Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Bayway, N. J.	18.2 (40)	
		Shell Chem. Co Base Chems.	Deer Park, Tex. Dominguez, Calif.	36.3 (80) 15.9 (35)	
		Union Carbide Corp Chems, & Plastics Div.	Institute & South Charleston, W. Va.	29.5 (65)	
				Total = 113.5 (250)	
Methyl- pentynol	Stabilizer in chlorinated solvents; viscosity re- ducer; electroplating	Air Products & Chems. Inc Acetylenic Chems. Div.	Calvert City, Ky.	-	-
	brightening; intermediate in syntheses of hyporties & isoprenoid chemicals; solvent for polyamide re- sins; acid inhibitor; prevention of hydrogen embrittlement; medicine (soporific & anesthetic)	Hoffman-La Roche Inc.	Nutley, N. J.	-	
Methyl- phenyl- carbinol	Perfumery; flavoring; dyes; laboratory reagent	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	-

<u>Chemical</u>	Usage ¹	Manufacturer(s) ^{2,3}	$Location(s)^{2,3}$	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
α-methyl- styrene	Polymerization monomer, especially for polyester	Allied Chem. Corp Specialty Chems. Div.	Frankford, Pa.	6.8 (15)	-
		Clark Oil & Refining Corp Clark Chem. Corp., subsid.	Blue Island, Ill.	2.3 (5)	
		Dow Chem. U.S.A.	Midland, Mich.	4.5 (10)	
		GaPacific Corp Chem. Div.	Plaquemine, La.	4.5 (10)	
		Skelly Oil Co.	El Dorado, Kans.	1 (2)	
		Union Carbide Corp Chems. & Plastics Div.	Bound Brook, N. J.	3.6 (8)	
		U.S. Steel Corp USS Chems., div.	Haverhill, Ohio	6.8 (15)	
				Total = 29.5 (65)	
Morpho- line	Rubber accelerator; solvent; organic	Texaco Inc Jefferson Chem. Co., Inc., subsid.	Conroe, Tex.	6.8 (15)	-
	synthesis; additive to boiler water; waxes & polishes; corro- sion inhibitor; optical brightener for detergents			Total = 6.8 (15)	
a-naphtha- lene sul- fonic	Starting point in the manufacture of alpha- naphthol, alpha-naph-	Chattem Drug & Chem. Co., Petrochems. Co., Inc., subsid.	Long Beach, Calif.	-	-
acid	tholsulfonic acid, alpha-naphthylamine- sulfonic acid; solvent (sodium salt) for	Diamond Shamrock Corp Diamond Shamrock Chem. Co Nopco Chem. Div.	Cedartown, Ga.	-	
	phenol in the manu-	Eastern Color & Chem. Co.	Providence, R. I.	-	
	facture of disinfectant soaps	Emkay Chem. Co.	Elizabeth, N. J.	-	
	<u>F</u> -	Toms River Chem. Corp.	Toms River, N. J.	-	
		Witco Chem. Corp Ultra Div.	Clearing, Ill.	-	

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM 1b)	Total ^{4,5.} production MM kg (MM lb) <u>for year of estimate</u>
β-naph- thalene sulfonic acid	Starting point in the manufacture of beta- naphthol, beta-naph- tholsulfonic acid, beta-naphthylamine- sulfonic acid; etc.	American Cyanamid Co Fine Chems. Dept. (See also a-naph- thalene sulfonic acid)	Bound Brook, N. J.	-	-
α-naphthol	Dyes; organic synthesis; synthetic perfumes	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	-
β-naphthol	Dyes; pigments; anti- oxidants for rubber, fats, oils; insecticide; synthesis of fungicides; pharmaceuticals, per- fumes	American Cyanamid Co Organic Chems, Div.	Willow Island,	-	10.8 (23.8) -1 955
Neo- pentanoic acid	Intermediate, as a replacement for some natural materials	Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Baton Rouge, La.	-	-
Nitroanisole	Organic synthesis; manufacture of inter- mediates for dyes & pharmaceuticals	E. I. du Pont de Ne- mours & Co., Inc Organic Chems. Dept Dyes & Chems. Div.	Deepwater, N. J.	-	-
		Monsanto Co Monsanto Indust. Chems, Co.	St. Louis, Mo.	-	
Nitro- benzene	Manufacture of aniline; solvent for cellulose	Allied Chem. Corp Specialty Chems. Div.	Moundsville, W. Va.	25 (55)	250.2 (551.2) -1972
	ethers; modifying es- terification of cellu- lose acetate; ingredient of metal polishes & shoe polishes; manufacture of benzidine, quino- line, azobenzene, etc.	American Cyanamid Co Organic Chems. Div.	Bound Brook, N. J. Willow Island, W. Va.	38.6 (85) 27.2 (60)	
		E. I. du Pont de Ne- mours & Co., Inc Elastomer Chems. Dept Indust. Chems. Dept.	Beaumont, Tex. Gibbstown, N. J.	90.8 (200)	
		First Miss. Corp First Chem. Corp., subsid.	Pascagoula, Miss.	61.3 (135)	
		Mobay Chem. Corp Indust. Chems. Div.	New Martinsville, W. Va.	61.3 (135)	
		Monsanto Co Monsanto Indust. Chems. Co.	Sauget, Ill.	4.5 (10)	
		Rubicon Chems. Inc.	Geismar, La.	34 (75) Total = 483.5 (1,065)	

<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM_kg (MM_lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Nitro-	Organic synthesis;	Bofors Indust., Inc.	Linden, N. J.	-	-
benzoic acid (m,o,p)	preparation of anes- thetics & as intermed- iate in the manufacture of dyes & sun-screening agents	E. I. du Pont de Ne- mours & Co., Inc Organic Chems. Dept Dyes & Chems. Div.	Deepwater, N. J.	Ŧ	
	agenta	Salsburý Labs.	Charles City, Iowa	-	
		Sterling Drug Inc The Hilton-Davis Chem. Co., div.	Cincinnati, Ohio	-	
Nitro- ethane	Propellant; solvent for nitrocellulose, cellulose acetate, céllulose ace-	Commercial Solvents Corp.	Sterlington, La.	-	-
	topropionate, cellulose acetobutyrate, vinyl, alkyd, & many other resins, waxes, fats & dyestuffs; chemical synthesis				
Nitro- toluen e	Organic synthesis; for production of teluidine, tolidine, fuchsin, & various synthetic dyes	E. I. du Pont de Ne- mours & Co., Inc Organic Chems. Dept Dyeş & Chems. Div.	Deepwater, N. J.	-	-
		First Miss. Corp First Chem. Corp., subsid.	Pascagoula, Miss.	-	
Nonene	Organic synthesis; wet- ting agent; lube oil	Atlantic Richfield Co ARCO Chem, Co., div.	East Chicago, Ind.	-	-
	additive; polymer gasoline	Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Baton Rouge, La.	٦	
	•	The Humphrey Chem. Co.	North Haven, Conn.	-	
		Sun Qil Co Sun Oil Co. of Penn., subsid.	Marcus Hook, Pa.	-	
		Union Oil Co. of Calif,	Beaumont, Tex.	-	

<u>Chemical</u>	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM_lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Nonyl- phenol	Non-ionic surfactant (nonbiodegradable); lube oil additives; stabili-	Borg-Warner Corp Borg-Warner Chems Weston Div.	Morgantown, W. Va.	9.1 (20)	-
	zers, petroleum demulsi- fiers, fungicides; bacte- ricides; dyes; drugs; ad- hesives; rubber chemicals;	Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Bayway, N. J.	4.1 (9)	
	phenolic resins & plasticizers	GAF Corp Chem. Div.	Calvert City, Ky. Linden, N. J.	2.3 (5) 9.1 (20)	
		Monsanto Co Monsanto Indust. Chems. Co.	Kearny, N. J.	11.3 (25)	
		Productol Chem. Co.	Sante Fe Springs, Calif.	1 (2)	
		Rohm & Haas Co Rohm & Haas Texas Inc., subsid.	Philadelphia, Pa. Deer Park, Tex.	9.1 (20) 2.3 (5)	
		Texaco Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	13.6 (30)	
		Uniroyal, Inc Uni- royal Chem., div.	Naugatuck, Conn.	4.5 (10)	
				Total = 66.3 (146)	
Octyl-	Nonionic surfactants;	GAF Corp Chem. Div.	Linden, N. J.	-	_
phenol	plasticizers; antioxi- dants; fuel oil stabi-	Productol Chem. Co.	Santa Fe Springs, Calif.	-	
	lizer; intermediate for resins, fungicides, bactericides, dyestuffs	Schenectady Chems., Inc.	Rotterdam Junction, N. Y.	-	
	adhesives, rubber chemicals	Rohm & Haas Co Rohm & Haas Texas Inc., subsid.	Philadelphia, Pa. Deer Park, Tex.	-	
Paralde-	Substitute for acetalde-	Lonza Inc.	Mapleton, Ill.	-	-
hyde	hyde; rubber accelera- tors; rubber antioxi- dants; synthetic or- ganic chemicals; dye- stuff intermediates; medicine; solvent for fats, olls, waxes, gums, resins; leather; solvent mixtures for cellulose derivatives	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	

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Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Penta- erythritol	Alkyd resins; rosin & tall oil esters; special	Celanese Corp Cela- nese Chem. Co., div.	Bishop, Tex.	34 (75)	46.8 (103.2) -1973
	varnishes; pharmaceuti- cals; plasticizers; insecticides: synthetic	Commercial Solvents Corp.	Seiple, Pa.	11.3 (25)	
	lubricants; explosives; paint swelling agents	Hercules Inc Synthetics Dept.	Louisiana, Mo.	18.2 (40)	
		Pan American Chem. Corp.	Toledo, Ohio	11.3 (25)	
				Total = 74.9 (165)	
ethylene vapor-deg vent; dry metals & solids; v transfer p	Dry cleaning solvent; vapor-degreasing sol- vent; drying agent for	Diamond Shamrock Corp Diamond Shamrock Chem. Co Electro Chems. Div.	Deer Park, Tex.	72.6 (160)	332.8 (733) - 1974
	metais & certain other solids; vermifuge; heat- transfer medium, mfg. of fluorocarbons	Dow Chem. U.S.A.	Freeport, Tex. Pittsburg, Calif. Plaquemine, La.	54.5 (120) 9.1 (20) 68.1 (150)	
		E. I. du Pont de Ne- mours & Co., Inc Organic Chems. Dept Freon® Products Div.	Corpus Christi,	72.6 (160)	
		Ethyl Corp.	Baton Rouge, La.	22.7 (50)	
		Occidental Petroleum Corp Hooker Chem. Corp., subsid Hooker Chems. & Plastics Corp., subsid Electrochemical & Specialty Chems. Div.	Taft, La.	22.7 (50)	
		PPG Indust., Inc Chem. Div Indust. Chem. Div.	Lake Charles, La.	90.8 (200)	
		Stauffer Chem. Co Indust. Chem. Div.	Louisville, Ky.	31.8 (70)	
		Vulcan Materials Co Chems. Div.	Geismar, La. Wichita, Kans.	68.1 (150) 22.7 (50)	
				Total = 535.7 (1,180)	
l-pentene	Organic synthesis; blending agent for high octane motor fuel	Phillips Petroleum Co Petrochem. & Supply Div.	Phillips, Tex.	-	-

<u>Çhemical</u>	<u>Usage¹</u>	Manufgcturer(s) ^{2,3}	Location(s)2,3	1975 capacity² MM kg (MM_1b)	Total4)5. production MM kg (MM lb) for year of estimate
2-pentene	Polymerization inhibitor; organic synthesis	-	- `	-	-
o-phene- tidine	Manuf acture of dyes; laboratory reagent	Monsanto Co Monsanto Indust. Chems. Co.	St. Louis, No.	-	*
p-p hene- tidene	Dyestuffs intermediate; pharmaceuticals; medi-	Monsanto Co. ~ Monsanto Indust. Chems. Co.	St. Lòuis, Mo. Sauget, Ill.	-	-
	cine; laboratory reagent	Salsbury Labs,	Wilmington, N. C.	-	
Pheno1	Phenolic resins; epoxy resins (bisphenol-A);	Allied Chem, Corp Specialty Chems. Div.	Frankford, Pa.	238.3 (525)	1,103.2 (2,430)-1974
	nylon-6 (caprolactam); 2,4-D; selective solvent for refining lubricating oils; adipic acid; sali-	Clark Dil & Refining Corp Clark Chem. Corp., subsid.	Blue Island, Ill.	40 (88)	
	cylic acid; phenolphtha- lein; pentachlorophenol;	Dow Chem. U.S.A.	Midland, Mich. Oyster Creek, Tex.	45.4 (100) 181.6 (400)	
	acetophenetidine; picric acid; germicidal paints; pharmaceuticals; labora-	Georgia-Pacific Corp Chem. Div.	Plaquemine, La.	130.3 (287)	
	tory reagent; dyes &	Kalama Chem. Inc.	Kalama, Wash.	25 (\$5)	
	indicators; slimicide	Koppers Co., Inc	Follansbee, W. Va,	-	
		The Merichem Co.	Houston, Tex.	-	
		Monsanto Co Monsanto Polymers & Petrochems. Co.	Chocolate Bayou, Tex.	204.3 (450)	
		Productol Chem. Co.	Sante Fe Springs, Calif.	-	
		Reichhold Chems., Inc.	Tuscaloosa, Ala.	61.3 (135)	
		Skelly Oil Co.	El Dorado, Kans.	43.1 (95)	•
		Standard 011 Co. of Calif Chevron Chem. Co., subsid Oronite Additives & Indust. Chems. Div Indust. Chems.	Richmond, Calif.	25 (55)	
		Stimson Lumber Co Northwest Petrochem. Corp., div.	Anacortes, Wash.	-	
		Union Carbide Corp Chems. & Plastics Div Union Carbide Caribe, Inc., subsid.	Bound Brook, N. J. Penuelas, P. R.	68.1 (150) 90.8 (200)	
		U.S. Steel Corp USS Chems., div.	Clairton, Pa. Haverhill, Ohio	127.1 (280)	
				Total = 1,260.3 (2,820)	

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<u>Chemical</u>	Usage 1	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM <u>lb)</u>	Total4,5. production MM kg (MM lb) for year of estimate
Phenol- sulfonic	Water analysis; labora- tory reagent; electro-	Productol Chem. Co.	Sante Fe Springs, Calif.	-	-
acids	plated tin coatings baths; manufacture of intermediates & dyes; pharmaceuticals	Jim Walter Corp U.S. Pipe & Foundry Co., subsid Chem. Div.	Birmingham, Ala.	-	
	·····	Witco Chem. Corp Ultra Div.	Paterson, N. J.	-	
Phenyl anthra- nilic acid	-	Sterling Drug Inc	Rensselaer, N. Y.	-	-
Phenylene- diami <i>n</i> e	Azo dye intermediate; photographic develop- ing agent; fur dyes; photochemical measure- ments; intermediate in manufacture of	Fairmount Chem. Co.,	Deepwater, N. J. Newark, N. J.	-	29.1 (64) -1971
		The Sherwin-Williams Co. — Sherwin-Williams Chems. Div.	St. Bernard, Ohio	-	
	antioxidants & ac-	Toms River Chem. Corp.	Toms River, N. J.	-	
	celerators for rubber; detection of nitrous acid; textile developing agent; organic synthesis; laboratory reagent	E. I. du Pont de Ne- mours & Co., Inc Organic Chems. Dept Dyes & Chems. Div.	Deepwater, N. J.	-	
		The B. F. Goodrich Co B. F. Goodrich Chem. Co., div.	Henry, Ill.	-	
		Martin Marietta Corp Martin Marietta Chems. Sodyeco Div.	Sodyeco, N. C.	-	
		Ashland Oil, Inc Ashland Chem. Co., div Chem. Products Div.	Great Meadows, N. J.	-	
		GAF Corp Chem. Div.	Rensselaer, N. Y.	-	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM 1b)	Total ^{4,5,} production MM kg (MM lb) for year of estimate
Phosgene	Organic synthesis, es- pecially of isocyanates	Allied Chem. Corp Specialty Chems. Div.	Moundsville, W. Va.	44.5 (98)	330.6 (728.2) -1973
	polyurethane & poly- carbonate resins, car- bamates, organic car-	BASF Wyandotte Corp Indust. Chems. Group	Geismar, La.	25 (55)	
	bonates, & chloroform ates; pesticides; herbicides; dye manu	Chemetron Corp Chems. Group - Organic Chems. Div.	La Porte, Tex.	9.1 (20)	
	facture	E. I. du Pont de Ne- mours & Co., Inc Elastomer Chems. Dept.	Deepwater Point, N. J.	61.3 (135)	
		FMC Corp Chem. Group - Indust. Chem. Div.	Baltimore, Md.	2.7 (6)	
		Gen. Electric Co Plastics Business Div Engineering Plastics Product Dept.	Mount Vernon, Ind.	27.2 (60)	
		Mobay Chem, Corp Indust, Chems, Div.	Cedar Bayou, Tex. New Martinsville, W. Va.	59 (130) 111.2 (245)	
		Olin Corp Agri-	Lake Charles, La.	54.5 (120)	
		cultural Chems. Div. Designed Products Div.	Ashtabula, Ohio	22.7 (50)	
		PPG Indust., Inc Chem. Div Indust. Chem. Div.	Barberton, Ohio	2.3 (5)	
		Rubicon Chems. Inc.	Geismar, La.	56.7 (125)	
		Stauffer Chem. Co Agricultural Chem. Div.	Cold Creek, Ala.	11.3 (25)	
		Story Chem. Corp Ott Div.	Muskegon, Mich.	4.5 (10)	
		Texa co Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	13.6 (30)	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	50 (110)	
		The Upjohn Co Polymer mer Chems. Div.	La Porte, Tex.	90.8 (200)	
		Van De Mark Chem. Co., Inc.	Lockport, N. Y.	3.6 (8) Total =	
				650.1 (1,432)	

