

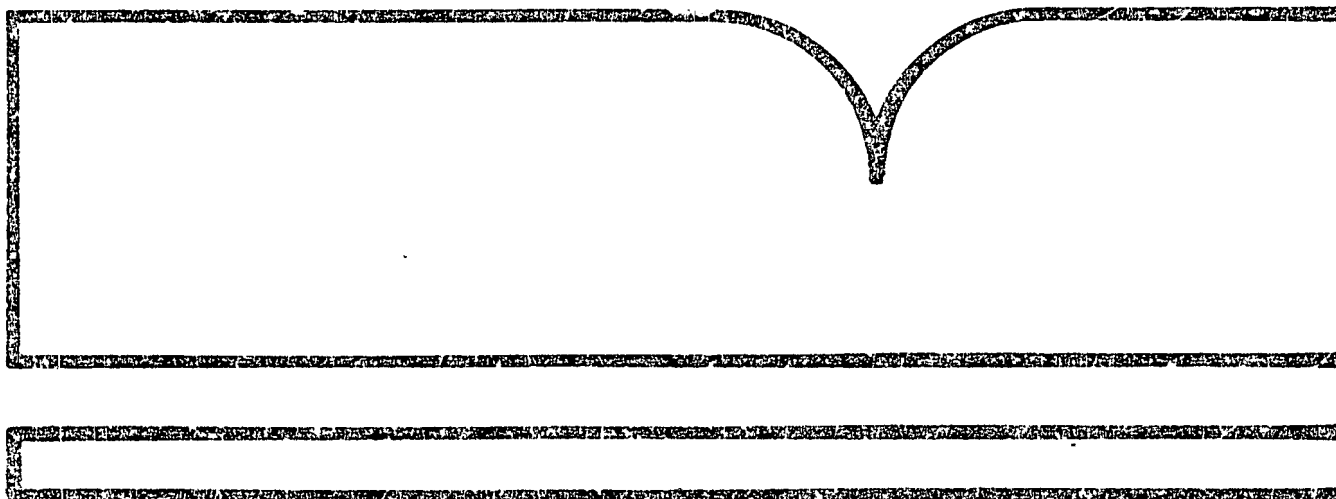
Alternative Treatment of Organic  
Solvents and Sludges from Metal  
Finishing Operations

Monsanto Research Corp., Dayton, OH

Prepared for

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ALTERNATIVE TREATMENT OF ORGANIC SOLVENTS AND SLUDGES  
FROM METAL FINISHING OPERATIONS  
FINAL REPORT

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## SECTION 1

### INTRODUCTION

Disposal of organic wastes from metal finishing is an increasingly costly alternative to reprocessing and reuse. Resulting in materials suitable for in-plant reuse, use as fuel, or resale to and reuse by other uses, secondary processing of these wastes could conserve raw material consumption and thus reduce the amount of waste that ultimately would enter the environment. Under EPA contract 68-03-3025 Monsanto Research Corporation (MRC) assembled data on the nature of metal finishing industry, current practices in using, recycling, and disposal of organic fluids, type and quantity of organic fluids used and organic wastes generated by the metal finishing industry categories including metalworking (metal rolling, cutting, grinding, and heat treating), solvent cleaning (degreasing), and surface coating (painting and rust prevention) (refer to Section 4.1 for further definition of those metal finishing operations included and excluded from this study), and technologies available for recovery, reuse, and disposal of organic fluids and wastes.

To collect relevant information, a thorough literature search was conducted followed by limited industry contacts and visits to environmental regulatory agencies in several industrial states. Waste sampling and analyses were not included in the program scope.

The purpose of this report is to summarize program findings. The report is organized into six sections. Following the summary, and the conclusions and recommendations in Sections 2 and 3, Section 4 gives information on the size, growth, SIC code distribution, and geographic distribution of the metal finishing industry. In Section 5, the metal finishing industry and operations are described including raw materials used, and wastes produced. Section 6 describes technologies for refining, reclamation, reuse, and disposal of metal finishing waste products.

Raw data on industry waste characteristics collected from state agent files are appended.

## SECTION 2

### SUMMARY

Approximately 150,000 industrial plants in SIC Codes 25 and 33-39 comprise the United States metal finishing industry. The purposes of this study were (1) to describe the metal finishing industry and its use of organic materials, (2) to describe the quantity and composition of organic wastes from metal finishing, (3) to describe the current technologies used to recover or dispose of these materials, and (4) to draw conclusions and make recommendations as to future work that needs to be done to improve the ways in which organic residues from the metal finishing industry are reused or disposed of.

#### 2.1 INDUSTRY DESCRIPTION

This study of the metal finishing industry focuses on processes which use significant amounts of organic materials. These are (1) the metalworking processes, (2) solvent cleaning, and (3) product coating processes.

Metalworking processes use oils. They are of four types: (1) metal removal, (2) metal forming, (3) heat treating, and (4) rust preventive coating.

Metal cutting operations, such as machining, require oils both as lubricants and coolants. Emulsified oils or soluble synthetic fluids are sold as concentrates, then diluted with water before use. Metal forming operations use oils primarily for lubrication. The hot and cold-rolling operations used for production of steel and aluminum strip and sheet use many different types of oils. Heat treating operations, such as quenching, use mineral and emulsified oils to quickly reduce metal temperatures. Straight mineral oils are used to coat steel coil as a rust preventive.

Degreasing or solvent metal cleaning uses nonaqueous solvents to clean surfaces of all of the common ferrous and nonferrous metals. The four main types of organic solvents used for solvent metal degreasing operations are: alcohols, halogenated solvents, hydrocarbons, and ketones.