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Phthalic anhydride	Alkyd resins; plastici- zers; hardener for	Allied Chem. Corp Specialty Chems. Div.	El Segundo, Calif.	15.9 (35)	444.5 (979) -1974
	resins; polyesters; syn- thesis of phenolphthalein & other phthaleins, many	BASF Wyandotte Corp Colors & Chems. Group	South Kearny, N. J.	59 (130)	
	other dyes; chlorinated products; pharmaceutical intermediates; insecti-	Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Baton Rouge, La.	40.9 (90)	
	cides; diethyl phthalate; dimethyl phthalate; laboratory reagent	Koppers Co., Inc Organic Materials Div.	Bridgeville, Pa. Cicero, Ill.	40.9 (90) 59 (130)	
	Tablandly Teagent	Monsanto Co Monsanto Indust, Chems, Co.	Bridgeport, N. J. Texas City, Tex.	3 8. 6 (85) 59 (130)	
		Occidental Petroleum Corp Hooker Chem. Corp., subsid Hooker Chems. & Plastics Corp., subsid Puerto Rico Chem. Co., subsid.	Arecibo, P. R.	45.4 (100)	
		Standard Oil Co. of Calif Chevron Chem. Co., subsid Oronite Additives & Indust. Chems. Div Indust. Chems.	Richmond, Calif.	22.7 (50)	
		Stepan Chem. Co Surfactant Dept.	Anaheim, Calif. Elwood, Ill. Fieldsboro, N. J.	22.7 (50) 22.7 (50)	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	45.4 (100)	
		U.S. Steel Corp USS	Neville Island, Pa.	68.1 (150)	
				Total = 517.6 (1,140)	
Phthali- mide	Synthetic indigo, via anthranilic acid; fungicide; organic synthesis; laboratory reagent	The Sherwin-Williams Co Sherwin-Williams Chems. Div.	St. Bernard, Ohio	-	-

Total4,5

<u>Chemical</u>	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM lb)	production MM kg (MM lb) for year of estimate
Phthalo- nitrile	Intermediate in organic synthesis, especially pigments & dyes; base material for high temperature lubricants & coatings; insecticide	-	-	-	-
Piperazine	Corrosion inhibitor;	Fleming Labs., Inc.	Charlotte, N. C.	-	-
	anthelmintic; insecti- cide; accelerator for curing polychloroprene	Texaco Inc Jefferson Chem. Co., Inc., subsid.	Conroe, Tex.	-	
		Union Carbide Corp Chems. & Plastics Div.	Taft, La. Texas City, Tex.	-	
Poly- butenes	Hot-melt adhesives; sealing tapes; special sealants; cable in-	American Petrofina, Inc Cosden Cil & Chem. Co., subsid.	Big Spring, Tex.	9.1 (20)	104.4 (230) -1967
	sulation; polymer modi- fier; viscosity index improvers; lube oil additive	Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Bayway, N. J.	20.4 (45)	
		The Lubrizol Corp.	Deer Park, Tex.	40.9 (90)	
		Standard Oil Co. of Calif Chevron Chem. Co., subsid Oroníte Additives & Indust. Chems. Div Indust. Chems.	Richmond, Calif.	20.4 (45)	
		Standard Oil Co. (Ind.) Amoco Chems, Corp., subsid.	Texas City, Tex. Wood River, Ill.	77.2 (170) 40.9 (90)	
				Total = 208.8 (460)	
Polyethy- lene glycol	Chemical intermediates (lower molecular weight varieties); plasticizers;	Ashland Oil, Inc Ash- land Chem. Co., div Chem. Products Div.	Janesville, Wisc.	-	-
	softeners & humectants; lubricants; bases for cosmetics & pharmaceu-	BASF Wyandotte Corp Indust. Chems. Group	Wyandotte, Mich.	-	
	ticals; solvents; bin-	Dow Chem. U.S.A.	Freeport, Tex.	-	
	ders; metal & rubber processing; permissible	Hodag Chem. Corp.	Skokie, Ill.	-	
	additives to foods & animal feed; laboratory	Olin Corp Designed Products Div.	Brandenburg, Ky.	-	
	reagent	Texaco Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	-	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	

<u>Chemical</u>	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5.} production MM kg (MM lb) for year of estimate
Poly- ethylene glycol chloride	Solvents for cleaning extracting, & dewaxing	-	-	-	-
Poly- propylene	Hydraulic fluids; rubber lubricants; antifoam	BASF Wyandotte Corp Indust. Chems. Group	Washington, N. J. Wyandotte, Mich.	-	38.8 (85.5) -1973
glycol	agents; intermediates in urethane foams, ad- hesives, coatings, elastomers; plastici-	E. R. Carpenter Co., Inc Choate Chem. Co., subsid.	Bayport, Tex.		
	zers; paint formula- tions; laboratory	Dow Chem. U.S.A.	Freeport, Tex. Midland, Mich.	:	
	reagent	Hodag Chem. Corp.	Skokie, Ill.	-	
		ICI United States Inc Specialty Chems. Div.	New Castle, Del.	-	
		Nalco Chem. Co Petroleum & Process Chem. Div Visco Chems.	Sugar Land, Tex.	-	
		Olin Corp Designed Products Div.	Brandenburg, Ky.	-	
		Pelron Corp Texaco Inc Jefferson Chem. Co., Inc., subsid.	Conroe, Tex.	-	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
		Witco Chem. Corp Organics Div.	Clearing, Ill.	-	
Propane	Organic synthesis; household & industrial fuel; manufacture of ethylene, extractant;	Air Products & Chems. Inc Specialty Gas - Dept. Chemicals - Intermediates Mktg.	Allentown, Pa.	-	21,802 (48,022)-1971
	solvent; refrigerant; gas enrichener; aerosol	Matheson Gas Products	Lyndhurst, N. J.	-	
	propellant; mixture for bubble chambers	Phillips Petroleum Co Petrochemical & Supply Div Customer Ser- vice Center	Borger, Tex.	-	
		Technical Petroleum Co.	Chicago, Ill.	-	

Chemical	Usage 1	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM_kg (MM_lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Propion- adlehyde	Manufacture of poly- vinyl acetals & other plastics; synthesis	Eastman Kodak Co Eastman Chem. Products, Inc., subsid.	Longview, Tex.	-	-
	of rubber chemicals; disinfectant; preservative	Union Carbide Corp Chems. & Plastics Div.	Seadrift, Tex. Texas City, Tex.	Ξ	
Propionic acid	Propionates, some of which are used as mold	Celanese Corp Celanese Chem. Co., div.	Pampa, Tex.	5.4 (12)	27.4 (60.4) -1973
(propanoic acid)	inhibitors in bread & fungicides in general;	Commercial Solvents Corp.	Sterlington, La.	1.4 (3)	
atiu)	emulsifying agents; solutions for electro- plating nickel; per- fume esters; artifical	Eastman Kodak Co. – Eastman Chem. Products Inc., subsid. – Tenn. Eastman Co., div.	Kingsport, Tenn.	9.1 (20)	
	fruit flavors; pharma- ceuticals; solvent mix- tures for cellulose derivatives; pretreat- ment of zinc oxide	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	11.3 (25)	
				Total = 27.2 (60)	
Propyl- amine	Intermediate; laboratory reagent	Pennwalt Corp Chem. Div.	Wyandotte, Mich.	-	7.6 (16.7) -1972
		Va. Chems. Inc Indust. Chems. Dept.	Portsmouth, Va.	-	
Propyl chloride	Solvent; intermediate propylamine	Publicker Indust. Inc.	Philadelphia, Pa.	-	-
Propylene	Isopropyl alcohol, poly-	Amerada Hess Corp.	Port Reading, N. J.	59 (130)	4,544 (10,010) -1974
	propylene, synthetic glycerol, acrylonitrile, propylene oxide, heptene,	American Petrofina, Inc Cosden Oil & Chem. Co., subsid.	Big Spring, Tex. Eldorado, Tex. Mount Pleasant, Tex.	59 (130) 15 (33) 25 (55)	
	cumene, polymer gasoline, anticipated use for	ARCO/Polymers, Inc.	Houston, Tex.	68.1 (150)	
	acrylic acid & in vinyl resins	Ashland Oil, Inc Ashland Chem. Co., div., Petrochems. Div.	Ashland, Ky. Louisville, Ky. North Tonawanda	75 (165) 13.6 (30) 22.7 (50)	
		Atlantic Richfield Co ARCO Chem. Co., div.	Channelview, Tex. East Chicago, Ind. Wilmington, Calif.	6.8 (15) 30 (66) 45.4 (100)	
		BASF Wyandotte Corp Indust. Chems. Group	Geismar, La.	22.7 (50)	

Chemical	<u>Usage 1</u>	Manufacturer(s) ^{2,3}	Location(s)2:3	1975 capacity² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Probylene (cont'd)	(See previous page)	The Charter Co Charter Oil Co., subsid Charter Internat'l Oil Co., subsid.	Houston, Tex.	34 (75)	(See previous page)
		Chemplex Co.	Clinton, Iowa	61.3 (135)	
		Cities Service Co., Inc North American Petroleum Group	Lake Charles, La.	240.6 (530)	
		Clark Oil & Refining Corp Clark Chem. Corp., subsid.	Blue Island, Ill.	20.4 (45)	
		Coastal States Gas Corp Coastal States Marketing, Inc., subsid.	Corpus Christi, Tex.	25 (55)	
		Continental Oil Co Conoco Chems.	Westlake, La.	18.2 (40)	
		Dow Chem. U.S.A.	Bay City, Mich. Freeport, Tex. Plaquemine, La.	45.4 (100) 200 (440) 72.6 (160)	
		E. I. du Font de Ne- mours & Co., Inc Plastics Dept.	Orange, Tex.	68.1 (150)	
		Eastman Kodak Co Eastman Chem. Froducts, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	136.2 (300)	
		El Paso Natural Gas Co., El Paso Products Co., subsid.	Odessa, Tex.	79.4 (175)	
		Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Baton Rouge, La. Baytown, Tex. Bayway, N. J.	710.5 (1,565) 249.7 (550) 145.3 (320)	
		Getty Oil Co.	Delaware City,	81.7 (180)	
		The B. F. Goodrich Co B. F. Goodrich Chem. Co., div.	Calvert City, Ky.	63.6 (140)	
		Gulf Oil Corp Gulf Oil Chems. Co., div Petrochems. Div.	Cedar Bayou, Tex. Philadelphia, Pa. Port Arthur, Tex.	56.7 (125) 84 (185) 252 (555)	
		Marathon Oil Co.	Detroit, Mich. Texas City, Tex.	45.4 (100) 129.4 (285)	
			Beaumont, Tex.	220.2 (485)	

<u>Chemical</u>	<u>Usage 1</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Propy- lene (cont'd)	(See previous page)	Mobil Oil Corp Mobil Chem. Co., div Petrochems. Div.	Beaumont, Tex.	220.2 (485)	(See previous page)
		Monsanto Co Monsanto Polymers & Petrochems. Co.	Chocolate Bayou,	250 (550)	
		Northern Natural Gas Co Northern Petro- chem., subsid Polymers Div.	Morris, Ill.	90.8 (200)	
		Novamont Corp.	Kenova, W. Va.	84 (185)	
		The Oil Shale Corp Lion Oil Co., subsid.	El Dorado, Ark.	-	
		Petro Gas Producing Co.	Groves, Tex.	25 (55)	
		Phillips Petroleum Co.	Sweeny, Tex.	68.1 (150)	
		Puerto Rico Olefins Co.	Penuelas, P. R.	295.1 (650)	
		Shell Chem. Co Base Chems.	Deer Park, Tex. Dominguez, Calif. Norco, La.	499.4 (1,100) 79.5 (175) 100 (220)	
		Skelly Oil Co.	El Dorado, Kans.	11.8 (26)	
		Standard Oil Co. of Calif Chevron Chem. Co., subsid Oronite Additives & Indust. Chems. Div Indust. Chems.	El Segundo, Calif. Richmond, Calif.	18.2 (40) 93.1 (205)	
		Standard Oil Co. (Ind.) -	Chocclate Bayou,	179.3 (395)	
		Amoco Chems. Corp., subsid.	Tex. Texàs City, Tex. Wood River, Ill.	172.5 (380) 59 (130)	
		The Standard Oil Co. (Ohio)	Lima, Ohio Toledo, Ohio	81.7 (180) 88.5 (195)	
		Sun Oil Co Sun Oil Co. of Penn., subsid. Suntide Refining Co., subsid.	Duncan, Okla. Marcus Hook, Pa. Toledo, Ohio Corpus Christi, Tex.	36.3 (80) 154.4 (340) 25 (55) 91 (200)	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Propy- lene	(See previous page)	Texaco Inc.	Port Arthur, Tex. Westville, N. J.	11.3(25) 25(55)	(See previous page)
(cont'd)		Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	59 (130)	
		Texas City Refining Inc.	Texas City, Tex.	45.4 (100)	
		Union Carbide Corp Chems. & Plastics Div.	Seadrift, Tex. Taft, La. Texas City, Tex. Torrance, Calif. Whiting, Ind.	50 (110) 90.8 (200) 109 (240) - 125 (275)	
		Union Carbide Caribe,	Penuelas, P. R.	208.8 (460)	
		Union 011 Co. of Calif.	Beaumont, Tex.	43.1 (95)	
				Total = 6,751 (14,870)	
Propylene chloro- hydrin	Organic synthesis (introducing hydroxy- propyl group)	Eastman Kodak Co Eastman Organic Chems.	Rochester, N. Y.		-
Propy- lene	Intermediate for per- chloroethylene &	Dow Chem. U.S.A.	Freeport, Tex. Plaquemine, La.	11.3 (25) 4.5 (10)	-
dichloride	carbon tetrachloride; lead scavenger for antiknock fluids;	Olin Corp Designed Products Div.	Brandenburg, Ky.	-	
	solvents for fats, oils, waxes, gums, &	Texaco Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	6.8 (15)	
	resins; solvent mix- tures for cellulose esters & ethers;	Union Caribde Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	11.3 (25)	
	esters a ethers; scouring compounds; spotting agents; metal degreasing agents; soil fumigant for nematodes			Total = 315.5 (695)	
Propy- lene	Propylene glycol & other glycols; urethane	BASF Wyandotte Corp Indust. Chems. Group	Wyandotte, Mich.	79.4 (175)	808 (1,780) -1974
oxide	foams; surfactants & detergents; isopropanol amines; fumigant; syn-	Dow Chem. U.S.A.	Freeport, Tex. Plaquemine, La.	340.5 (750) 100 (220)	
	thetic elastomer (homopolymer)	Olin Corp Designed Products Co.	Brandenburg, Ky.	59 (130)	
		Oxirane Chem. Co.	Bayport, Tex.	404 (890)	
		Texaco Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	68.1 (150)	
				Total =	

1,051 (2,315)

<u>Chemical</u>	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Pyridine (natural &	Synthesis of vitamins & drugs; solvent; water- proofing; rubber chemi-	Natural: Crowley Tar Products, Inc.	Baltimore, Md. Houston, Tex.	:	3.4 (7.42) -1968
synthetic)	cals; denaturant for alcohol & antifreeze mixtures; dyeing assist-	Koppers Co., Inc Organic Materials Div.	Follansbee, W. Va.	-	
	ant in textiles; fumgicides	Synthetic: Reilly Tar & Chem. Corp.	Indianapolis, Ind.	16 (35)	
		Warner-Lambert Co	Harriman, N. Y.	2.3 (5)	
		Nepera Chem. Co., Inc., subsid.		Synthetic Total 18.3 (40)	=
Quinone	Mfg, of dyes & hydro- quinone	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	-	-
		Frank Enterprises	Columbus, Ohio	-	
Resorcinol	Resorcinol-formaldehyde resins; dyes; pharma-	Koppers Co., Inc Organic Materials Div.	Petrolia, Pa.	11.3 (25)	11.8 (26) -1970
	ceuticals; cross-link- ing agent for neoprene; rubber tackifier; ad- hesives for wood veneers & rubber-to-textile com- posites; medicine; mfg. of styphnic acid			Total = 11.3 (25)	
Resor-	Dyestuff & pharmaceuti-	Aldrich Chem. Co., Inc.	Milwaukee, Wisc.	-	-
cylic acid	<pre>cal intermediate; chemi- cal intermediate in synthesis of fine or- ganic chemicals; light stabilizers; resins</pre>	Koppers Co., Inc Organic Materials Div.	Petrolia, Pa.	-	
Sal1-	Mfg. of aspirin & other	Dow Chem. U.S.A.	Midland, Mich.	7.7 (17)	6.2 (13.6) -1969
cylic acid	medicinals; preserva- tive; dyes; perfumes; prevulcanization inhib- itor; organic inter- mediate; fungicide	Monsanto Co Monsanto Indust, Chems, Co.	St. Louis, Mo.	9.1 (20)	

<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Sali- cylic acid	(See previous page)	Sterling Drug Inc The Hilton-Davis Chemical Co., div.	Cincinnati, Ohio	3.2 (7)	(See previous page)
(cont'd)		Tenneco Inc Tenneco Chems., Inc Organics & Polymers Div.	Garfield, N. J.	4.5 (10)	
				Total = 24.5 (54)	
Sodium acetate	Dye & color intermed- iate; pharmaceuticals;	Allied Chem. Corp Specialty Chems. Div.	Marcus Hook, Pa.	-	-
	cinnamic acid; soaps; photography; purifica-	Dan River, Inc.	Danville, Va.	-	
	<pre>photography, purifica- tion of glucose; meat preservation; medicine; electroplating; tanning; dehydrating agent; buf- fer in foods; laboratory reagent</pre>	Howerton Gowen Chems., Inc.	Roanoke Rapids, N. C.	-	
		Mallinckrodt, Inc Indust. Chems. Div.	St. Louis, Mo.	-	
		Washine Div.	Lodi, N. J.	-	
	-	Ritter Chem. Co., Inc.	Amsterdam, N. Y.	-	
		Union Carbide Corp Chems. & Plastics Div.	Niagara Falls, N. Y.	-	
Sodium carboxy-	Detergents, soaps, food products (especially	BASF Wyandotte Corp Indust. Chems. Group	Wyandotte, Mich.	1.8 (4.0)	29.5 (64.9) -1970
methyl cellulose	dietetic foods & ice cream), where it acts as	Brown Co.	Berlin, N. H.	-	
Gellulose	water binder, thickener, suspending agent, & emul- sion stabilizer; textile	Hercules Inc Coatings & Specialty Products Dept.	Harbor Beach, Mich. Hopewell, Va.	4.5 (10.0) 18 (40.0)	
	<pre>manufacturing (sizing); coating paper & paper board to lower porcsity;</pre>	H. Kohnstamm & Co., Inc.	Camden, N. J. Clearing, Ill.	0.9 (2.0) 0.5 (1.0)	
	drilling muds; emulsion paints; protective colloid; pharmaceuticals;	The Procter & Gamble Co The Buckeye Cel- lulose Corp., subsid.	Memphis, Tenn.	3.2 (7.0)	
	cosmetics	United Aircraft Corp Essex Internat'l Inc., subsid.	Muncie, Ind.	1.1 (2.5)	
				Total = 30.2 (66.5)	

<u>c</u>	Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total4,5 production MM kg (MM lb) for year of estimate
	odium Cormate	Reducing agent; medicine; manufacture of	Commercial Solvents Corp.	Seiple, Pa.	-	-
		formic acid & oxalic acid; organic chemicals; mordant; tanning; wall-	Hercules Inc Synthetics Dept.	Louisiana, Mo.	-	
		paper printing; plating	Pan American Chem. Corp.	Toledo, Ohio	-	
			Tenneco Inc Tenneco Chems., Inc Organics & Polymers Div.	Fords, N. J.	-	
	odium henate	Antiseptic; salicylic acid; organic synthesis	American Petrofina, Inc American Petrofina Co. of Texas, subsid.	Port Arthur, Tex.	-	-
			Colt Indust., Inc Crucible Stainless Steel & Alloy Div.	Midland, Pa.	-	
			National Steel Corp Great Lakes Steel Div B. F. Div.	Zug Island (River Rouge), Mich.	-	
			Republic Steel Corp Iron & Chem. Div.	Chicago, Ill. Cleveland, Ohio	_	
			Sharon Steel Corp Fairmont Coke Works	Fairmont, W. Va.	-	
			Shenango Inc.	Neville Island, Pa.	-	
			Wheeling-Pittsburgh Steel Corp.	Monessen, Pa.	-	
	orbic	Fungicide; food pre- servative; copolymeri-	American Hoechst Corp Dyes & Pigments Div.	Coventry, R. I.	-	-
		zation; upgrading of drying oils; cold rub- ber additive; inter- mediate for plastici- zers & lubricants	Pfizer Inc Chems. Div.	Groton, Conn.	-	

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estim</u> a	
SBR,	Polystyrene plastics; SBR, ABS, & SAN res- ins; protective coatings	American Petrofina, Inc Cosden Oil & Chem. Co., subsid.	Big Spring, Tex.	54.5 (120)	2,724 (6,000) -	1974
	(styrene-butadiene latex; alkyds); styrenated poly- esters; rubber-modified	alkyds); styrenated poly- ARCO/Polymers, inc. Beav	Beaver Valley, Pa. Houston, Tex.	199.8 (440) 54.5 (120)		
	polystyrene; copolymer	Cos-Mar, Inc.	Carville, La.	272.4 (600)		
resins; intermediate	resins; intermediate	Dow Chem. U.S.A.	Freeport, Tex. Midland, Mich.	749.1 (1,650) 181.6 (400)		
		El Paso Natural Gas Co El Paso Co., subsid.	Odessa, Tex.	54.5 (120)		
		Foster Grant Co., Inc.	Baton Rouge, La.	372.3 (820)		
		Gulf Oil Corp. + Gulf Oil Chems. Co., div Petrochems. Div.	Welcome, La.	227 (500)		
		Monsanto Co Monsanto Polymers & Petrochems. Co.	Texas City, Tex.	590.2 (1,300)		
		Standard 011 Co. (Ind.) - Amoco Chems. Corp., subsid.	Texas City, Tex.	385.9 (850)		
		Sun Oil Co Sun Oil Co. of Penn., subsid. Suntide Refining Co., subsid.	Corpus Christi, Tex,	36.3 (80)		
		Union Carbide Corp	Seadrift, Tex.	136,2 (300)		
		Chemș. & Plastics Div.		Total ≠ 3,314.2 (7,300)		
Succinic acid	Medicine; organic Synthesis; mfg. of lac-	Allied Chem. Corp Specialty Chems. Div.	Marcus Hook, Pa.	-	-	
	quers, dyes, esters for perfumes, succinates; photography; in foods as a sequestrant, buffer, neutralizing agent	Richardson-Merrell, Inc J. T. Baker Chem. Co., subsid.	Phillipsburg, N. J.	-		

Succino- nitrile	Organic synthesis	Guardian Chem. Corp Eastern Chem. Div.	Hauppauge, N. Y.	-		-	
		R.S.A. Corp.	Ardsley, N. Y.	-			
Sulfo- lane	Extraction of aromatic hydrocarbons from oil	Phillips Petroleum Co., Petrochem. & Supply Div.	Phillips, Tex,	-		-	
	refinery streams; fractionation of wood tars, tall oil, & other fatty acids; polymeriza- tion solvent; plastici- zer; component of hydrau- lic fluid; textile finishing	Shell Chem. Co Base Chems.	Norco, La.	-			
Synthesis gas	Organic synthesis; mfg. of alcohols (Oxo process); low-Btu fuel gas	-	-	-		-	
Tere- phthalic acid	Production of linear, crystalline polyester resins, fibers & films by combination with	Eastman Kodak Co 'Eastman Chem. Products, Inc., subsid Tenn. Eastman Co., div.	Kingsport, Tenn.	-	1,557	(3,430)	-1974
	glycols, e.g., "Dacron,' "Mylar," "Terylene;" also used as a reagent for alkali in wool; ad- ditive to poultry feeds	Hercules Inc Synthetics Dept.	Wilmington, N. C.	113.5			
			Decatur, Ala. Joliet, Ill.	363.2 (800) 45.4 (100)			
				Total = 522.1 (1,150)			
Tetra- chloro- ethane	Solvent; cleansing & degreasing metals; paint removers, varnishes, lac- quers, photographic film; resins & waxes; extraction of oils & fats; alcohol denatu- rant; organic synthesis; insecticides; weed kil- ler; fumigant	Occidental Petroleum Corp Hocker Chem. Corp., subsid Hocker Chems. & Plastics Corp., subsid Electrochemical & Specialty Chems. Div.	Taft, La.	-		-	
Tetra- chloro- phthalic anhydride	Intermediate in dyes, pharmaceuticals, plasti- cizers, & other organic materials; flame- retardant in epoxy resins	Monsanto Co Monsanto Indust. Chems. Co.	Bridgeport, N. J.	-		-	

Chemical	<u>Usage¹.</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) <u>for year of estimate</u>
Tetra- ethyl lead (TEL)	Antiknock gasoline ad- ditive; certain ethyl- ation operations	E. I. du Pont de Ne- mours & Co., Inc Oganic Chemicals Dept Petroleum Chems. Div.	Antoich, Calif. Deepwater, N. J.	154.4 (340) _	246.7 (543.4) -1968
		Ethyl Corp.	Baton Rouge; La. Pasadena, Tex.	158.9 (350)	
		Nalco Chem. Co Petroleum & Process Chem. Div.	Freeport, Tex.	18.2 (40)	
		PPG Indust., Inc Chem. Div Houston Chem. Co., div.	Beaumont, Tex.	45.4 (100)	
				Total [#] = 376.8 (830)	
Tetra- hydro- naphtha-	Solvent; chemical intermediate	E. I. du Pont de Ne- mours & Co., Inc Dyes & Chems. Div.	Deepwater, N. J.	-	-
lene		Lonza Inc.	Mapleton, Ill.	-	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
Tetra- hydro- phthalic anhydride	Chemical intermediate for light-colored al- kyds, polyesters, plasticizers & ad- hesives; intermediate for pesticides; hardener for resins	Petro-Tex Chem. Corp Petro-Tex Chem. Co., subsid.	Houston, Tex.	-	~
Tetra- methylene- diamine	Chemical intermediate	BASF Wyandotte Corp Indust. Chems. Group	Wyandotte, Mich.	~	-
Toluene -2,4-	Dye intermediate; direct oxidation black for furs	Air Products & Chems., Inc.	Pasadena, Tex.	-	-
diamine	& hair; source for toluene-2,4-diisocya-	American Cyanamid Co Organic Chems. Div.	Bound Brook, N. J.	-	
	nate	E. I. du Pont de Ne- mours & Co., Inc Organic Chems. Dept Dyes & Chems. Div.	Deepwater, N. J.	-	
		GAF Corp Chem. Div.	Rensselaer, N. Y.	-	
		Olin Corp Agricul-	Lake Charles, La.	-	
		tural Chems. Div Designed Products Div.	Ashtabula, Ohio Brandenburg, Ky. Rochester, N. Y.	-	
		Rubicon Chems. Inc.	Geismar, La.	-	
		Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	

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* Includes TEL, TML and mixtures.

<u>Chemical</u>	<u> Usage 1</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2 > 3}	1975 capacity ² MM kg (NM 15)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Toluene- sulfonic	Dyes; organic synthesis; acld catalyst	American Cyanamid Co Organic Chems. Div.	Bound Brook, N. J.	-	-
acids		Cities Šervice Co., Inc North American Chems. & Metals Group - Indust. Chems. Div.	Copperhill, Tenn.	-	
		Monšanto Co Monsanto Indust. Chems. Co.	St. Louis, Mo.	-	
		Nease Chem. Co., Inc.	State College, Pa.	-	
		Jim Walter Corp U.S. Pipe & Foundry Co., subsid Chem. Div.	Birmingham, Ala.	÷	
Toluene- sulfon- amide	Organic synthesis; plasticizers & resins; fungicide & mildewcide in paints & coatings	Monsanto Co. ∸ Monsanto Indust. Chems, Co.	St. Louis, Mo.	-	-
Toluene- sulfonyl chloride	Organic synthesis; inter- mediate in the synthesis of saccharin & dyestuffs	Monsanto Co Monsanto Indust, Chems, Co.	St. Louis, Mov	-	-
Trichloro-	Solvent in chemical	Dow Chem. U.S.A.	Midland, Mich.	-	-
benzene	mfg.; dyes & inter- mediates; dielectric fluid; synthetic trans- former oils; lubricants; heat-transfer medium; insecticides	Occidental Petroleum Corp Hooker Chem. Corp., subsid Hooker Chems. & Plastics Corp., subsid Electrochemical & Specialty Chems. Div.	Niagara Falls, N. Y.	-	
		Sobin Chems., Inc Montrose Chem. Div.	Newark, N. J.	-	
		Solvent Chem. Co., Inc.	Malden, Mass. Niagara Falls, N. Y.	Ξ	
		Standard Chlorine Chem. Co., Inc.	Delaware City, Del. Kearny, N. J.	-	

<u>Chemical</u>	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM_kg (MM_1b)	Total ^{4,5.} production MM kg (MM lb) <u>for year of estimate</u>
Trichloro-	Solvent for cleaning	Dow Chem. U.S.A.	Freeport, Tex.	154.4 (340)	170.1 (374.6) -1971
ethane	precision instruments; aerosol propellant;	Ethyl Corp.	Baton Rouge, La.	22.7 (50)	
	metal degreasing; pesticide; solvent for fats, oils, waxes,	PPG Indust., Inc Chem. Div Indust. Chem. Div.	Lake Charles, La.	79.4 (175)	
	resins, other products; organic synthesis	Vulcan Materials Co Chems, Div.	Geismar, La.	29.5 (65) Total = 286 (630)	
Trichloro- ethylene	Metal degreasing; ex- traction solvent for oils, fats, waxes; sol- vent dyeing; dry clean-	Diamond Shamrock Corp Diamond Shamrock Chem. Co Electro Chems. Div.	Deer Park, Tex.	45.4 (100)	-
	ing; refrigerant & heat exchange liquid;	Dow Chem. U.S.A.	Freeport, Tex.	68.1 (150)	
	organic syntheses;	Ethyl Corp.	Baton Rouge, La.	22.7 (50)	
	fumigant; medicine (anesthetic); clean- ing & drying electronic parts	Occidental Petroleum Corp Hooker Chem Corp., subsid Hooker Chems. & Plastics Corp., subsid Electrochemi- cal & Specialty Chems. Div.	Taft, La.	18.2 (40)	
		PPG Indust., Inc Chem. Div Indust. Chem. Div.	Lake Charles, La.	127.1 (280)	
				Total = 281.5 (620)	
1,2,3-Tri-	Paint & varnish remover;	Dow Chem. U.S.A.	Freeport, Tex.	-	-
chloro- propane	solvent; degreasing agent	Shell Chem. Co Base Chems.	Deer Park, Tex.	-	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
l,1,2-Tri- chloro-	Dry cleaning solvent; fire extinguishers; re-	Allied Chem. Corp Specialty Chems. Div.	Baton Rouge, La.	-	-
l,2,2-tri- fluoro- ethane	frigerant; air-condi- tioning units; to make chlorotrifluoroethylene; blowing agent; polymer intermediate; solvent	E. I. du Pont de Ne- mours & Co., Inc Organic Chems. Dept Freon® Products Div.	Antioch, Calif. Deepwater, N. J. East Chicago, Ind. Louisville, Ky. Montague, Mich.	-	
	drying; drying electro- nic parts & precision equipment	Union Carbide Corp Chems. & Plastics Div.	Institute & South Charleston, W. Va.	-	
Tri- ethanol- amine	Fatty acid soaps used in drycleaning, cosmet- ics, household deter- gents, & emulsions; wool scouring; textile antifume agent & water- repellent; dispersion agent; corrosion inhi- bitor; softening agent, humectant, & plastici- zer; insecticide; che- lating agent; rubber accelerator	(See diethanolamine)	-	-	49 (108) -1974
Triethyl- amine	Catalytic solvent in chemical synthesis; ac- celerator activators	Air Products & Chems., Inc.	Pensacola, Fla.	-	-
	for rubber; wetting, penetrating & water-	Pennwalt Corp Chem. Div.	Wyandotte, Mich.	-	-
	proofing agents of quarternary ammonium	Union Carbide Corp Chems. & Plastics Div.	Taft, La.	-	
	types; curing & harden- ing of polymers (e.g., core-binding resins); corrosion inhibitor propellant	Va. Chems. Inc Indust. Chems. Dept.	Portsmouth, Va.	-	
Tri- ethylene	Solvent for nitrocellu- lose; various gums &	Allied Chem. Corp Specialty Chems. Div.	Orange, Tex.	1.4 (3)	51.3 (113.1) -1973
glycol	resins; lacquers; or- ganic synthesis; air- conditioning units;	Celanese Corp Cela- nese Chem. Co., div.	Clear Lake, Tex.	1.4 (3)	
	bactericide (in vapor	Dixie Chem. Co.	Bayport, Tex.	0.9 (2)	
	form); humectant in printing inks; textile conditioner; fungicide	Dow Chem. U.S.A.	Freeport, Tex. Plaquemine, La.	15.9 (35)	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	$Location(s)^{2,3}$	1975 capacity ² MM kg (MM 1b)	Total4,5 production MM kg (MM lb) for year of estimate
Tri- ethylene glycol (cont'd)	(See previous page)	Eastman Kodak Co Eastman Chem. Products, Inc., subsid Texas Eastman Co., div.	Longview, Tex.	<0.5 (<1)	(See previous page)
		Olin Corp Designed Products Div.	Brandenburg, Ky.	<0.5 (<1)	
		PPG Indust., Inc Chem. Div Houston Chem. Co., div	Beaumont, Tex.	<0.5 (<1)	
		PPG Indust. (Caribe)	Guayanilla, P. R.	<0.5 (<1)	
		Shell Chem. Co Base Chems.	Geismar, La.	1.8 (4)	
		Texaco Inc Jefferson Chem. Co., Inc., subsid.	Port Neches, Tex.	4.5 (10)	
		Union Carbide Corp Chems. & Plastics Div. Union Carbide Caribe.	Institute & South Charleston, W. Va. Seadrift, Tex. Taft, La.	- 34 (75)	
		Inc., subsid.	Penuelas, P. R.	J Total = <61.7 (<136)	
Tri- ethylene glycol dimethyl ether	Solvent for gases; coupling immiscible liquids	The Ansul Co Chem. Div.	Marinette, Wisc .	-	-
Tr1- méthy1-	Organic synthesis, es- pecially of chlorine salts;	Air Products & Chems., Inc.	Pensacola, Fla.	-	13.1~(28.9) - 1973
amine	warning agent for natu- ral gas; manufacture of	Commercial Solvents Corp.	Terre Haute, Ind.	-	
	disinfectants; flota- tion agent; insect attractant; quaternary	E. I. du Pont de Ne- mours & Co., Inc Biochems. Dept.	Belle, W. Va. La Porte, Tex.	Ξ	
	ammonium compounds; plastics	GAF Corp Chem. Div.	Calvert City, Ky.	-	
	•	Rohm & Haas Co.	Philadelphia, Pa.	-	