Paints are classified in two major categories, as solvent-based or water-borne paints. The water-borne paints were developed to decrease the total amount of volatile solvent emissions and are

widely used as product coatings. However, solvent-borne enamels and lacquers remain the most widely used in the automotive industry. Six major methods are used for the application of product coatings in the metal finishing industry: (1) spray painting, (2) dip coating, (3) flow coating, (4) roll coating, (5) electrodeposition, and (6) powder coating.

## 2.2 ORGANIC WASTES

The annual quantities of organic materials used in metal finishing, the amounts of organic waste currently collected, and the estimated amounts that could be collected are shown below.

Use	Annual consumption, 10 <sup>6</sup> kg/yr	Waste collected, 10 <sup>6</sup> kg/yr	Waste potentially collectable, 10 <sup>6</sup> kg/yr
Metalworking (oils)	760	180	480
Degreasing (solvents)	670	580	630
Product coatings (paints)	<u>1,050</u>	<u>200</u>	<u>200</u>
TOTAL	2,480	960	1,310

The oils may be petroleum-based mineral oils (used straight), emulsified oils, or synthetic oils. Commonly used additive types include anti-oxidants, rust preventatives, extreme pressure additives, viscosity index improvers, pour point depressants, fatty oils, and emulsifiers.

Waste mineral oils may contain sulfur, chlorine, fluorides, nitrogen, phosphates, metal chips and fines, sediment, water, PCBs, oxidation products, and phenolic compounds as contaminants.

Waste emulsified and synthetic oils may contain metal particles, biodegradation products, tramp oil, nitrosamines, and residues from oil additives--including sulfur, phosphorus, chlorine, zinc, lead, copper, and phenolic compounds--as contaminants.

The waste solvents may be halogenated or nonhalogenated and may contain oil, grease, wax, metallic particles, etc.

Waste coating may contain high concentrations of organic solvents, resins, and heavy metals.

## 2.3 RECOVERY AND DISPOSAL

Environmental regulations usually prohibit the discharge of untreated organic wastes from the metal finishing industry into

surface waters because they contain unallowable concentrations of both organic and inorganic pollutants.

With increasingly restrictive environmental regulations, disposal of waste oils is becoming expensive. Therefore, refining/reclamation/alternate applications are viable options for waste oil generators.

Refining/reclamation technology for waste straight oils is well developed. Independent re-refiners accept waste oils for refining based on their composition and compatibility with refining technology used in their plants.

Waste emulsified oil treatment reclamation technology has been well developed in recent years. Economics of on-site or off-site treatment or disposal for a plant will depend on the volume of waste emulsified oil generated. Larger plants generally treat their waste prior to discharging wastewater to surface waters. Smaller plants exercise off-site treatment or disposal options. It is possible that some plants might still be illegally disposing of waste emulsified oil into sewers. The use of regional facilities to treat waste emulsified oils from small plants has been considered.

Synthetic fluids are expensive, so fluid maintenance and management programs in the plant are utilized to increase fluid life expectancy. Very limited technology is available at present to reclaim spent synthetic fluids. Synthetic fluids manufacturing firms are developing water soluble biodegradable synthetic fluids to avoid costly disposal problems. Disposal alternatives and costs are highly dependent on the chemical formulations of synthetic fluids, which are generally treated as proprietary information. For this reason, very limited information is available about treatment or disposal of spent synthetic fluids.

Waste solvents have high potentials for recovery and reuse. Also the Resource Conservation and Recovery Act (RCRA) lists waste solvents as hazardous waste, so they are to be disposed of in accordance with the regulations.

Reclamation technology for waste solvents is well developed. Due to RCRA regulations, disposal of waste solvents is becoming very expensive. For this reason more generators are starting to use the services of waste solvent reclaiming firms. Waste solvent reclaiming firms have been growing in number since RCRA regulations came into effect.

The major application method contributing to paint waste is the spray coating method. The waste is almost exclusively disposed of in either sanitary or secured landfills. A very small portion is incinerated.

Paint wastes have limited recovery or reuse potential. Waste coating may or may not be a hazardous waste depending on its composition. The disposal practice will depend on whether the waste is hazardous or nonhazardous. RCRA testing will be required to classify a waste coating as hazardous or nonhazardous.

#### 2.4 CONCLUSIONS

Conclusions from this work and recommendations based upon them are included. Specific batch scale studies, engineering studies, and economic studies which are needed are listed.

## SECTION 3

### CONCLUSIONS AND RECOMMENDATIONS

#### 3.1 CONCLUSIONS

- (1) The 150,000 metal finishing plants in the United States use 2,480 million kilograms of organic materials per year.
- (2) At present approximately 40 percent of these materials are collected for reclamation or disposal by processes such as incineration, landfill, or using in road paving. The other 60 percent which is not collected, is disposed of by processes such as vaporization losses, process losses on-site, and dumping.
- (3) The metal finishing industry is concentrated in ten heavily industrialized states: California, Illinois, New York, Ohio, Michigan, Pennsylvania, Texas, New Jersey, Massachusetts, and Indiana (in order of number of large plants).
- (4) These states are the ones with the most potential for setting up reclamation centers since they generate the largest amount of wastes.
- (5) The organic wastes from the metal finishing industry come primarily from the metalworking, solvent cleaning, and product coating processes.
- (6) The wastes from the metalworking and solvent cleaning processes generally contain sufficient concentrations of organic or inorganic contaminants to make them environmentally unacceptable for discharge to surface waters without treatment.
- (7) Paint wastes vary from innocuous to hazardous; hence, decisions must be made on each one individually to determine whether or not there are restrictions on the manner in which they are disposed of.
- (8) Waste oil compositions vary considerably, depending upon their initial composition, the process in which they are used, the severity of the operating conditions (temperature and pressure), and the degree of recycle or reuse.