<u>Chemical Usage¹</u>		Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
iscbuty- intermed lene compound oil addi material tion in p	s of resins, & late organic s; lubricating tive, raw for alkyla- producing ane motor fuels	The B. F. Goodrich Co B. F. Goodrich Chem. Co., div.	Port Neches, Tex.	-	-
	er; animal feed;	Agway Inc.	Olean, N. Y.	54.5 (120)	3,350 (7,380)-1974
mediate;	; chemical inter- stabilizer in es; medicine;	Air Products & Chems., Inc.	Pensacola, Fla.	22.7 (50)	
adhesive	s; separation of cons (as urea	Allied Chem. Corp Specialty Chems. Div	South Point, Ohio	63.6 (140)	
	; sulfamic luction; flame-		Geismar, La. Omaha, Neb.	204.3 (450) 127.1 (280)	
profing agents; vis- cosity modifier for starch or casein-based paper coatings; re- ported helpful in treat-	agents; vis- odifier for	American Cyanamid Co Agricultural Div.	New Orleans, La.	131.7 (290)	
	Borden Inc Borden Chem. Div Petrochems.	Geismar, La.	177.1 (390)		
ing sick.	le-cell anemia	CF Indust., Inc Chattanooga Nitrogen Complex - Donaldsonville Nitrogen Complex -	Tyner, Tenn. Donaldsonville, La.	36.3 (80) 331.4 (730)	
		Fremont Nitrogen Complex N. C. Nitrogen Complex	Fremont, Neb. Tunis, N. C.	18.2 (40) 154.4 (340)	
		Coastal States Gas Corp Colorado Inter- state Corp., subsid Wycon Chem. Co., subsid.	Cheyen ne, Wy o.	45.4 (100)	
		Columbia Nitrogen Corp.	Augusta, Ga.	27.2 (60)	
		Cooperative Farm Chems. Association	Lawrence, Kans.	181.6 (400)	
		Gardinier Big River, Inc.	Helena, Ark.	59 (130)	
		Gen. Amer. 011 of Tex Premier Petrochem. Co., subsid.	Pasadena, Tex.	95.3 (210)	
		Goodpasture, Inc.	Dimmitt, Tex.	22.7 (50)	
		W. R. Grace & Co Agricultural Chems. Group	Memphis, Tenn.	122.6 (270)	
		Hercules Inc Synthe- tics Dept.	Hercules, Calif. Louisiana, Mo.	36.3 (80) 86.3 (190)	

<u>Chemical</u>	<u>Usage 1</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Urea (cont'd)	(See previoùs page)	Kaiser Aluminum & Chem. Corp Kaiser Agri- cultural Chems. Div.	Savannah, Ga.	72.6 (160)	(See previous page)
		Lone Star Gas Co Nipak, Inc., subsid.	Kerens, Tex. Pryor, Okla.	77.2 (170) 122.6 (270)	
		Miss. Chem. Corp.	Yazoo City, Miss.	168 (370)	
		Mobil Oil Corp Mobil Chem. Co., div Petrochems. Div.	Beaumont, Tex.	45.4 (100)	
		N-Ren Corp Cherokee Nitrogen Div High Plains Div.	Pryor, Okla. Plainview, Tex.	18.2 (40) 54.5 (120)	
		Olin Corp Agricul- tural Chems. Div.	Lake Charles, La.	145.3 (320)	
		Phillips Pacific Chem. Co.	Kennewick, Wash.	40.9 (90)	
		Phillips Petroleum Co Fertilizer Div.	Beatrice, Neb.	50 (110)	
		Reichhold Chems., Inc.	St. Helens, Ore.	50 (110)	
		St. Paul Ammonia Pro- ducts, Inc.	East Dubuque, Ill.	72.6 (160)	
		J. R. Simplot Co Minerals & Chem. Div.	Pocatello, Idaho	-	
		Skelly Oil Co Hawk- eye Chem. Co., subsid.	Clinton, Iowa	54.5 (120)	
		The Standard Oil Co. (Ohio) - Vistron Corp., subsid Chems. Dept.	Lima, Ohio	217.9 (480)	
		Tenn. Valley Authority	Muscle Shoals, Ala.	63.6 (140)	
		Terra Chems. Internat'l, Inc.	Port Neal, Iowa	154.4 (340)	
		Triad Chem.	Donaldsonville, La.	449.5 (970)	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Urea (con'd)	(See previous page)	Tyler Corp Atlas Powder Co., subsid.	Joplin, Mo.	59 (130)	(See previous page)
		Union Oil Co, of Calif. Collier Carbon & Chem. Corp., subsid.	Brea, Calif. Kenai, Alas.	50 (110) 308.7 (680)	
		U.S. Steel Corp USS Agri-Chems, div.	Cherokee, Ala.	22.7 (50)	
		Valley Nitrogen Pro- ducers, Inc.	El Centro, Calif. Helm, Calif.	140.7 (310) 31.8 (70)	
		The Williams Companies - Agrico Chem. Co., subsid.	Blytheville, Ark. Donaldsonville, La.	299.6 (660) 299.6 (660)	
				Total = 5,057.6 (11,140))
Vinyl acetate	Polyvinyl acetate, polyvinyl alcohol, poly- vinyl butyral, & poly- vinyl chloride-acetate resins (q.v.); these are used particularly in latex paints; paper coating; adhesives; textile finishing; safety glass inter- layers	Borden Inc Borden Chem. Div Petrochems.	Geismar, La.	68.1 (150)	635.6 (1,400) -1974
		Celanese Corp Cela- nese Chem. Co., div.	Bay City, Tex. Clear Lake, Tex. Pampa, Tex.	136.2 (300) 158.9 (350) 29.5 (65)	
		E. I. du Pont de Ne- mours & Co., Inc Plastics Dept.	La Porte, Tex.	158.9 (350)	
		National Distillers & Chem. Corp Chems. Div U.S. Indust. Chems. Co., div.	Deer Park, Tex.	170.2 (375)	
		National Starch & Chem. Corp.	Long Mott, Tex.	31.8 (70)	
		Reichhold Chems., Inc Reichhold Chem. Del Caribe, Inc., subsid.	Rio Piedras, P. R.	6.8 (15)	
		Union Carbide Corp Chems. & Plastics Div.	Texas City, Tex.	120.3 (265)	
				Total = 880.8 (1,940)	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM lb)	Total ^{4,5} production MM kg (MM lb) for year of estimate
Vinyl chloride	Polyvinyl chloride (q.v.) & copolymers; organic	Allied Chem. Corp Indust. Chems. Div.	Baton Rouge, La.	136.2 (300)	2,542 (5,600) -1974
	synthesis; adhesives for plastics	Borden Inc Borden Chem. Div Petrochems.	Geismar, La.	-	
		Continental Oil Co Conoco Chems.	Westlake, La.	295.1 (650)	
		Dow Chem. U.S.A.	Freeport, Tex. Oyster Creek, Tex. Plaquemine, La.	90.8 (200) 317.8 (700) 177.1 (390)	
		Ethyl Corp.	Baton Rouge, La. Pasadena, Tex.	136.2 (300) 68.1 (150)	
		The B. F. Goodrich Co B. F. Goodrich Chem., Co., subsid.	Calvert City, Ky.	454 (1,000)	
		Monochem, Inc.	Geismar, La.	136.2 (300)	
		PPG Indust., Inc Chem. Div Indust.	Lake Charles, La.	181.6 (400)	
		Chem, Div PPG Indust. (Caribe)	Guayanilla, P. R.	227 (500)	
		Shell Chem, Co Base Chems,	Deer Park, Tex. Norco, La.	381.4 (840) 317.8 (700)	
		Stauffer Chem, Co Plastics Div Poly- mers West	Carson, Calif.	79.5 (175)	
		Tenneco Inc Tenneco Chems., Inc Organics & Polymers Div.	Houston, Tex.	102.1 (225)	
		Union Carbide Corp	Texas City, Tex.	68.1 (150)	
		Chems. & Plastics Div.		Total = 3,169 (6,980)	

Chemical	<u>Usage¹</u>	Manufacturer(s) ^{2,3}	$Location(s)^{2,3}$	1975 capacity² MM kg (MM 1b)	Total ^{4,5,5} production MM kg (NM lb) <u>for year of estimate</u>
Vinyli- dene	Copolymerized with vinyl chloride or acryloni-	Dow Chem. U.S.A.	Freeport, Tex. Plaquemine, La.	-	77.2 (170) -1974
chloride	trile to form various kinds of saran; other copolymers are also made; adhesives; component of synthetic fibers	PPG Indust., Inc Chem. Div Indust. Chem. Div.	Lake Charles, La.	-	
Vinyl	Solvent; intermediate	Dow Chem.' U.S.A.	Midland, Mich.	-	-
toluene		Foster Grant Co., Inc.	Baton Rouge, La.	-	
m≁xylene	Solvent; intermediate for dyes & organic synthesis, especially isophthalic acid; insecticides; aviation fuel	Atlantic Richfield Co ARCO Chem. Co., div.	Channelview, Tex.	15.9 (35)	35.4 (78) -1970
o-xylene	Mfg, of phthalic an- hydride; vitamin & pharmaceutical synthesis;	American Petrofina, Inc Cosden Oil & Chem. Co., subsid.	Big Spring, Tex.	8.2 (18)	374.4 (824.8) -1970
	dyes; insecticides; motor fuels	Atlantic Richfield Co ARCO Chem. Co., div.	Houston, Tex.	95.3 (210)	
		Cities Service Co., Inc North American Petroleum Group	Lake Charles, La.	54.5 (120)	
		Coastal States Gas Corp Coastal States Marketing, Inc., subsid.	Corpus Christi,	18.2 (40)	
		Commonwealth 011 Refin- ing Co., Inc Common- wealth Petrochems., Inc., subsid.	Penuelas, P. R.	63.6 (140)	
		Crown Central Petroleum Co rp.	Pasadena, Tex.	34 (75)	
		Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Baytown, Tex.	222.5 (490)	
		Kerr-McGee Corp South- western Refining Co., Inc., subsid.	Corpus Christi, Tx.	45.4 (100)	

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity² MM kg (MM 1b)	Total ^{4,5} production MM kg (MM lb) for year of estimate
o-xylene (cont'd)	(See previous page)	Monsanto Co Monsanto Polymers & Petrochems. Co.	Chocolate Bayou, Tex.	13.6 (30)	(See previous page)
		Phillips Petroleum Co Phillips Puerto Rico Core, Inc., subsid.	Gu aya ma, P. R.	59 (130)	
		Shell Chem. Co Base Chems.	Deer Park, Tex.	90.8 (200)	
		Standard Oil Co. of Calif Chevron Chem. Co., subsid Oronite Additives & Indust. Chems. Div Indust. Chems.	Richmond, Calif.	67.2 (148)	
		Sun Oil Co Sun Oil Co. of Penn., subsid Suntide Refining Co., subsid.	Corpus Christi, Tex.	72.6 (160)	
		Tenneco Inc Tenneco 011 Co., div.	Chalmette, La.	70.4 (155)	
				Total = 915.3 (2,016)	
p-xylene	Synthesis of tere- phthalic acid for polyester resins & fibers ("Dacron," "Mylar," "Terylene"); vitamin & pharmaceu- tical syntheses; insecticides	Atlantic Richfield Co ARCO Chem. Co., div.	Houston, Tex.	181.6 (400)	1,216.7 (2,680) -1974
		The Charter Co Charter Oil Co., subsid., Charter Internat'l Co., subsid.	Houston, Tex.	6.8 (15)	
		Cities Service Co., Inc North American Petroleum Group	Lake Charles, La.	15.9 (35)	
		Exxon Corp Exxon Chem. Co., div Exxon Chem. Co. U.S.A.	Baytown, Tex.	181.6 (400)	
		Hercor Chem. Corp.	Penuelas, P. R.	238.3 (525)	
		Phillips Petroleum Co Phillips Puerto Rico Core Inc., subsid.	Guayama, P. R.	34 (75)	

Chemical	Usage ¹	Manufacturer(s) ^{2,3}	Location(s) ^{2,3}	1975 capacity ² MM kg (MM lb)	Total ^{4,5} production MM kg(MM lb) <u>for year of estimate</u>
p-xylene (cont'd)	(See previous page)	Shell Chem. Co Base Chems.	Deer Park, Tex.	45.4 (100)	(See previous page)
		Standard Oil Co. of Callf Chevron Chem. Co., subsid Oronite Additives & Indust. Chems. Div Indust. Chems.	El Segundo, Calif. Pascagoula, Miss. Richmond, Calif.	140.7 (310) 50 (110)	
		Standard Oil Co. (Ind.) - Amoco Chems. Corp., subsid.	Decautur, Ala. Texas City, Tex.	124.8 (275) 124.8 (275)	
		Sun Oil Co Sun Oil Co. of Penn., subsid. Suntide Refining Co., subsid.	Corpus Christi,	136.2 (300)	
		Tenneco Inc Tenneco Oil Co., div.	Chalmette, La.	45.4 (100)	
		-		Total = 1,325.7 (2,920)	
Xylenol (mixed 2,	Disinfectants; solvents, pharmaceuticals, insect- icides & fungicides; plasticizers; rubber chemicals; additives to	Koppers Co., Inc Organic Materials Div.	Follansbee, W. Va.	-	-
4~; 2,5~; 3,4-;		Productol Chem. Co.	Santa Fe Springs, Calif.	-	
3,5-)	<pre>lubricants & gasoline; manufacture of poly- phenylene oxide (2,6-isomer only); wetting agents; dyestuffs</pre>	Stimson Lumber Co	Anacortes, Wash.	-	
Xylidine (mixed 2,3-; 2,4-; 2,5-; 2,6-)	Dye intermediates; organic syntheses; pharmaceuticals	E. I. du Pont de Ne- mours & Co., Inc. ~ Organic Chems. Dept Dyes & Chems. Div.	Deepwater, N. J.	-	-

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APPENDIX B

RAW MATERIALS

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Table B-1. RAW MATERIALS FOR THE INDUSTRIAL ORGANIC CHEMICALS INDUSTRY

*Acetaldehyde *Acetaldol *Acetanilide *Acetic acid *Acetic anhydride *Acetone *Acetone cyanohydrin *Acetonitrile Acetyl chloride *Acetylene *Acrolein *Acrylic acid *Acrylonitrile Air Alkyl amines Alkyl benzenes aroup names Alkyl chlorides *Allyl alcohols *Allyl chlorides Alumina gel Aluminum chloride Ammonia Ammonium salts (e.g., carbonate) *Amyl alcohols *Amyl chlorides *Aniline *Aniline hydrochloride Aniline sulfate Antimony (III) fluoride Aromatics, C_8 -groups

*Benzaldehyde *Benzene *m-Benzene disulfonic acid *Carbon disulfide *p-Benzene disulfonic acid *Carbon tetrachloride *Benzene sulfonic acid *Benzil *Benzoic acid *Benzoin *p-Benzoquinone *Benzotrichloride *Benzoyl chloride *Benzyl chloride Bromine *Bromobenzene *1,3-Butadiene *n-Butane 2-Butanone *1-Butene *2-Butene *n-Butenes *n-Butyraldehyde *n-Butyl alcohol *sec-Butyl alcohol *tert-Butyl alcohol *tert-Butyl toluene *Butyric acid

Calcium carbonate Calcium hydroxide Calcium oxide Carbon

Carbon dioxide Carbon monoxide Catalytic gas oils α -Cellulose Charcoal Chlorine (dry) *Chloracetic acid *Chlorobenzene *Chloroform *Chlorotoluene Coal tars Cobalt toluate *Crotonaldehyde *Cumene *Cumene hydroperoxide *Cyanogen chloride *Cyclohexane *Cyclohexanol *Cyclohexanone

*Diacetone alcohol Diallyl ether - group name *o-Dichlorobenzene *m-Dichlorobenzene *Dichlorohydrin *Diethylene glycol dibutyl ether Diethylene glycol monoethers - group name *Diethyl ether

Table B-1 (Continued). RAW MATERIALS FOR THE INDUSTRIAL ORGANIC CHEMICALS INDUSTRY

Diethyl oxalate *1,1-Difluoroethane *Diisobutylene Dimethyl acetal *Dimethyl sulfate *Dimethyl sulfide *Dinitrobenzenes *Dinitrobenzoic acid *Dinitrotoluene *Diphenyl oxide *Dodecene Drip oils

*Epichlorohydrin *Ethane *Ether *Ethyl acetate *Ethvl alcohol *Ethyl benzene *Ethyl chloroacetate *Ethyl chloride Ethyl formate Ethyl sulfate Ethyl toluene Ethylene *Ethylene chlorohydrin *Ethylene diamine *Ethylene dibromide *Ethylene dichloride *Ethylene glycol *Ethylene oxide

Flue gas *Formaldehyde *Formic acid *Fumaric acid Furfural

*Glyceraldehyde *Glycerol

*Heptene Hexyl alcohol Hydrochloric acid Hydrofluoric acid Hydrogen Hydrogen bromide Hydrogen chloride *Hydrogen cyanide Hydrogen fluoride Hydrogen peroxide *Hydroquinone Hypochlorous acid

Iron sulfate *Isoamylenes Isobutane Isobutene *Isobutyl alcohol Isobutylene *Isobutyraldehyde Isopentane *Isopropyl alcohol *Isopropyl chloride

*Ketene

Lead Lead amalgam Light cycle oils

*Maleic acid *Maleic anhvdride Manganese dioxide *Mesityl oxide *Methallyl chloride Methane *Methyl acetate *Methyl alcohol *Methyl chloride *Methyl cyclohexane *Methyl ethyl ketone *Methyl formate Methyl iodide *Methyl isobutyl ketone Methyl propene *Methylene chloride Monoethylene glycol monoether group name *Naphthalene *1-Naphthalene sulfonic acid *2-Naphthalene sulfonic acid Natural gas Nitric acid

Table B-1 (Continued). RAW MATERIALS FOR THE INDUSTRIAL ORGANIC CHEMICALS INDUSTRY

*Nitrobenzene m-Nitrochlorobenzene Nitrogen Nitrogen dioxide (dinitrogen tetraoxide) *o-Nitroanisole *p-Nitroanisole *o-Nitrophenol *p-Nitrophenol Nitrosylsulfuric acid *Nitrotoluene *Nonene

Octyl alcohol "Olefins" Oxalic acid (dihydrate) Oxygen

*Pentane Peracetic acid *Perchloroethylene *Phenol *Phosgene Phosphorous tribromide *Phthalic anhydride *Phthalic anhydride *Phthalimide Polychloroaromatics Potassium t-butoxide Potassium cyanide Potassium hydrosulfide Potassium hydroxide

Potassium sulfide *Propane, liquid *n-Propyl alcohol *n-Propyl chloride Propylene *Propylene chlorohydrin Propylene glycol *Propylene oxide *Pyridine Refinery gas caustic extract Reformer bottoms Silica gel Sodium *Sodium acetate Sodium bicarbonate Sodium bisulfite Sodium carbonate Sodium carbonate emulsifier *Sodium chloroacetate Sodium chloride Sodium cyanide Sodium dichromate

Sodium ethoxide

Sodium hydrosulfide

Sodium hydrosulfite

Sodium hydroxide

Sodium perborate

*Sodium formate

*Sodium phenate Sodium "salt" Sodium stearate Sodium sulfide Sodium sulfite Sulfur, organic derivatives Sulfur dioxide Sulfur dioxide, liquid Sulfur trioxide Sulfuric acid 01eum Sulfuric acid, monohydrate Synthesis gas *1,1,2,2-Tetrachloroethane Tetrahydrofuran *Trichloroaniline *1,1,2-Trichloroethane *Trichloroethylene 2,4,6-Trichlorophenol Toluene *Toluene sulfonyl chloride *Toluidine Tolunitrile *Urea Water

Water, demineralized Water, distilled Water, steam

Table B-1 (Continued). RAW MATERIALS FOR THE INDUSTRIAL ORGANIC CHEMICALS INDUSTRY

*m-Xylene
*o-Xylene
*p-Xylene
Zeolite, synthetic
Zinc

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* Indicates chemical is also a product of this industry.

APPENDIX C

CATALYSTS

Table C-1. CATALYSTS USED IN THE PRODUCTION OF INDUSTRIAL ORGANIC CHEMICALS

Acetic acid Alkali metals Alumina Alumina, modified anhydrous Gamma Alumina, gel Alumina-chromia Aluminum turnings Aluminum alkoxides Aluminum chloride Amine bases Ammonium chloride Ammonium metavanadate Ammonium persulfate-ammonium bromide Aniline hydrochloride Antimony, partially fluorinated Antimony (III) chloride Antimony (V) chloride Antimony (V) fluoride

Barium chloride on carbon Barium hydroxide Bauxite Bismuth-molybdenum Boric acid Boron trifluoride Brass Bromine

Calcium carbide Calcium chloride Calcium nickel phosphate stabilized with 2% Chromium oxide Calcium oxide Carbon

Carbon, activated Carboxyl salts of divalent transition metals, e.g., zinc isovalerate Chromic acid Cobalt acetate Cobalt carbonyl compounds Cobalt carbonyl compounds, phosphorus promoted Cobalt compounds Cobalt-manganese activated by bromine Cobalt-manganese activated by acetaldehyde Cobalt-manganese activated by methyl ethyl ketone Cobalt naphthenate Cobalt oxides Cobalt "salts" Cobalt "salts" activated by bromine Cobalt stearate Copper Copper, solid, promoted by cobalt or chromium on asbestos Copper-silica Copper acetate Copper chromite Cuprammonium nitrate Cupric chloride Cupric chloride impregnated on a fluid or fixed-bed support Cupric oxide Cupric sulfate Cuprous oxide Diatomaceous earth Dichlorohydrin Disulfides

Dowex 50 ion exchange resin

Table C-1. (Continued). CATALYSTS USED IN THE PRODUCTION OF INDUSTRIAL ORGANIC CHEMICALS

Ethyl acetate

Ferric acetate Ferric bromide Ferric chloride Ferric oxide-chromium oxide-potassium oxide Friedel-Crafts reagents Fuller's earth

Gamma radiation from Cobalt-60

Heavy metal salts Hydrochloric acid

Ion exchange resins Iron turnings Iron-molybdenum oxide

Lewis acid catalyst Light Lithium arsenate Lithium phosphate Lithium "salt"

Magnesium Magnesium oxide Manganese acetate Manganese butyrate Manganese oxide Mercaptans Metaboric acid Molybdenum chloride Molybdenum oxides Molybdenum sulfide Nickel Nickel, activated Nickel, activated, on asbestos carrier Nickel-chromium catalyst, reduced Nickel acetate Nickel oxide in refractory cement Nickel chromite Nickel chromate Nickel, Raney Nickel sulfide

Oleic acid

Palladium Palladium catalyst, supported Palladium chloride promoted for metal oxidation by cooper chloride Phosphoric acid, solid Phosphoric acid, on kieselguhr Phosphorus, red Phosphorous trichloride Phosphorous pentachloride Platinum Platinum-rhodium mesh Platinum oxide Potassium carbonate Potassium cyanide Potassium hydroxide Potassium sulfate Rhodium-carbonyl complex

Silica-alumina Silica gel catalyst

Table C-1. (Continued). CATALYSTS USED IN THE PRODUCTION OF INDUSTRIAL ORGANIC CHEMICALS

Silica-zerconia Sodamine Sodium Sodium hydroxide Silver Silver, crystalline Silver oxide Sulfuric acid

Tin

p-Toluene sulfonic acid Triethyl phosphate Tungsten Tungsten sulfide Tungstic acid

UV light from mercury vapor lamps Uranium oxide

Vanadium Vanadium pentoxide

Water

Zinc chloride Zinc compounds Zmc oxide promoted with alumina and chromates Zmc oxide on pumice Zirconium chloride APPENDIX D

INDUSTRIAL ORGANIC CHEMICALS

ACETAL ACETALDEHYDE ACETALDOL ACETAMIDE ACETANILIDE ACETIC ACID ACETIC ANHYDRIDE ACETONE ACETONE CYANOHYDRIN ACETONITRILE ACETOPHENDNE ACETYL CHLORIDE ACETYLENE ACROLEIN ACRYLAMIDE ACRYLIC ACID AND ACRYLATE ESTERS ACRYLONITRILE ADIPIC ACID ADIPONITRILE ALKYLNAPHTHALENES (METHYLD ALLYL ALCOHOL ALLYL CHLORIDE AMINOBENZOIC ACID (M,P) AMINOETHYLETHANOLAMINE P-AMINOPHENOL AMYL ACETATES AMYL ALCOHOLS (8 ISOMERS) AMYLAMINE AMYL CHLORIDE AMYL MERCAPTANS AMYL PHENOL ANILINE ANILINE HYDROCHLORIDE ANISIDINE ANISOLE ANTHRANILIC ACID ANTHRAQUINONE BENZALDEHYDE

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BENZAMIDE BENZENE BENZENEDISULFONIC ACID BENZENESULFONIC ACID BENZIL BENZILIC ACID BENZOIC ACID BENZOIN BENZONITRILE BENZOPHENONE BENZOTRICHLORIDE BENZOYL CHLORIDE BENZYL ALCOHOL BENZYLAMINE BENZYL BENZOATE BENZYL CHLORIDE BENZYL DICHLORIDE BIPHENYL BISPHENOL A BROMOBENZENE BROMONAPHTHALENE BUTADIENE 1-BUTENE N-BUTYLACETATE N-BUTYLACRYLATE N-BUTYL ALCOHOL SEC=BUTYL ALCOHOL TERT-BUTYL ALCOHOL N-BUTYLAMINE SEC-BUTYLAMINE TERT-BUTYLAMINE P-TERT-BUTYLBENZOIC ACID 1,3 BUTYLENE GLYCOL TERT-BUTYLPHENOL N-BUTYRALDEHYDE N-BUTYRIC ACID N-BUTYRIC ANHYDRIDE N=BUTYRONITRILE

CAPROLACTAM CARBON DISULFIDE CARBON TETRABROMIDE CARBON TETRACHLORIDE CELLULOSE ACETATE CHLOROACETIC ACID M-CHLOROANILINE **O=CHLORDANILINE P=CHLORDANILINE** CHLOROBENZALDEHYDE CHLOROBENZENE CHLOROBENZOIC ACID CHLOROBENZOTRICHLORIDE (0,P) CHLOROBENZOYL CHLORIDE CHLORODIFLUOROETHANE CHLORODIFLUOROMETHANE CHLOROFORM CHLORONAPHTHALENE O-CHLORONITROBENZENE P-CHLORONITROBENZENE CHLOROPHENOLS CHLOROSULFONIC ACID M+CHLOROTOLUENE O-CHLOROTOLUENE **P-CHLOROTOLUENE** CHLOROTRIFLUOROMETHANE CROTONALDEHYDE CROTONIC ACID CUMENE CUMENE HYDROPEROXIDE CYANDACETIC ACID CYANOGEN CHLORIDE CYANURIC ACID CYANURIC CHLORIDE CYCLOHEXANE CYCLOHEXANOL CYCLOHEXANONE CYCLOHEXENE

INDUSTRIAL ORGANIC CHEMICALS

NAME

CYCLOHEXYLAMINE CYCLOOCTADIENE DECANOL DIACETONE ALCOHOL DIAMINOBENZOIC ACID DICHLOROANILINE M-DICHLOROBENZENE 0+DICHLOROBENZENE **P=DICHLOROBENZENE** DICHLORODIFLUOROMETHANE 1.2=DICHLOROETHANE DICHLOROETHYL ETHER DICHLOROHYDRIN DICHLOROPROPENE DICYCLOHEXYLAMINE DIETHYLAMINE DIETHYLENE GLYCOL DIETHYLENE GLYCOL DIETHYL: ETHER DIETHYLENE GLYCOL DIMETHYL ETHER DIETHYLENE GLYCOL MONOBUTYL ETHER DIETHYLENE GLYCOL MONOBUTYL ETHER ACETATE DIETHYLENE GLYCOL MONDETHYL ETHER DIETHYLENE GLYCOL MONOETHYL ETHER ACETATE DIETHYLENE GLYCOL MONOMETHYL ETHER DIETHYL SULFATE DIFLUORDETHANE DIISOBUTYLENE DIKETENE DIMETHYLAMINE N, N=DIMETHYLANILINE DIMETHYL ETHER N,N=DIMETHYLFORMAMIDE DIMETHYL HYDRAZINE DIMETHYL SULFATE DIMETHYL SULFIDE DIMETHYL SULFOXIDE DIMETHYL TEREPHTHALATE 3,5=DINITROBENZOIC ACID

NAME

2,4=DINITROPHENOL DINITROTOLUENE DIOXANE DIDXOLANE DIPHENYLAMINE DIPHENYL OXIDE DIPHENYLTHIOUREA DIPROPYLENE GLYCOL DODECENE DODECYLANILINE DODECYLPHENOL EPICHLOROHYDRIN ETHANOL EHTANDLAMINE ETHYL ACETATE ETHYL ACETOACETATE ETHYL ACRYLATE ETHYLAMINE ETHYLBENZENE ETHYL BROMIDE ETHYL CELLULOSE ETHYL CHLORIDE ETHYL CHLOROACETATE ETHYLCYANOACETATE ETHYLENE CARBONATE ETHYLENE CHLOROHYDRIN ETHYLENE DIAMINE ETHYLENE DIBROMIDE ETHYLENE GLYCOL ETHYLENE GLYCOL DIACETATE ETHYLENE GLYCOL DIMETHYL: ETHER ETHYLENE GLYCOL MONOBUTYL ETHER ETHYLENE GLYCOL MONOBUTYLE ETHER ACETATE ETHYLENE GLYCOL MONOETHYL: ETHER ETHYLENE GLYCOL MONDETHYL ETHER ACETATE ETHYLENE GLYCOL MONOMETHYL ETHER ETHYLENE GLYCOL MONOMETHYL ETHER ACETATE ETHYLENE GLYCOL MONOPHENYL ETHER

Table D-1. (Continued). INDUSTRIAL ORGANIC CHEMICALS

NAME

ETHYLENE GLYCOL MONOPROPYL ETHER ETHYLENE OXIDE ETHYL ETHER 2+ETHYL HEXANOL ETHYL ORTHOFORMATE ETHYL OXALATE ETHYL SODIUM OXALACETATE FORMALDEHYDE FORMAMIDE FORMIC ACID FUMARIC ACID GLYCEROL (NATURAL&SYNTHETIC) GLYCEROL DICHLOROHYDRIN GLYCEROL TRI (POLYOXYPROPYLENE) ETHER GLYCINE GLYDXAL HEPTENE HEXACHLOROBENZENE HEXACHLOROETHANE HEXADECYL ALCOHOL HEXAMETHYLENEDIAMINE HEXAMETHYLENE GLYCOL HEXAMETHYLENE TETRAMINE HYDROGEN CYANIDE HYDROQUINONE P-HYDROXYBENZOIC ACID ISOAMYLENE ISOBUTANOL ISOBUTYL ACETATE **ISOBUTYLENE ISOBUTYLRALDEHYDE** ISOBUTYRIC ACID **ISODECANOL** ISOOCTYL ALCOHOL ISDPENTANE **ISOPHORONE** ISOPHTHALIC ACID ISOPRENE

ISOPROPANOL ISOPROPYL ACETATE ISOPROPYLAMINE (MONO) ISOPROPYL CHLORIDE **ISOPROPYLPHENOL** KETENE MALEIC ACID MALEIC ANHYDRIDE MALIC ACID MESITYL OXIDE METANILIC ACID METHACRYLIC ACID METHALLYL CHLORIDE NETHANOL METHYL ACETATE METHYL ACETOACETATE METHYLAMINE NEMETHYLANILINE METHYL BUTYNOL NETHYL CHLORIDE METHYLCYCLOHEXANE METHYLCYCLOHEXANONE METHYLENE CHLORIDE METHYLENE DIANILINE NETHYL ETHYL KETONE METHYL FORMATE METHYLISOBUTYL CARBINOL METHYLISOBUTYL KETONE METHYL METHACRYLATE METHYLPENTYNOL A.METHYLSTYRENE MORPHOLINE A-NAPHTHALENE SULFONIC ACID B-NAPHTHALENE SULFONIC ACID ANNAPHTHOL 8-NAPHTHOL NEOPENTANDIC ACID **O=NITROANILINE**

+ + z

NAME

P+NITROANILINE **GENITROANISOLE** PENITROANISOLE NITROBENZENE NITROBENZOIC ACID (M,O,P) NITROETHANE NITROMETHANE NITROPHENOL NITROPROPANE NITROTOLUENE NONENE NONYLPHENOL OCTYLPHENOL PARALDEHYDE PENTAERYTHRITOL NOPENTANE **1**-PENTENE PERCHLORDETHYLENE PERCHLOROMETHYL MERCAPTAN **O**=PHENETIDINE **P**-**PHENETIDINE** PHENOL PHENOLSULFONIC ACIDS PHENYL ANTHRANILIC ACID PHENYLENEDIAMINE PHOSGENE PHTHALIC ANHYDRIDE PHTHALIMIDE 8-PICOLINE PIPERAZINE POLYBUTENES POLYETHYLENE GLYCOL POLYPROPYLENE GLYCOL PROPIONALDEHYDE PROPIONIC ACID N=PROPYL ALCOHOL PROPYLAMINE PROPYL CHLORIDE