- (9) Waste mineral oil refining and reclamation technology is well developed technically, but their economic practicality is in question. At present only a small fraction of the oil which could be re-refined is processed for reuse. The relatively small volume of oil being processed and its fluctuating quantities produce uncertainty in the economic viability of this approach. As long as there are few regulations requiring or strongly encouraging re-refining, it will continue to be a solution for only a small fraction of oil disposal problems.
- (10) The costs of disposing of waste oil are increasing, making re-refining or reclamation more attractive economically.
- (11) High-priced synthetic metalworking fluids are increasingly used in the industry. The recovery potential for synthetic fluids is unknown at present.
- (12) Few reclaimers handle waste oil water emulsions, or synthetic or water-based metal working fluids.
- (13) Solvent recovery is handicapped by the diversity of solvents available and the small quantities of specific solvents at some locations. Some solvent recovery companies are not well qualified, and they are frequently underfinanced.
- (14) Some solvents are complex mixtures of chemicals that are difficult to recycle.
- (15) Disposal companies are basically incinerating waste solvents at high cost. Disposal costs are so high that waste solvent generators are reluctant to call them.
- (16) Most solvent recyclers only process a limited number of solvents. They may not provide a service to many small waste solvent generators.

### 3.2 RECOMMENDATIONS

#### 3.2.1 Bench-Scale Studies

- (1) Establish a bench-scale or pilot-scale demonstration project for treatment or reuse of metalworking fluid wastes of the types and amounts that would be generated in small metalworking plants. A study of an emulsion treatment process would be appropriate since this type of process currently is presenting problems.
- (2) Conduct a bench-scale or pilot-scale study to determine the influence of oil additives on re-refining processes, and the feasibility of recycle or reuse of metalworking fluids after changing the additive composition.



- (3) Through laboratory analysis and bench-scale studies, investigate the effects on fluid performance characteristics and hazard potential of increased concentrations of additives (as in repeatedly recycled or reused fluids).
- (4) Conduct bench-scale studies to determine effective methods for breaking the emulsions and oil/water separation.
- (5) Investigate on a bench-scale method for removing water from emulsified oils without breaking the emulsion, reconditioning the oil, rediluting with fresh makeup water, and returning the oils to service with minimal treatment.
- (6) Conduct a bench-scale or pilot-scale study to determine the types of metalworking fluids most effectively re-refined.
- (7) Conduct bench- or pilot-scale studies to investigate the recovery potential of synthetic metalworking fluids, and identify appropriate recovery technologies.

### 3.2.2 Engineering Studies

- (8) Conduct a survey of large metalworking plants (large-volume users of metalworking fluids) to determine the present extent of metalworking fluid recycle or reuse; identify and categorize by type of fluid, type of operation, type of machine, type of metal, etc. Conduct a study of plant metalworking operations to determine costs associated with in-plant vs. external analysis and treatment of metalworking fluids, and cost-effective process improvements to conserve fluid usage.
- (9) Identify alternative uses for recycled metalworking fluids, degreasing solvents, and waste paints.
- (10) Investigate technologies for dewatering or concentration of metalfinishing sludges.
- (11) Identify alternative uses for nonhazardous metalfinishing sludges, still bottoms, etc.
- (12) Investigate alternative disposal methods for hazardous metalfinishing sludges and still bottoms, such as burning paint sludges in a cement kiln.
- (13) Through an in-plant engineering study of metalworking operations, recommend a preventive maintenance program to prolong the working life of synthetic metalworking fluids.
- (14) Conduct a wastestream sampling program to establish pre-treatment standards for disposal of waste oil.

- (15) Based on the results of sampling, design a waste treatment system to increase the recoverable portion of waste metalworking fluids.
- (16) Conduct an in-plant engineering study to improve the segregation of metalworking fluids preparatory to recycle, reuse, or re-refining.

### 3.2.3 Economic Studies

- (17) Investigate small metalworking plants (<20 employees) to determine the feasibility of metal finishing fluid reuse or recycle and identify economical alternatives for the small user.
- (18) Initiate and demonstrate economic incentives (tax-sheltered, depreciation-acceleration) for these small metalworking plants to practice recycle or reuse as a cost-effective alternative to disposal.
- (19) Investigate the effectiveness of financial incentives on the establishment of regional metal finishing waste fluid recycling centers and waste exchangers in the more heavily industrialized areas of the United States identified in this report.
- (20) Investigate the economic feasibility of emulsified oil treatment or reclamation in small plants.
- (21) Conduct an economic study of the oil re-refining and solvent and paint reclaiming industries.
- (22) Conduct a study to identify the recoverable portion of metal-finishing wastes and determine the economic value and potential uses for recovered materials.
- (23) Identify present disposition of wastes and ascertain the degree of hazard presented for each, particularly if they are currently disposed of in improper ways.
- (24) Aid both large and small manufacturers in complying with nonpolluting program by encouraging safe disposal, recycle, or re-refining in a practical and economic manner. Essentially develop a handbook for metalworking fluid and cleaning solvents recycle, re-refining, reclamation or disposal. It would present practical methods, economics of operation and provide the manufacturers with acceptable alternatives.
- (25) Considering the disposal problems of different localities and size of industrial operations, set in motion a project to encourage recyclers by demonstrating the market, suggesting processing alternatives and showing the economic advantages for the communities.