Table D-1. (Continued). INDUSTRIAL ORGANIC CHEMICALS

NAME

PROPYLENE PROPYLENE CHLOROHYDRIN PROPYLENE DICHLORIDE PROPYLENE GLYCOL PROPYLENE OXIDE PYRIDINE (NATURAL & SYNTHETIC) QUINONE RESORCINOL RESORCYLIC ACID SALICYLIC ACID SDDIUM ACETATE SODIUM BENZOATE SODIUM CARBOXYMETHYL CELLULOSE SODIUM CHLOROACETATE SODIUM FORMATE SODIUM PHENATE SORBIC ACID STYRENE SUCCINIC ACID SUCCINONITRILE SULFANILIC ACID SULFOLANE TANNIC ACID TEREPHTHALIC ACID TETRACHLOROETHANE TETRACHLOROPHTHALIC ANHYDRIDE TETRAETHYL LEAD TETRAHYDRONAPHTHALENE TETRAHYDROPHTHALIC ANHYDRIDE TETRAMETHYLENEDIAMINE TETRAMETHYLETHYLENEDIAMINE TOLUENE TOLUENE=2,4=DIAMINE 2,4-TOLUENE DIISOCYANATE TOLUENE DIISOCYANATES(MIXTURE) TOLUENESULFONAMIDE TOLUENESULFONIC ACIDS TOLUENESULFONYL CHLORIDE:

Table D-1. (Continued). INDUSTRIAL ORGANIC CHEMICALS

NAME

TOLUIDINES TRICHLOROBENZENE 1,1,1=TRICHLOROETHANE 1,1,2-TRICHLORDETHANE TRICHLOROETHYLENE TRICHLOROFLUOROMETHANE 1,2,3=TRICHLOROPROPANE 1,1,2=TRICHLORO=1,2,2=TRIFLURDETHANE TRIETHYLAMINE TRIETHYLENE GLYCOL TRIETHYLENE GLYCOL DIMETHYL ETHER TRIISOBUTYLENE TRIMETHYLAMINE UREA VINYL ACETATE VINYL CHLORIDE VINYLIDENE CHLORIDE VINYL TOLUENE XYLENES, MIXED 0=XYLENE PEXYLENE XYLENOL XYLIDINE

APPENDIX E

INDUSTRIAL ORGANIC CHEMICAL PRODUCERS

NAME ASBOTT LABORATORIES ACETO CHEMICAL CO, INC. ACME=HARDESTY CO, INC. ADD PROCESSING CORP. AGWAY, INC AIRCO CHEMICALS AND PLASTICS AIR PRODUCTS AND CHEMICALS INC. AIR PRODUCTS AND CHEMICALS INC. AIR PRODUCTS AND CHEMICALS INC. AIR PRODUCTS AND CHEMICALS INC. AIR PRODUCTS AND CHEMICALS INC. ALCO STANDARD CORP. ALLIED CHEMICAL CO. ALLIED CHEMICAL CORP. ALLIED CHEMICAL CORP. AMERICAN NILINE AND EXTRACT CO. AMERICAN CYANAMID CO. AMERICAN CYANAMID CO. AMERICAN CYANAMID CO. AMERICAN CYANAMID CO. AMERICAN HOECHST CORP. AMERICAN HOECHST CORP. AMERICAN HOECHST CORP. AMERICAN PETROFINA INC.	CITY	STATE
ASBOTT LABORATORIES	NORTH CHICAGO	IL
ACETO CHEMICAL CO. INC.	CARLSTADT	NJ
ACME=HARDESTY CO. INC.	JENKINTOWN	PÅ
ADD PROCESSING CORP.	ABBEVILLE	LA
AGWAY, INC	OLEAN	NY
AIRCO CHEMICALS AND PLASTICS	LOUISVILLE	KY
AIR PRODUCTS AND CHEMICALS INC.	CALVERT CITY	KY
AIR PRODUCTS AND CHEMICALS INC.	HOMETOWN	PÅ
ATR PRODUCTS AND CHEMICALS INC.	PASADENA	TX
AIR PRODUCTS AND CHEMICALS INC.	PENSACOLA	FL
AKZONA INC.		TN
ALBA MANUFACTURING CO.	AUDOPA	Ti.
ALCO STANDARD CORP.	FDDYSTONE	PA
ALORICH CHEMICAL CO.	MTEWAHKEE	
ALLTEN CHENTCAL CORP.	BATON ROUGE	
ALLTED CHEMICAL CORP.	RIFEALO	
ALLTED CHEMICAL CORP.	DANUTLIE	71 Ti
ALLIED CHEMICAL CORFS	EL TARETH	1L N.T
ALLIED CHEMICAL CORF.	EL RECHNON	С. А.
ALLER CHEMICAL CORFS	FRANKFORD	
ALITED CHEMICAL CONFI	CETSMAD	
ALLIED CHEMICAL CODO	CIDHAN CEIDHAN	
ALLIED CHEMICAL CORC:	NADČUS HOOK	
CLAIED CHEMICAL CORF.	MARGUS HUUR	
ALLIED CHEMICAL CORF.		
ALLIED CHEMICAL CORF:		
AFFICA CUENTON CODA	CRANGE Bouth Botht	1 A
ALLIED CHEMICAL CURPS	SUUIM FUINI	
ALLIEU UNENIUAL CURFA	STRALUSE Shiti Adël Shita	
AMERICAN ANILINE AND EXTRACT CU,	THILAUELPHIA	PA
AMERICAN COLOR AND CHEMICAL CURPS	LUCK HAVEN	PA
AMERICAN CTANAMID CU.	BUUNDBRUDK	NJ
AMERIÇAN CYANAMID CO.	CHARLUTTE	NG
AMERICAN CYANAMID CO.	LINDEN	NJ
AMERICAN CYANAMID CO.	MARIETTA	DH
AMENICAN CYANAMID CO.	NEW ORLEANS	ĻA
AMERICAN CYANAMID CD.	WILLOW ISLAND	WV
AMERICAN HOECHST CORP.	COVENTRY	RI
AMERICAN PETROFINA INC.	BIG SPRING	TX

NAME AMERICAN POLYMERS INC, AMES LABORATORIES INC, ANSUL CO. ARCO CHEMICAL CO. ARCO CHEMICAL CO. ARCO CHEMICAL CO. ARCO CHEMICAL CO. ARCO CHEMICAL CO. ARCO CHEMICAL CO. ARCO/POLYMERS INC, ARMOUR AND COMPANY ASHLAND CHEMICAL CO. ASHLAND CHEMICAL CO. ASHLAND CHEMICAL CO. ASHLAND CHEMICAL CO. BASF WYANDOTTE CORP. BASF WYANDOTTE CORP. B	CITY	STATE
AMERICAN POLYMERS INC.	PATTERSON	NJ
AMES LABORATORIES INC.	MILFORD	CT
ANSUL CO.	MARINETTE	WI
ARCO CHEMICAL CO.	BEAVER VALLEY	PA
ARCO CHEMICAL CO.	CHANNELVIEW	TX
ARCO CHEMICAL CO.	EAST CHICAGO	IN
ARCO CHEMICAL CO.	HOUSTON	TX
ARCO CHEMICAL CO.	PORT ARTHUR	TX
ARCO CHEMICAL CO.	WILMINGTON	CA
ARCO/POLYMERS INC.	HOUSTON	TX
ARMOUR AND COMPANY	MONTGOMERY	IL
ASHLAND CHEMICAL CO.	ASHLAND	κŸ
ASHLAND CHEMICAL CO.	GREAT MEADOWS	NJ
ASHLAND CHEMICAL CO.	HAMMOND	IN
ASHLAND CHEMICAL CD.	JANESVILLE	WI
ASHLAND CHEMICAL CO.	MAPLETON	IL
BASE WYANDOTTE CORP.	GEISMAR	LĀ
BASE WYANDDITE CORP.	KEARNY	NJ
BASE WYANDOTTE CORP.	WASHINGTON	NJ
BASE WYANDOTTE CORP.	WYANDOTTE	MĪ
BECKMAN INSTRUMENTS, INC.	PALO ALTO	ĊĂ
BEKER INDUSTRIES CORP.	CARLSGAD	NM
BETHLEHEM STEEL CORP.	SPARROWS POINT	MD
BID-RAD LABORATORIES	RICHMOND	CA
BLUE SPRUCE CO.	EDISON	NJ
BOFORS INDUSTRIES INC.	LINDEN	NJ
BORDEN CHEMICAL	BAINBRIDGE	NÝ
BORDEN CHEMICAL	COMPTON	CA
BORDEN CHEMICAL	DEMOPOLIS	AL
BORDEN CHEMICAL	DIBOLL	TX
BORDEN CHEMICAL	FAYETTEVILLE	NC
BORDEN CHEMICAL	FREMONT	CA
BORDEN CHEMICAL	GEISMAR	LA
BORDEN CHEMICAL	ILLIOPOLIS	ĨL
BORDEN CHEMICAL	KENT	WÁ
BORDEN CHEMICAL	LA GRANDE	OR
BORDEN CHEMICAL	LEOMINSTER	MA
BORDEN CHEMICAL	LOUISVILLE	KY

NAME BORDEN CHEMICAL BORDEN CHEMICAL BORGEWARNER CORP. BORGEWARNER CORP. BOUCKMAN LABORATORIES INC. BUCKMAN LABORATORIES INC. BUCKMAN LABORATORIES INC. CALCASIEU CHEMICAL CORP. CALUS CORP. CELANESE CHEMICAL CO. CELANESE CHEMICAL CO. CF INDUSTRIES CF INDUSTRIES CF INDUSTRIES CF INDUSTRIES CF INDUSTRIES CHARTER CHEMICALS CHARTER CHEMICALS CHEMICAL FORMULATORS INC. CHEMICAL FORMULATORS INC. CHEMICAL PRODUCTS CO. CHEMICAL PRODUCTS CO. CHEMICAL PRODUCTS CO. CHEMICAL PRODUCTS CO. CHEMICAL PRODUCTS CO. CHEMICAL COPP CITIES SERVICE CO INC CITIES SERVICE CO INC	CITY	STATE
BORDEN CHEMICAL	MISSOULA	МТ
BORDEN CHEMICAL	SHEBOYGAN	ΗI
BORDEN CHEMICAL	SPRINGFIELD	OR
BORGEWARNER CORP.	MORGANTOWN	WV
BROWN CO.	BERLIN	NH
BUCKMAN LABORATORIES INC.	CADET	MO
BUCKMAN LABORATORIES INC.	MEMPHIS	TN
CALCASTEU CHEMICAL CORP.	LAKE CHARLES	LA
CAPTRE ISOPRENE CORP.	PONCE	PR
CAPIES CORP.	LASALLE	IL
CELANESE CHEMICAL CO.	BAY CITY	TX
CELANESE CHEMICAL CO.	BISHOP	TX
CELANESE CHEMICAL CO.	CLEAR LAKE	TX
CELANESE CHEMICAL CO.	NARROWS	¥ A
CELANESE CHEMICAL CO.	NEWARK	NJ
CELANESE CHEMICAL CO.	PAMPA	TX
CELANESE CHEMICAL CO.	ROCK HTLL	SC
CELANESE CHEMICAL CO.	ROME	GA
CELANDOL DHENICHE CO,	DONAL DSONVILLE	LA
CF INDUSTRIES	FREEMONT	NE
CF INDUSTRIES	TUNTS	NC
CE TADUGINILU	TYNER	TN
CHARTER CHEMICALS	HOUSTON	TX
CHARTEN BRIG AND CHEMICAL CO.	CHATTANODGA	TN
CHATTEM DRUG AND CHEMICAL CO.	LONG BEACH	CA
CHEMETRON CHEMICALS	LAPORTE	TX
CHENTCAL FORMULATORS INC.	NITRO	WV
CHEMICAL & POLLUTION SCIENCES. INC.	DLD BRIDGE	NJ
CHEMICAL PRODUCTS CORP.	CARTERSVILLE	GA
CHEMICAL FRODUCTO BORT	GREENSBORD	NC
CHENDIEA CU Chendiea The	CLINTON	IA
CHEVPON CHEMICAL CO	FL SEGUNDO	ĈĂ
DICUMOND CHEMICAL COG	RICHMOND	ČÂ
CHICAGO SANTIARY PRODUCTS CO.	CHICAGO	ĨĹ
CHILAGO SANTIANI FRODULIO CO:	MCINIOSH	ĂĹ
CIDWADETRI COVL	ST. GARRIFI	
CIDWARETRI PAKL	COPPERHILL	ŤN
PIALED SERVICE CO INC	LARE CHADLES	LA
CTITED DEKATCE CO TMC	LAKE GRANEED	L ~

NAME CLARK CHEMICAL CO. CLORAY NJ CORP. CDASTAL STATES GAS CO. COASTAL STATES GAS CO. COLGATE PALMOLIVE CO. COLGATE PALMOLIVE CO. COLGATE PALMOLIVE CO. COLGATE PALMOLIVE CO. COLGATE PALMOLIVE CO. COLGATE PALMOLIVE CO. COLUMBIA NITROGEN CORP. COMMERCIAL SOLVENTS CORP. COMMERCIAL SOLVENTS CORP. COMMERCIAL SOLVENTS CORP. COMMERCIAL SOLVENTS CORP. COMMERCIAL SOLVENTS CORP. COMMERCIAL SOLVENTS CORP. COMMERCIAL OIL COMPANY CONTINENTAL OIL COMPANY CONTINENTAL OIL COMPANY COOPERATIVE FARM CHEMICAL ASSOC. COPOLYMER RUBBER AND CHEMICAL CORP. COS+MAR INC CROMPTON & KNOWLES CORP. CROMLEY HYDROCARBON CHEMICALS INC. CROWLEY HYDROCARBON CHEMICALS INC. CROWLEY HYDROCARBON CHEMICALS INC. CROWLEY TAR PRODUCTS CROWLEY TAR PRODUCTS CROWN ZELLERBACH CORP. CROWN ZELLERBACH CORP. CROWN ZELLERBACH CORP. CROWN ZELLERBACH CORP. CARLING AND CO. DART INDUSTRIES INC. OIAMOND SHAMROCK CORP. DIAMOND SHAMROCK CORP. DIAMOND SHAMROCK CORP. DIAMOND SHAMROCK CORP. DIAMOND SHAMROCK CORP. DIXIE CHEMICAL CO CON CHEMICAL CO. DOW BADISCHE CO. DOW CHEMICAL CO.	CITY	STATE
CLARK CHEMICAL CO.	BLUE ISLAND	IL
CLORAY NJ CORP.	NEWARK	NJ
COASTAL STATES GAS CO.	CHEVENNE	WY
COASTAL STATES GAS CO.	CORPUS CHRISTI	TX
COLGATE PALMOLIVE CD.	REPKELY	CA
COLGATE PALMOLIVE CO.	JEFEERSONVILLE	IN
COLGATE PALMOLIVE CO.	JERSEV CITY	NJ
COLGATE PALMOLIVE CO.	KANSAS CITY	KA
COLT INDUSTRIES INC.	MIDLAND	PA
COLUMBIA NITROGEN CORP.	AUGUSTA	GA
COMMERCIAL SOLVENTS CORP.	SETPL F	PA
COMMERCIAL SOLVENTS CORP.	STERI INGTON	LA
COMMERCIAL SOLVENTS CORP.	TERRE HAUTE	IN
COMMONWEALTH OIL REFINING CO.	PENIIFI AS	PR
CONTINENTAL OIL COMPANY	NEWARK	NJ
CONTINENTAL OTL COMPANY	WESTLAKE	LĂ
COOPERATIVE FARM CHEMICAL ASSOC.	LAWRENCE	KA
COPOLYMER RUBBER AND CHEMICAL CORP.	BATON ROUGE	LA
COS-MAR INC	CARVILE	LA LA
CROMPTON & KNOWLES CORP.	GIBRALTAR	PA
CROMPTON & KNOWLES CORP.	READING	PA
CROWLEY HYDROCARBON CHEMICALS INC.	HOUSTON	TX
CROWLEY HYDROCARBON CHEMICALS INC.	KENT	OH
CROWLEY HYDROCARBON CHEMICALS INC.	OKLAHOMA CITY	OK
CROWLEY TAR PRODUCTS	BALTIMORE	ND
CROWLEY TAR PRODUCTS	HOUSTON	TX
CROWN ZELLERBACH CORP.	BOGALUSA	LA
CROWN ZELLERBACH CORP.	CAMAS	WA
DAN RIVER INC.	DANVILLE	VA
DARLING AND CO.	CHICAGO	IL
DART INDUSTRIES INC.	ELYRIA	ÖH
DIAMOND SHAMPOCK CORP.	BELLE	WV
DIAMOND SHANROCK CORP.	CEDARTOWN	GA
DTAMOND SHAMPOCK CORP.	DEER PARK	TX
DIVIE CHEMICAL CO	BAYPORT	TX
DON CHEMICAL CO.	ANCHORAGE	AK
DOW BADTSCHE CO.	FREEPORT	TX
CROWLEY HYDROCARBON CHEMICALS INC, CROWLEY TAR PRODUCTS CROWN ZELLERBACH CORP. CROWN ZELLERBACH CORP. OAN RIVER INC. DARLING AND CO. DART INDUSTRIES INC. DIAMOND SHAMROCK CORP. DIAMOND SHAMROCK CORP. DIAMOND SHAMROCK CORP. DIAMOND SHAMROCK CORP. DIXIE CHEMICAL CO. DON CHEMICAL CO. DOW BADISCHE CO.	BAY CITY	MI
AAU RUPUSAN PAS		•••

NAME DOW CHEMICAL CO. DOW CHEMICAL CO. DOW CHEMICAL CO. DOW CHEMICAL CO. DOW CHEMICAL CO. DOW CHEMICAL CO. DOW CORNING EI DU PONT DE NEMOURS & CO EI DU PONT DE N	CITY	STATE
DOW CHENICAL CO.	CITY FREEPORT MAGNOLIA MIDLAND OYSTER CREEK PITTSBURG PLAQUEMINE CARROLLTON MIDLAND ANTIOCH BEAUMONT BELLE CAPE FEAR CORPUS CHRISTI DEEPWATER POINT EAST CHICAGD GIBBSTOWN HEALING SPRINGS LAPLACE LAPORTE LINDEN LOUISVILLE MEMPHIS MONTAGUE NIAGARA FALLS ORANGE TOLEDO VICTORIA	TX
DOW CHEMICAL CO.	MAGNOLIA	AR
DOW CHEMICAL CO.	MIDLAND	MI
DOW CHENICAL CO.	DYSTER CREEK	TX
DOW CHENICAL CO.	PITTSBURG	CA
DOW CHENICAL CO.	PLAQUEMINE	LA
DOW CORNING	CARROLLTON	KY
	MIDLAND	MI
ET DU PONT DE NEMOURS & CO	ANTIOCH	CA
ET DU PONT DE NEMOURS & CO	BEAUMONT	TX
ET DU PONT DE NEMOURS & CO	BELLE	WV
ET DU FUNT DE NEMOURS & CO	CARE FEAR	NC
ET DU PONT DE NEMOURS & CO	COPPUS CHRISTI	TX
ET DU PONT DE NEMOURS & CO	DEEPWATER POINT	NJ
EL DU FUNT DE NEMOURS & CO	FAST CHICAGD	IN
ET DU PONT DE NEMOURS & CO	CTRESTOWN	NJ
ET DU PUNT DE NEMOURS & CO	HEALTNG SPRINGS	NC
EI UU PUNI DE NEMOURS à CO		LA
ET DU FUNI DE NEMOURS & CO		TX
EI DU FUNI DE NEMOURS & CO		NJ
EI DU PUNI DE NEMOURS à CO		KY
EL DU FUNT DE NEHOURS & CD	MENDU46 C001311CCC	TN
EI DU PUNI DE NEMOURS & CU	MONTACIE	MI
EL DU PUNT DE NEMOURS & CO	NTACADA FALLS	NY
EI DU PONT DE NEMOURS à CU	NIAUARA FALLO	TX
EI DU PONT DE NEMOURS & CU	URANGE Tol EDO	OH
EI DU PONT DE NEMOURS & CU		TX
EI DU PONT DE NEMOURS & CU	VICIURIA	VÂ
EI DU PONT DE NEMOURS & CU	WAYNESDURU	NJ
DYE SPECIALTIES INC	JERSET LITT .	NJ
EASTERN COLOR AND CHEMICAL CO	PROVIDENCE	RI
EASTMAN KODAK CO.	KINGSPURT	TN
EASTMAN KODAK CO,		TX
EASTMAN KODAK CO.	ROCHESTER	NY
EL PASO NATURAL GAS CO,	ODESSA	TX
EMERY INDUSTRIES INC.	CINCINNATI	ОН
EMERY INDUSTRIES INC,	CITY OF COMMERCE	CA
EMKAY CHEMICAL CO.	ELIZABETH	NJ
ENSERCH CORP.	KERENS	TX

NAME ENSERCH CORP, ESMARK, INC, ESMARK, INC, ETHYL CORP, ETHYL CORP, ETHYL CORP, ETHYL CORP, ETHYL CORP, EXXON CHEMICAL CO, EXXON CHEMICAL CO, EXXON CHEMICAL CO, FAIRMONT CHEMICAL CO, FAIRMONT CHEMICAL CO, FERRO CORP, FERRO CORP, FIRESTONE TIRE AND RUBBER CO, FIRESTONE TIRE AND RUBBER CO, FIRESTONE TIRE AND RUBBER CO, FIRESTONE TIRE AND RUBBER CO,	CITY	STATE
ENSERCH CORP.	PRYOR	OK
ESMARK, INC.	BEAUMONT	TX
ESMARK, INC.	WINCHESTER	MA
ETHYL CORP.	BATON ROUGE	LA
ETHYL CORP.	MAGNOLIA	AR
ETHYL CORP.	ORANGEBURG	SC
ETHYL CORP.	PASADENA	TX
EXXON CHEMICAL CO.	BATON ROUGE	LA
EXXON CHEMICAL CO.	BAYTOWN	TX
EXXON CHEMICAL CO.	RAVWAV	NJ
FATRMONT CHEMICAL CO.	NFWARK	NJ
FERRO CORP.	BATON ROUGE	LĂ
FERRO CORP.	SANTA FF SPRINGS	CA
FIRESTONE TIRE AND RUBBER CO.	DRANGE	TX
FIRST MISSISSIPPI CORP.	PASCAGOULA	MS
FLEMING LABORATORIES INC.	CHAROLITE	NC
FMC CORP.	BALTIMORE	MD
FNC CORP.	BAYPORT	TX
FMC CORP.	MEADVILLE	PA
FNC CORP.	SOUTH CHARLESTON	ŴŴ
FOSTER#GRANT CO. INC.	BATON ROUGE	LA
FRANK ENTERPRIESES	COLUMBUS	OH
FRITZCHE DODGE & OLCOTT INC.	EAST HANDVER	NJ
SAF CORP.	CALVERT CITY	KY
GAF CORP.	LINDEN	NJ
GAF COPP.	RENNSFLEAR	NY
GARDINIER ATG RIVER. INC.	HELENA	AR
GENERAL AMERICAN OTI OF TEXAS	PASADENA	TX
CENERAL ANERICAN OIL OF TERRO	MOUNT VERNON	IN
CENERAL ELECTRIC CO.	SFLKTRK	NY
CENERAL ELECTRIC CO	WATEREARD	NY
THE CENEDAL TIDE & DURRED CO.	ASHTABILA	DH
GEODETA DARTETE RODDEN CUL	ALRANY	OR .
CEADOIA PACIFIC CORFS	BELL TNGHAM	WA
FERRO CORP. FIRESTONE TIRE AND RUBBER CO. FIRST MISSISSIPPI CORP. FLEMING LABORATORIES INC. FMC CORP. FMC CORP. FMC CORP. FMC CORP. FMC CORP. FMC CORP. FMC CORP. FOSTER GRANT CO. INC. FRANK ENTERPRIESES FRITZCHE DODGE & OLCOTT INC. GAF CORP. GAF CORP. GAF CORP. GAF CORP. GAF CORP. GAF CORP. GENERAL ELECTRIC CO. GENERAL ELECTRIC CO. GEORGIA PACIFIC CORP. GEORGIA PACIFIC CORP. GEORGIA PACIFIC CORP. GEORGIA PACIFIC CORP. GEORGIA PACIFIC CORP. GEORGIA PACIFIC CORP. GEORGIA PACIFIC CORP.		ÖH
GEODOIA PACIFIC CONF.	COOS BAY	0R
CEARCIA FALIFIC CORR	CRASSETT	AR .
CENCIA FALIFIL LUKF:	PLACHEMTNE	LA
GEURGIA FAGIFIG GURFS	E P M M P M P M P M P M P M P M P M P M	L A

NAME GEORGIA PACIFIC CORP. GEORGIA PACIFIC CORP. GEORGIA PACIFIC CORP. GETTY OIL CO. GIVAUDAN CORP. GOODPASTURE, INC. BF GOODRICH CHEMICAL CO. BF GOODRICH CHEMICAL CO. BF GOODRICH CHEMICAL CO. GOODYEAR TIRE AND RUBBER CO. W. R. GRACE AND CO. W. R. GRACE AND CO. W. R. GRACE AND CO. W. R. GRACE AND CO. GRAIN PROCESSING CORP. GREAT LAKES CHEMICAL CORP. GULF OIL CO. GULF OIL CO. HERCULES, INC. HERCULES, INC. HUMPHREY CHEMICAL CO.	CITY	STATE
GEORGIA PACIFIC CORP.	RUSSELLVILLE	SC
GEORGIA PACIFIC CORP.	TAYLORSVILLE	MS
GEORGIA PACIFIC CORP.	VIENNA	GA
GETTY OIL CO.	DELAWARE CITY	DE
GIVAUDAN CORP.	CLIFTON	NJ
GOODPASTURE, INC.	DIMMITT	TX
BF GOODRICH CHEMICAL CO,	CALVERT CITY	KY
BF GOODRICH CHEMICAL CO.	HENRY	IL
BF GOODRICH CHEMICAL CO.	PORT NECHES	TX
GOODYEAR TIRE AND RUBBER CO.	BAYPORT	TX
GOODYEAR TIRE AND RUBBER CO.	BEAUMONT	TX
W. R. GRACE AND CO.	FORDS	NJ
W, R, GRACE AND CO.	MEMPHIS	TN
W. R. GRACE AND CO.	NASHUA	NH
GRAIN PROCESSING CORP,	MUSCATINE	IA
GREAT LAKES CHEMICAL CORP.	EL DORADO	AR
GUARDIAN CHEMICAL CORP.	HAUPPAUGE	NY
GULF OIL CO.	ALLIANCE	LA
GULF DIL CO.	CEDAR BAYOU	TX
GULF OIL CO.	PHILADELPHIA	PA
GULF OIL CO.	PORT ARTHUR	TX
GULF OIL CO,	VICKSBURG	MS
GULF OIL CO.	WELCOME	LA
HARDWICKE CHEMICAL CO.	ELGIN	SC
HEICO, INC.	DELAWARE WATER GAP	PA
HERCULES, INC.	BURLINGTON	NJ
HERCULES, INC.	GIBBSTOWN	NJ
HERCULES, INC.	GLENN FALLS	NY
HERCULES, INC,	HARBOR BEACH	MI
HERCULES, INC.	HERCULES	CA
HERCULES, INC.	HOPEWELL	VA
HERCULES, INC.	LOUISIANA	MO
HERCULES, INC.	PLAQUEMINE	LÅ
HERCULES, INC.	WILMINGTON	NC
HODAG CHEMICAL CORP.	SKOKIE	IL
HOWERTOWN GOWEN CHEMICALS, INC.	ROANOKE RAPIDS	NC
HUMMEL CHENICAL CO.	SOUTH PLAINFIELD	NJ
HUMPHREY CHEMICAL CO.	NORTH HAVEN	СТ

, NAME	CITY	STATE
ICC INDUSTRIES, INC. ICC INDUSTRIES, INC. ICI UNITED STATES INLAND CHEMICAL CORP. INLAND CHEMICAL CORP. JEFFERSON CHEMICAL CO., INC. JEFFERSON CHEMICAL CO., INC.	DOVER NIAGARA FALLS NEW CASTLE JUNEAU MANATI CONRDE PORT NECHES HOUSTON CINCINNATI SAVANNAH KALAMA STONY POINT GLOUCESTER CITY	он
ICC INDUSTRIES, INC.	NIAGARA FALLS	NY
ICI UNITED STATES	NEW CASTLE	DE
INLAND CHEMICAL CORP.	JUNEAU	WI
INLAND CHEMICAL CORP.	MANATI	PR
JEFFERSON CHEMICAL CO., INC.	CONRDE	TX
JEFFERSON CHEMICAL CO., INC.	PORT NECHES	TX
JOC OIL, INC.	HOUSTON	TX
ANDREW JERGENS CO.	CINCINNATI	OH
KAISER CHEMICALS	SAVANNAH	GA
KALAMA CHEMICALS, INC.	KALAMA	WA
KAY-FRIES CHEMICALS, INC.	STONY POINT	NY
KEWANEE INDUSTRIES, INC.	GLOUCESTER CITY	NJ
H. KOHNSTAMM AND CD., INC.	CAMDEN	NJ
H. KOHNSTAMM AND CD., INC.	CLEARING	IL
KOPPERS CO., INC.	BRIDGEVILLE	PA
KOPPERS CO., INC.	CICERO	IL
KOPPERS CO., INC.	FOLLANSBEE	WV
KOPPERS CO., INC.	PETROLIA	PA
KRAFTCO CORP.	MEMPHIS	TN
LACAT CHEMICALS INC.	CHICAGO HEIGHTS	IL
LEVER BROTHERS CO.	BALTIMORE	MŌ
LEVER BROTHERS CO.	EDGEWATER	NJ
LEVER BROTHERS CO.	HAMMOND	IN
LEVER BROTHERS CO.	LOS ANGELES	CA
LEVER BROTHERS CO.	ST. LOUIS	MO
ELI LILLY AND CO.	LAFAYETTE	IN
LONZA, INC.	MAPLETON	IL
LUBRIZOL CORP.	DEER PARK	ŤX
LUBRIZOL CORP.	DEER PARK	ТХ
MALLINCKRODT, INC.	LODI	NJ
MALLINCKROOT, INC.	RALEIGH	NC
MALLINCKRODT, INC.	ST, LOUIS	MO
MARATHON DIL CO.	ROBINSON	IL
MARATHON DIL CO.	TEXAS CITY	TX
MARTIN MARIETTA CORP.	SODYECO	NC
MERCK AND COMPANY INC.	ALBANY	GA
JEFFERSUN CHEMICAL CO., INC. JOC OIL, INC. ANDREW JERGENS CO. KAISER CHEMICALS KALAMA CHEMICALS, INC. KAY-FRIES CHEMICALS, INC. KAY-FRIES CHEMICALS, INC. H. KOHNSTAMM AND CO., INC. H. KOHNSTAMM AND CO., INC. KOPPERS CO., INC. KOPPERS CO., INC. KOPPERS CO., INC. KOPPERS CO., INC. KAFTCO CORP. LACAT CHEMICALS INC. LEVER BROTHERS CO. LEVER BROTHERS CO. MALLINCKROOT, INC. MALLINCKROOT, INC. MARATHON OIL CO. MARATHON OIL CO. MARATHON OIL CO. MARATHON OIL CO. MARATHON OIL CO. MARATHON CO. MERICHEM CO.	HOUSTON	TX

NAME	CITY	STATE
NAME MIDDLEBORO INDUSTRIES, INC. MILES LABORATORIES, INC. MILLMASTER ONYX CORP. MISSISSIPPI CHEMICAL CORP. MOBAY CHEMICAL CO. MOBAY CHEMICAL CO. MOBAY CHEMICAL CO. MONSANTO CO.	MIDDLEBORD ZEELAND Newark Yazoo Cedar Bayou New Martinsville	MA
MILES LABORATORIES, INC.	ZEELAND	MI
MILLMASTER ONYX CORP.	NEWARK	NJ
MISSISSIPPI CHENICAL CORP.	YAZOO	MS
MOBAY CHEMICAL CO.	CEDAR BAYOU	TX
NOBAY CHEMICAL CO.	NEW MARTINSVILLE	WV
NOBIL OIL CORP.	BEAUMONT	TX
MONOCHEM, INC.	GEISMAR	LA
MONSANTO CO.	ADDYSTON	OH
MONSANTO CO	ANNISTON	AL
MONGANTO CO.	BRIDGEPORT	NJ
MONGANTO CO.	CHOCOLATE BAYDU	TX
MONGANTO COS Monganto Co	DECATUR	AL
MONGANTO CO	FUGENE	OR
MONRANTO CO	FVFRFTT	MA
MUNSANIU, LUR Monranto co	KFARNY	LN
MUNGANTO CO:		LÅ
MUNJANIU CUA Monganto Co	NITRO	ŴV
MONRANTO CO	PENSACOLA	FL
MONGANTO CO	ST. LOUIS	MO
MONRÁNTO CO.	SAUGET	IL
MONRANTO CO	SPRINGFIELD	MA
MUNDANIU CU:	TEXAS CITY	TX
MONSANTO CO.	TRENTON	MI
MONTROSE CHEMICAL CORP. OF CALIFORNIA	HENDERSON	NV
MURRO CHEMICAL CO.	PORTSMOUTH	VA
NALCO CHEMICAL CO.	FREEPORT	TX
NALCO CHEMICAL CO.	SUGARLAND	TX
NAPP CHEMICALS, INC.	LODI	N.J.
NATIONAL DISTILLERS AND CHEMICAL CORP.	DEER PARK	TX
NATTONAL OTOTTLEEDE AND PHEMIPAL COPP	TUSCULA	ĨL.
NATIONAL STADCH AND CHENTCAL CORP.	LONG MOTT	ŤŸ
NATIONAL SPARCH AND CHEMICAL CONF.	7UG TSLAND	MT
NATIONAL STEEL CONF.	FERNAL D	пн
NEADE CHEMICAL COST INCO	STATE COLLEGE	PA
NATIONAL STARCH AND CHEMICAL CORP, NATIONAL STEEL CORP. NEASE CHEMICAL CO., INC. NEASE CHEMICAL CO., INC. NECHES BUTANE PRODUCTS CO. NIPRO, INC. NORDA, INC.	CEDAR BAYOU NEW MARTINSVILLE BEAUMONT GEISMAR ADDYSTON ANNISTON BRIDGEPORT CHOCOLATE BAYOU DECATUR EUGENE EVERETT KEARNY LULING NITRO PENSACOLA ST. LOUIS SAUGET SPRINGFIELD TEXAS CITY TRENTON HENDERSON PORTSMOUTH FREEPORT SUGARLAND LODI DEER PARK TUSCULA LONG MOTT ZUG ISLAND FERNALD STATE CDLLEGE PORT NECHES AUGUSTA BOONTON	ŤŸ
NECHER BUIANE FRUDUCIS CU.	AUGUSTA	C A
NIPRU, INC,	BOONTON	
NORDA, INC,		N J