- (26) Catalog present commercial services, listing by manufacturer, locality, and types of solvent and oils processed. Note deficiencies and consider problems. Frequently, it is difficult for a waste generator to find a recycler. If inadequacies are identified and publicized, private industry may fill the void.
- (27) Investigate the available processes and methods for recycling solvents and metalworking fluids to determine their:
- Effectiveness for EPA Compliance
  - Effectiveness of process economics
  - Note deficiencies and address research to correcting deficiencies so that acceptable processes will be available to control pollution.
- (28) Review present recycle and disposal methods used by the industry and compare them with present EPA regulations. Note degree of environmental insult and injury occurring and recommend a practical approach to reducing injury. Consider the effect of more regulation, improved recycling and disposal technology or economic incentives. In effect, develop a program to correct the problem where it exists.

## SECTION 4

### CHARACTERIZATION OF METAL FINISHING INDUSTRY

#### 4.1 METAL FINISHING INDUSTRY CATEGORIES

Nearly half of the total industrial activity in the United States is classified as metal finishing. Metal finishing thus comprises the largest single industry segment. It spends 45 percent of total dollars expended by industrial plants for materials, makes 40 percent of all capital expenditures, employs 47 percent of all industrial workers, accounts for 53 percent of the total industry payroll [1] and includes 148,719 plants [2].

The U.S metal finishing industry is classified into eight major groups and 58 subgroups under Standard Industrial Classification (SIC) codes 25 and 33 through 39, as shown in Table 1 [2]. Based on the 1977 Census of Manufacturers [3], except for Alaska, the metal finishing industry was found in all states and the District of Columbia as shown in Table 2 [3]. Seventeen states and the District of Columbia list plant population of less than 1,000. California has the largest metal finishing plant population, 22,296, and is followed by New York with 12,888 plants. An additional 7 states--Illinois, Massachusetts, Michigan, New Jersey, Ohio, Pennsylvania, and Texas--have plant populations of more than 5,000. This is illustrated in Figure 1.

Although all plants use organic fluids and produce organic wastes, it is the larger plants that are likely to generate waste quantities significant enough for economic segregation, reprocessing, and reuse. Out of the total of 148,719 plants, 48,907 (one-third

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- [1] Richards, D. W.; and Suprenant, K. S. Study to support new source performance standards for solvent metal cleaning operations. Appendix reports. U.S. Environmental Protection Agency; 1976 July 30. Contract 68-02-1329, Task Order No. 9.
  - [2] Development document for effluent limitations guidelines and standards for the metal finishing point source category. Washington, DC; U.S. Environmental Protection Agency; 1980 June; 557 p. EPA 440/1-80-091a.
  - [3] 1977 Census of Manufactures, Geographic Area Series MC77-A-1 through MC77-A-51. Washington, DC; U.S. Department of Commerce, Bureau of the Census; 1978.

TABLE 1. SIC CODES COMPRISING THE METAL FINISHING CATEGORY INDUSTRY [2]

<u>SIC major group and subcategory of manufacture with definition</u>	
<u>Major Group 25 Metal Furniture, Except Laboratory and Hospital Furniture</u>	
251	Household Furniture
252	Office Furniture
253	Public Building and Related Furniture
254	Partitions and Fixtures
259	Miscellaneous Furniture and Fixtures
<u>Major Group 33 Primary Metal Products, Except Metal Forgings and Stampings</u>	
331	Blast Furnace and Basic Steel Products
332	Iron and Steel Foundries
333	Primary Nonferrous Metals
334	Secondary Nonferrous Metals
335	Nonferrous Rolling and Drawing
336	Nonferrous Foundries
339	Miscellaneous Primary Metal Products
<u>Major Group 34 Fabricated Metal Products, Except Machinery and Transportation Equipment</u>	
341	Metal Cans and Shipping Containers
342	Cutlery, Hand Tools, and General Hardware
343	Heating Equipment (except Electric and Warm Air, Plumbing Fixtures)
344	Fabricated Structural Metal Products
345	Screw Machine Products, and Bolts, Nuts, Screws, Rivets and Washers
346	Metal Forgings and Stampings
347	Coating, Engraving and Allied Services
348	Ordnance and Accessories, except Vehicles and Guided Missiles
349	Miscellaneous Fabricated Metal Products

(continued)

TABLE 1 (continued)

<u>SIC major group and subcategory of manufacture with definition</u>	
<u>Major Group 35 Machinery, Except Electrical</u>	
351	Engines and Turbines
352	Farm and Garden Machinery and Equipment
353	Construction, Mining and Materials Handling Machinery and Equipment
354	Metalworking Machinery and Equipment
355	Special Industry Machinery, except Metalworking Machinery
356	General Industrial Machinery and Equipment
357	Office, Computing, and Accounting Machines
358	Refrigeration and Service Industry Machinery
359	Miscellaneous Machinery, except Electrical
<u>Major Group 36 Electrical and Electronic Machinery, Equipment and Supplies</u>	
361	Electric Transmission and Distribution Equipment
362	Electrical Industrial Apparatus
363	Household Appliances
364	Electric Lighting and Wiring Equipment
365	Radio and Television Receiving Equipment, except Communication Types
366	Communication Equipment
367	Electronic Components and Accessories
369	Miscellaneous Electrical Machinery, Equipment, and Supplies
<u>Major Group 37 Transportation Equipment</u>	
371	Motor Vehicles and Motor Vehicle Equipment
372	Aircraft and Parts
373	Ship and Boat Building and Repairing
374	Railroad Equipment
375	Motorcycles, Bicycles, and Parts
376	Guided Missiles and Space Vehicles and Parts
379	Miscellaneous Transportation Equipment

(continued)