NAME NORSE LABS, INC. NORTHERN FINE CHEMICALS NORTHERN NATURAL GAS CO. NORTHWEST INDUSTRIES INC. NORTHWEST INDUSTRIES INC. NORTHWEST INDUSTRIES INC. NORTHWEST INDUSTRIES INC. NAREN CORP. OCCIDENTAL PETROLEUM OCCIDENTAL PETROLEUM OCCIDENTAL PETROLEUM OCCIDENTAL PETROLEUM OCCIDENTAL PETROLEUM OCCIDENTAL PETROLEUM OLIN CORP. OLIN CORP. OLIN CORP. OLIN CORP. OLIN CORP. OLIN CORP. OXIRANE CHEMICAL CO. OXOCHEM ENTERPRISE PACIFIC SOAP CO. PAN AMERICAN CHEMICAL CORP. PENNWALT CORP. PENNWAL	CITY	STATE
NORSE LABS, INC.	SANTA BARBARA	CA
NORTHERN FINE CHEMICALS	FRANKLIN	NJ
NORTHERN NATURAL GAS CD.	MORRIS	ĨĹ
NORTHWEST INDUSTRIES INC.	BEALMONT	TX
NORTHWEST INDUSTRIES INC.	CHATTANOGA	ŤN
NORTHWEST INDUSTRIES INC.	FL DORADO	ÅR
NORTHWEST INDUSTRIES INC.	ST. LOUIS	MI
NHREN CORP.	PLATNVTFW	TX
N-REN CORP.	PRVNP	ÖK
OCCIDENTAL PETROLEUM	ARECTBO	PR
OCCIDENTAL PETROLEUM	NTAGARA FALLS	NY
OCCIDENTAL PETROLEUM	NORTH TANAWANDA	NY
OCCIDENTAL RETROLEUM	TAFT	LÀ
OLIN CORP.	ASHTABULA	ÖH
ALTN CORP_	BRANDENBURG	KY
OLIN CORP.	LAKE CHARLES	LÀ
ALTN CORP.	ROCHESTER	NY
ARATS PRODUCTS CORP.	NEWARK	NJ
DXIRANE CHEMICAL CO.	BAYPORT	TX
NXICHEM ENTERPRISE	PENUELAS	PR
PACIFIC SNAP CO.	VERNON	CA
PAN AMERICAN CHEMICAL CORP.	TOLEDO	ŌH
PARKEDAVIS & CO.	HOLLAND	MI
PFIRON CORP.	LYONS	IĹ
PENNWALT CORP.	BEAUMONT	TX
PENNWALT CORP.	CALVERT CITY	KY
PENNWALT CORP.	GENESEO	NY
PENNWALT CORP.	GREENS BAYOU	TX
PENNWALT CORP.	THOROFARE	NJ
PENNWALT CORP.	WYANDOTTE	MĪ
PETRO-TEX CHEMICAL CORP.	HOUSTON	TX
PEANSTIENE LABROATORIES, INC	WAUKEGAN	IL
CHAS. PETZER & CO., INC	GREENSBORD	NČ
CHAS. PFIZER & CO INC	GROTON	CT
CHAS. PETTER & CO., INC	TERRE HAUTE	IN
PHYLLIPS PARTETS CHEMITAL CO.	KENNENECK	WA
	BEATRICE	NE
	BORGER	TX
LUTPTLO LEIMOPEON CO ⁸		1.0

NAME	CITY	STATE
NAME PHILLIPS PETROLEUM CO. PHILLIPS PETROLEUM CO. PHILIPS PETROLEUM CO. PILOT CHEMICAL CO. PILOT CHEMICAL CO. PILOT CHEMICAL CO. PIONEER SOAP CO. PLASTICS ENGINEERING CORP. PPG INDUSTRIES, INC. PPG INDUSTRIES, INC. PPG INDUSTRIES, INC. PPG INDUSTRIES, INC. PPG INDUSTRIES, INC. PPG INDUSTRIES, INC. PROCTOR & GAMBLE CO. PROCTOR & GAMBL	GUAYAMA	PR
PHILLIPS PETROLEUM CO.	PHILLIPS	ТХ
PHILLIPS PETROLEUM CO.	SWEENEY	TX
PIERCE CHEMICAL CO.	ROCKFORD	IL
PILOT CHEMICAL CO,	HOUSTON	TX
PIONEER SDAP CO.	SAN FRANCISCO	ĈA
PLASTICS ENGINEERING CORP.	SHEBOYGAN	WI
PPG INDUSTRIES, INC.	BARBERTON	OH
PPG INDUSTRIES, INC.	BEAUMONT	ТХ
PPG INDUSTRIES, INC.	GUAYANILLA	PR
PPG INDUSTRIES, INC.	LAKE CHARLES	LA
PPG INDUSTRIES, INC.	NATRIUM	WV
PROCTOR & GAMBLE CO,	BALTIMORE	MD
PROCTOR & GAMBLE CO.	CHICAGO	IL
PROCTOR & GAMBLE CO.	DALLAS	TX
PROCTOR & GAMBLE CO.	DAYTON	OH
PROCTOR & GAMBLE CO,	IVORYDALE	OH
PROCTOR & GAMBLE CO,	KANSAS CITY	KA
PROCTOR & GAMBLE CO.	LONG BEACH	CA
PROCTOR & GAMBLE CO.	MEMPHIS	TN
PROCTOR & GAMBLE CO.	SACRAMENTO	CA
PUBLICKER INDUSTRIES INC.	GRETNA	LA
PUBLICKER INDUSTRIES INC.	PHILADELPHIA	PA
PUERTO RICO OLEFINS CO.	PENUELAS	PR
PUREX CORP,	BRISTOL	PA
PUREX CORP.	OMAHA	NE
PYO INTERNATIONAL, INC.	BOONTON	NJ
REICHOLD CHEMICALS, INC.	AUSTIN	TX
REICHOLD CHEMICALS, INC.	ELIZABETH	NJ
REICHOLD CHEMICALS, INC.	HAMPTON	SC
REICHOLD CHEMICALS, INC.	HOUSTON	TX
REICHOLD CHEMICALS, INC.	KANSAS CITY	KA
REICHOLD CHEMICALS, INC.	MALVERN	AR
REICHOLD CHEMICALS, INC.	MONCURE	NC
REICHOLD CHEMICALS, INC.	MORRIS	IL
REICHOLD CHEMICAL INC.	ST. HELENS	OR
REICHOLD CHEMICALS, INC.	TACOMA	WA
REICHOLD CHEMICALS, INC.	TUSCALOOSA	AL
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NAME REICHOLD CHEMICALS, INC. REILY TAR & CHEMICAL CORP. REPUBLIC STEEL CORP. REPUBLIC STEEL CORP. RICHARDSON-HEREELL INC. RITTER CHEMICAL CO. ROHM & HAAS CO. ROHM & HA	CITY	STATE
REICHOLD CHEMICALS, INC.	WHITE CITY	OR
REILY TAR & CHEMICAL CORP.	INDIANOPOLIS	ĪN
REPUBLIC STEEL CORP.	CHICAGO	ĪL
REPUBLIC STEEL CORP.	CLEVELAND	OH
RICHARDSON-MERRELL INC.	PHILLIPSBURG	NJ
RITTER CHEMICAL CO.	AMSTERDAM	NY
ROBINSON-WAGNER INC.	MAMARONECK	NY
ROHM & HAAS CO.	BRISTOL	PA
ROHM & HAAS CO.	DEFR PARK	TX
ROHM & HAAS CO.	KNOXVILLE	TN
ROHM & HAAS CO.	LOUISVILLE	KY
ROHM & HAAS CO.	PHILADELPHIA	PÅ
R.S.A. CORP.	ARDSLEY	NY
RUBICON CHEMICALS INC.	GEISMAR	LA
SALISBURY LABS	CHARLES CITY	ĪA
SALISBURY LABS	WILMINGTON	NC
SCHENECTADY CHEM. INC.	ROTTERDAM JUNCTION	NJ
G.D.SEARLE & CO.	NORWOOD	OH
SHARON STEEL CORP.	FAIRMONT	WV
SHELL OIL CO.	DEER PARK	TX
SHELL OIL CO.	DOMINGUEZ	CA
SHELL OIL CO.	GEISMAR	LA
SHELL DIL CO.	MARTINEZ	CA
SHELL OIL CO.	NORCO	ĻA
SHELL OIL CO.	HOOD RIVER	IL
SHENANGO INC.	NEVILLE ISLAND	PA
SHERWIN WILLIAMS CO	ST, BERNARD	OH
J. R. SIMPLOT CO.	POCATELLO	ID
SKELLY OIL CO.	CLINTON	IA
SKELLY OIL CO.	EL DORADO	KA
SKELLY OIL CO.	SPRINGFIELD	OR
SKELLY OIL CO.	WINNFIELD	LA
SOLVENT CHEMICAL CO.	MALDEN	MA
SOLVENT CHEMICAL CO.	NIAGRA FALLS	NY
SONOCO PRODUCTS CO.	HARTSVILLE	SC
SOUTH HAMPTON CO.	SILSBEE	TX
SPECIALTY ORGANICS, INC.	IRWINDALE	CA
SQUIBB CORP.	NEW BRUNSWICK	NJ

NAME		CITY DELAWARE CITY KEARNY CMOCOLATE BAYOU DECATURE JOLIET TEXAS CITY WOOD RIVER YORKTOWN LIMA CARSON COLD CREEK DELAWARE CITY EDISON MENDERSON LE MOYNE LOUISVILLE NIAGARA FALLS PERRY ANAHEIM ELWOOD FIELDSBORD CINCINATTI MEMPHIS RENSSELAER ANACORTES EAST DUBUQUE MUSKEGON CORPUS CHRISTI DUNCAN MARCUS HOOK TOLEDO CLAYMONT LYNDHURST NEWPORT CHALMETTE FOROS GARFIELD HOUSTON	STATE
STANDARD CHLORINE CHEMICAL	co.	DELAWARE CITY	DE
STANDARD CHLORINE CHEMICAL	60 .	KEARNY	NJ
STANDARD OF INDIANA		CHOCOLATE BAYOU	TX
STANDARD OF INDIANA		DECATURE	AL
STANDARD DE INDIANA		JOITET	ĨĹ
STANDARD OF INDIANA		TEYAS CITY	Ŧx
STANDARD DE INDIANA		WAAD PTVEP	ÎĹ
STANDARD OF INDIANA		VORTOWN	VĂ
STANDARD OF OHTO		1 TMA	0H
STAUEFER CHEMICAL CO.		CARSON	CA
STAUFFER CHEMICAL CO.		COLD CREEK	AL
STAUFFER CHEMICAL CO.		DELAWARE CITY	DE
STAUEPER CHEMICAL CO.		FDISON	NJ
STAUFFER CHEMICAL CO.		HENDERSON	NV
STAUFFER CHEMICAL CO.		LE MOYNE	AL
STAUFFER CHEMICAL CO.		LOUISVILLE	KY
STAUFFER CHEMICAL CO.		NIAGARA FALLS	NY
STAUFFER CHEMICAL CO.		PERRY	OH
STEPAN CHEMICAL CO.		ANAHEIM	CA
STEPAN CHEMICAL CO.		ELWOOD	IL
STEPAN CHEMICAL CO.		FIELDSBORD	NJ
STERLING DRUG, INC.		CINCINATTI	OĤ
STERLING DRUG, INC.		MEMPHIS	TN
STERLING DRUG, INC.		RENSSELAER	NY
STIMSON LUMBER COMPANY		ANACORTES	WA
ST. PAUL AMMONIA PRODUCTS,	INC.	EAST DUBUQUE	IL
STORY CHEMICAL CORP.		MUSKEGON	MI
SUNDED		CORPUS CHRISTI	TX
SUNDCO		DUNCAN	OK
SUNDED		MARCUS HODK	PA
SUNDCO		TOLEDO	OH
SUNDLIN CHEM. CO.		CLAYMONT	DE
SYBRON CORP.		LYNDHURST	NJ
SYNTEX CORP.		NEWPORT	TN
TENNECO CHEMICALS, INC.		CHALMETTE	LA
TENNECO CHEMICALS, INC.		FORDS	NJ
TENNECO CHEMICALS, INC.		GARFIELD	NJ
TENNECO CHEMICALS, INC.		HOUSTON	TX
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NAME TENNESSEE VALLEY AUTHORITY TERRA CHEM INTERNATIONAL, INC. TEXACO, INC. TEXAS-U.S. CHEMICAL CO. TOMS RIVER CHEMICAL CORP. TRIAD CHEMICAL TYLER CORP. UNION CAMBIDE CORP. UNION CARBIDE CO	CITY	STATE
TENNESSEE VALLEY AUTHORITY	MUSCLE SHOALS	AL
TERRA CHEM INTERNATIONAL, INC.	PORT NEAL	IA
TEXACO, INC.	PORT ARTHUR	TX
TEXACO, INC.	WESTVILLE	NJ
TEXAS-U.S. CHEMICAL CO.	PORT NECHES	TX
TOMS RIVER CHEMICAL CORP.	TOMS RIVER	NJ
TRIAD CHEMICAL	DONALDSONVILLE	LĂ
TYLER CORP.	JOPITN	Ma
UNION CAMP CORP.	DOVER	OH
UNION CARBIDE CORP.	ASHTABULA	QH
UNION CARBIDE CORP.	BOUND BROOK	NJ
UNION CARBIDE CORP.	BROWNSVILLE	TX
UNION CARBIDE CORP.	INSTITUTE AND SOUTH C	HARLESTONWV
UNION CARBIDE CORP.	MARIETTA	OH
UNION CARBIDE CORP.	NIAGRA FALLS	NY
UNION CARBIDE CORP.	PENUELAS	PR
UNION CARBIDE CORP.	SEADRIFT	TX
UNION CARBIDE CORP.	TAFT	LA
UNION CARBIDE CORP.	TEXAS CITY	TX
UNION OIL OF CALIFORNIA	BEAUMONT	TX
UNION OIL OF CALIFORNIA	BREA	CA
UNION OIL OF CALIFORNIA	KENAI	AL
UNION PACIFIC CORP. CHAMPLIN	CORPUS CHRISTI	TX
UNIROYAL, INC.	NAUGATUCK	CT
UNITED AIRCRAFT	MUNCIE	IN
UNITED STATES STEEL CORP.	CHEROKEE	AL.
UNITED STATES STEEL CORP.	CLAIRETON	PA
UNITED STATES STEEL CORP.	HAVERHILL	OH
UNITED STATES STEEL CORP.	NEVILLE ISLAND	ΡΑ
UNIVAR CORP.	EUGENE	OR
UNIVERSAL DIL PRODUCTS CO.	EAST RUTHERFORD	NJ
UNIVERSAL OIL PRODUCTS CO.	MCCOOK	IL
UPJOHN CO.	LAPORTE	TX
VALLEY NITROGEN PRODUCERS, INC.	EL CENTRO	CA
VALLEY NITROGEN PRODUCERS, INC.	HELM	CA
VAN DE MARK CHEM. CO.	LOCKPORT	NY
VIRGINIA CHEMICALS, INC.	PORTSMOUTH	VA
VULCAN MATERIALS CO,	GEISMAR	LA

NAME	CITY	STATE
VULÇAN MATERIALS CO.	WICHITA	KA
JIM WALTER CORP.	BIRMINGHAM	AL
WARNER LAMBERT CO.	HARRIMAN	NY
WHEELING PITTSBURG STEEL: CORP.	MONESSEN	PA
WHITE CHEHICAL CORP.	BAYONNE	NJ
WILLIAMS COMPANIES	BLYTHEVILLE	AR
WILLIAMS COMPANIES	CATOOSA	OK
WILLIAMS COMPANIES	DONALDSONVILLE	LA
WITCO CHEMICAL CORP.	CLEARING	IL
WITCO CHEMICAL CORP.	PATERSON	NJ
WOBURN CHEMICAL CO.	KEARNY	NJ
WOONSOCKET COLOR AND CHEMICAL CO.	WDONSOCKET	RĪ
WRIGHT CHEMICAL CO,	ACHE	NC

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The catalog of Industrial Process Profiles	for Environmental Use was	developed as an	
aid in defining the environmental impacts of			
Entries for each industry are in consistent		- (
study. Industrial organic chemicals are the			
in this industry and will undergo at least		- 4	
stream processing industry. These compound			
facture of such products as plastics, synth factants among others. The industry is dis			
benzene, butylenes, sources of cresylic aci		÷ •	
paraffins, propylene, toulene and xylenes.			
sheets and 365 process descriptions have be			
Within each process description available d			
materials, operating parameters, utilities,			
Code and references. Data related to the s		ompany, product	
and raw material data. are included as appe	endices.		
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