TABLE 1 (continued)

SIC major group and subcategory of manufacture with definition	
<u>Major Group 38 Measuring, Analyzing and Controlling Instruments: Photographic, Medical and Optical Goods; Watches and Clocks</u>	
381	Engineering, Laboratory, Scientific, and Research Instruments and Associated Equipment
382	Measuring and Controlling Instruments
383	Optical Instruments and Lenses
384	Surgical, Medical, and Dental Instruments and Supplies
385	Ophthalmic Goods
386	Photographic Equipment and Supplies
387	Watches, Clocks, Clockwork Operated Devices, and Parts
<u>Major Group 39 Miscellaneous Manufacturing Industries</u>	
391	Jewelry, Silverware, and Plated Ware
393	Musical Instruments
394	Dolls
395	Pens, Pencils, and Other Office and Artists' Materials
396	Costume Jewelry, Costume Novelties, Buttons and Miscellaneous Notions, except Precious Metal
399	Miscellaneous Manufacturing Industries.

TABLE 2. PLANT POPULATION FOR THE METAL FINISHING  
INDUSTRY BY SIC CODES AND BY STATE [3]

State	1977 SIC Code																	
	25		33		34		35		36		37		38		39		25, 33 thru 39	
									All established instruments								(total)	
	Total	With 20 employ- ees or more	Total	With 20 employ- ees or more	Total	With 20 employ- ees or more	Total	With 20 employ- ees or more	Total	With 20 employ- ees or more	Total	With 20 employ- ees or more	Total	With 20 employ- ees or more	Total	With 20 employ- ees or more		
Alabama	169	62	158	102	437	193	439	112	115	53	158	61	57	16	135	29	1,668	628
Alaska	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Arizona	103	21	64	36	261	62	380	77	159	50	100	23	78	13	219	26	1,364	308
Arkansas	124	51	52	26	216	78	301	65	90	51	121	35	27	6	100	23	1,031	345
California	1,752	570	794	358	4,366	1,396	6,711	1,278	3,047	1,131	1,906	626	1,458	430	2,262	392	22,296	6,181
Colorado	127	28	61	23	318	98	517	112	158	49	113	27	121	29	260	44	1,675	410
Connecticut	113	42	229	122	1,007	418	1,341	313	423	206	169	78	209	108	282	88	3,773	1,375
Delaware	9	1	9	6	47	15	58	12	12	5	12	6	13	5	31	1	191	51
District of Columbia	-	-	-	-	19	6	11	2	-	-	-	-	-	-	17	4	47	12
Florida	546	122	110	49	976	268	1,049	188	506	159	668	169	246	52	669	74	4,770	1,081
Georgia	228	94	85	47	464	180	624	153	165	74	169	61	75	21	207	47	2,017	677
Hawaii	30	6	-	-	36	9	38	3	-	-	21	4	-	-	83	11	208	33
Idaho	20	5	10	4	73	20	129	21	8	2	49	12	-	-	47	5	336	69
Illinois	142	55	583	327	2,647	1,148	3,480	1,036	1,082	557	300	140	484	185	842	255	9,558	3,703
Indiana	242	128	283	184	931	449	1,386	415	329	186	448	243	129	44	267	78	4,015	1,727
Iowa	65	23	77	41	293	118	564	210	95	44	102	38	51	14	142	37	1,289	525
Kansas	80	20	56	29	290	107	559	163	110	37	163	69	41	17	113	17	1,412	459
Kentucky	93	38	61	49	304	146	413	135	110	66	85	34	39	12	112	34	1,217	514
Louisiana	77	13	42	24	282	96	396	102	70	20	224	87	35	6	129	18	1,255	366
Maine	35	12	13	4	86	27	114	31	43	27	86	12	22	5	69	11	468	129
Maryland	108	30	62	30	310	111	346	99	179	80	117	29	107	26	154	34	1,385	439
Massachusetts	295	81	249	129	1,195	440	1,634	439	604	326	189	58	435	173	600	171	5,281	1,817
Michigan	317	132	581	329	2,439	1,060	3,983	1,206	479	201	624	304	261	96	464	89	9,148	3,417
Minnesota	133	38	112	64	609	250	1,112	322	279	120	151	56	145	57	266	59	2,807	966
Mississippi	159	76	36	25	161	70	233	70	73	48	77	36	25	9	70	21	814	355
Missouri	196	70	140	80	620	240	893	223	242	110	194	74	108	42	293	76	2,686	915
Montana	14	4	16	6	44	10	51	7	7	1	24	5	-	-	45	1	201	37

(continued)



TABLE 2 (continued)

1977 SIC Code																		
25		33		34		35		36		37		38		39		25, 33 thru 39 (total)		
State	Total	With 20 employees or more		With 20 employees or more		With 20 employees or more		All established instruments With 20 employees or more		With 20 employees or more		With 20 employees or more		With 20 employees or more		With 20 employees or more		
		Total	more	Total	more	Total	more	Total	more	Total	more	Total	more	Total	more	Total	more	
Nebraska	32	12	26	15	130	53	263	63	50	28	43	15	33	16	73	13	650	21
Nevada	24	5	12	3	65	10	68	7	37	9	21	3	16	3	69	16	310	5
New Hampshire	61	19	39	22	133	38	225	71	110	51	27	5	60	25	63	16	718	24
New Jersey	324	104	314	159	1,555	532	2,173	506	919	390	225	77	431	179	754	240	6,695	2,18
New Mexico	34	3	21	7	74	13	148	18	43	12	20	5	20	4	238	13	598	7
New York	1,028	257	466	223	2,542	780	2,871	636	1,527	581	430	134	854	312	3,170	721	12,888	3,64
North Carolina	664	391	87	45	469	192	841	208	200	98	177	53	78	27	234	49	2,750	1,06
North Dakota	-	-	-	-	23	4	92	25	-	-	11	3	-	-	25	6	151	3
Ohio	307	117	659	403	2,376	1,113	3,683	1,111	647	357	468	224	331	129	590	146	9,061	3,59
Oklahoma	95	16	82	44	448	171	650	154	121	47	184	59	80	21	160	20	1,820	53
Oregon	123	31	72	33	406	122	560	130	149	46	210	56	81	18	185	10	1,786	45
Pennsylvania	454	186	598	355	1,940	828	2,497	732	776	382	341	154	410	154	667	173	7,683	2,97
Rhode Island	36	8	110	38	414	112	319	60	67	35	46	17	48	22	1,051	274	2,031	56
South Carolina	63	29	52	27	232	85	382	112	79	41	70	27	27	11	93	27	998	35
South Dakota	-	-	-	-	35	10	75	23	9	5	26	6	7	4	31	4	183	5
Tennessee	341	132	118	68	522	224	587	162	240	104	198	81	74	18	265	77	2,345	86
Texas	512	184	324	151	1,933	707	2,794	713	674	220	635	198	352	105	733	130	7,957	2,40
Utah	67	20	35	15	164	55	193	48	73	20	57	16	53	13	81	14	723	20
Vermont	27	16	14	7	43	10	85	32	31	11	12	5	11	4	44	7	267	9
Virginia	175	85	64	34	279	118	414	123	175	68	131	49	80	27	130	29	1,448	53
Washington	144	45	55	30	478	124	642	129	205	53	343	89	86	17	278	47	2,231	53
West Virginia	22	11	49	28	151	59	227	50	26	15	29	11	18	6	48	9	549	19
Wisconsin	169	74	233	144	835	351	1,512	520	315	157	178	75	119	50	350	96	3,711	1,46
Wyoming	-	-	-	-	22	4	52	9	-	-	-	-	-	-	-	-	74	1
TOTALS	9,879	3,461	7,313	3,915	33,678	12,740	48,117	12,455	14,936	6,333	10,151	3,649	7,435	2,531	17,210	3,793	14,879	48 90

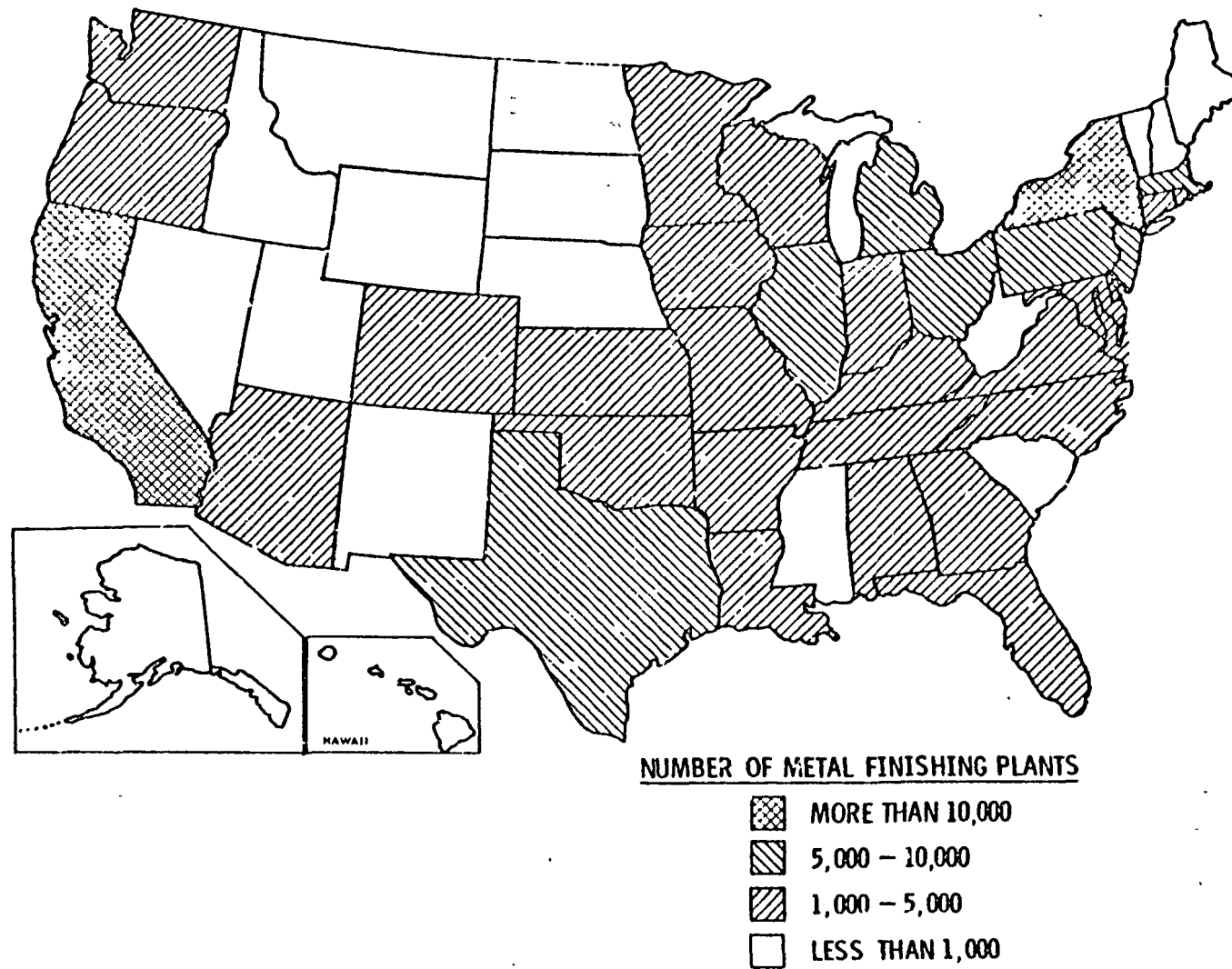


Figure 1. Geographic distribution of metal finishing plants by state [3].

of the total) employ 20 or more employees. The majority of the large plants ( 75 percent), are concentrated in 14 states (California, Connecticut, Florida, Illinois, Massachusetts, Michigan, New Jersey, New York, North Carolina, Ohio, Pennsylvania, Texas, and Wisconsin) with California, Illinois, Michigan, New York and Ohio having the largest populations. This is illustrated in Figure 2.

The metal finishing industry may be categorized on the basis of four factors: (1) plant size (related to the amount of waste produced); (2) type of metal finishing operation(s) used (cutting, cleaning, coating, etc.); (3) type of business association (independent job shop versus in-plant, captive shop); and (4) type of organic material used. Regardless of the size and type of business association (factors 1 and 3), the type of metal finishing operations in use will determine the type of organic waste produced. Metal finishing operations generate oil wastes, solvent cleaning operations generate degreasing solvents, and surface coating operations generate paint sludges. The following three subsections describe the metal finishing industry by these three types of operations.

There are many metal finishing processes and operations but not all of them are included in this study. The following processes are included: (1) metal forming, (2) metal removal, (3) heat treating, (4) coating, and (5) cleaning. These processes and operations included in each process are listed in Table 3. The processes excluded from the study are all metal plating processes, etching, and other chemical treatment processes. These and their respective operations are listed in Table 4. They are excluded either because they are known not to use organic fluids and produce organic wastes or because they have been included in other studies.

#### 4.2 METAL FINISHING INDUSTRY DESCRIPTION

Metal forming operations are not ordinarily included in the metal finishing category, but they are included within the scope of this report because the metal rolling and stamping operations consume an estimated 25 percent of all metal finishing oils [4,5].

Metal finishing oils are also used in metal removal operations (such as cutting), heat treating and rust preventive coating operations. The metal removal operations, such as cutting and grinding use half of all metal finishing oils [4,5]. Heat treating oils and rust protective oils each account for approximately

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[4] Sager, R. C. Comparing lube demand data. Hydrocarbon Processing. 60(7):141-147, 1981 July.

[5] Helm, J. L. Lube-supply problems to crop up in 1980s. Oil & Gas Journal. 89-94, 1979 December 10.

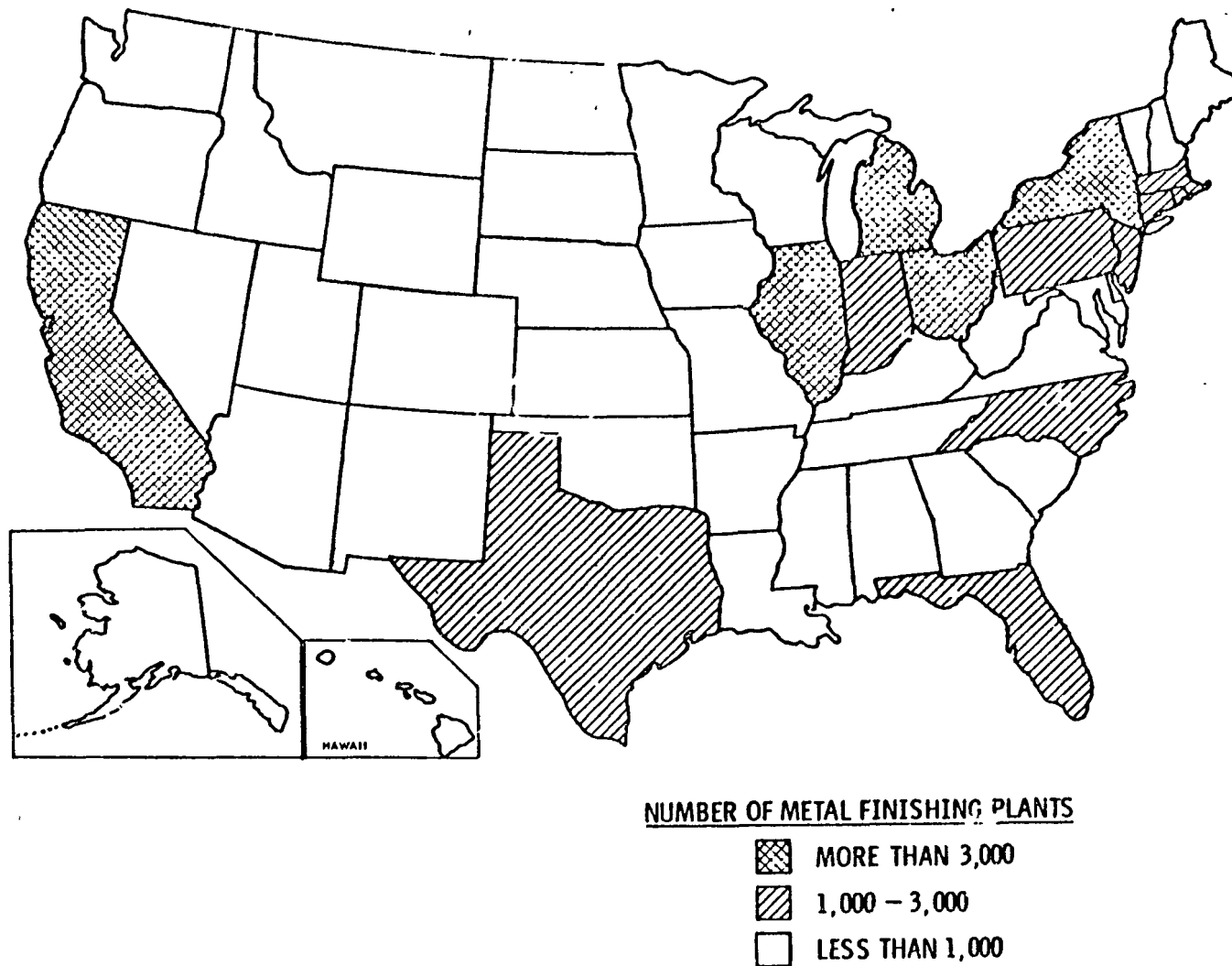


Figure 2. Geographic distribution of metal finishing plants with 20 or more employees by states [3].

TABLE 3. METAL FINISHING PROCESSES AND OPERATIONS INCLUDED IN THE STUDY

Process category				
Forming	Removal	Treatment	Coating	Cleaning
Rolling	Cutting	Quenching	Rust protection (oils)	Solvent cleaning
Casting	Grinding	Tempering	Undercoating	Degreasing
Molding	Polishing		Wax coating	
Stamping	Buffing		Painting	
Blanking	Barrel tumbling			
Drawing	Abrasive machining			
Extrusion				

TABLE 4. METAL FINISHING PROCESSES AND OPERATIONS EXCLUDED FROM THE STUDY

Process category					
Alteration	Removal	Coating	Cleaning	Plating	Chemical
Alloying	Shot blasting	Rubber	Acid	Immersion	Etching
Welding	Sand blasting	Plastic	Alkaline	Electroplating	Polishing
Brazing		Ceramic		Galvanizing	Acid pickling
Soldering		Chromating			Anodizing
		Phosphating			Bright-dipping
		Conversion			Passivating
					Paint curing

ten percent of the usage, while the remaining five percent is for other miscellaneous metalwork applications [4,5].

#### 4.2.1 Industry Size

On the basis of NPRA and U.S. DOE data, total sales of metal finishing oils in 1979 were estimated at 878 million liters (232 million gallons) [4,5].

#### 4.2.2 Growth Trends

Table 5 presents the 1979 sales estimates by metal finishing category, as well as projected demand for metal finishing oils from 1980 to 1990 [4]. Little growth is expected in the demand for metal finishing fluids. The ten-year growth rate for metal finishing oils is expected to average less than one percent per year [4]. By 1982 a no-growth status is predicted for removal oils because of the increased use of water base cutting and grinding fluids [4]. Although the use of treating oils is expected to increase, improved conservation practices are expected to extend fluid life. Forming, protecting, and other metal finishing oils are used in significant quantity for ferrous and nonferrous metal stampings, forgings, and extrusions in the automotive industry, and growth in these areas, if any, should relate directly to automobile production rates [4].

TABLE 5. ESTIMATED 1979 U.S. SALES AND PROJECTED U.S. DEMAND FOR METALWORKING OILS, 1980-1990 [4], MILLIONS OF LITERS

Metalworking category	Year					
	1979	1980	1981	1982	1985	1990
Removal	462	413	416	420	424	424
Forming	219	189	189	197	204	219
Treating	72	64	64	68	72	76
Protecting	98	91	95	98	102	106
Other	27	27	27	27	27	27
TOTAL	878	784	791	810	829	852

#### 4.2.3 SIC Code Description

Metal forming (metal rolling) operations are concentrated in SIC Code 33 (metal rolling) and SIC Code 34 (metal forging and stamping). Metal removal operations, associated with production of finished or semi-finished products, are widespread in SIC Codes 25 and 34-39. Rust preventative (oil) coating and heat treating operations are conducted in all SIC categories. Table 1 in Section 4.1 provides a brief description of the major three digit SIC Codes included in these eight 2-digit SIC Codes.

#### 4.2.4 Geographic Distribution

Figure 3 depicts the nationwide geographic distribution of 1977 sales of all lubricating and industrial oils, including automotive, aviation, and all industrial oils, including metal finishing oils [6]. The metal finishing operations are widespread across the country, although specific regions of the United States have characteristic industries; i.e., automotive production and assembly industries in Ohio and Michigan, steelmaking industries in Illinois and Indiana and aviation-related industries in California [4].

#### 4.3 SOLVENT CLEANING INDUSTRY DESCRIPTION

Industrial cleaning processes can be classified as acid cleaning, alkali cleaning or solvent cleaning. Acid cleaning and alkaline cleaning processes are important in the metal finishing industry but are not included within the scope of this study. Those processes which generate significant amounts of organic wastes are characterized as solvent metal cleaning or degreasing.

There are two basic processes for solvent cleaning: (1) cold cleaning (generally a simple soak, spray or wipe cleaning), and (2) vapor degreasing (cleaning by condensing vaporized solvent on a metal surface).

Degreasing or solvent metal cleaning employs nonaqueous solvents to clean all of the common industrial metals, including malleable, ductile, and gray cast iron; carbon and alloy steel; stainless steel; copper; brass; bronze; zinc; aluminum; magnesium; tin; lead; nickel; and titanium. The degreasing process is adaptable to items of a wide range of sizes and shapes, from transistor components to aircraft sections. The process is also used to clean metal strip and wire at speeds from 45 m/min to 60 m/min [7].

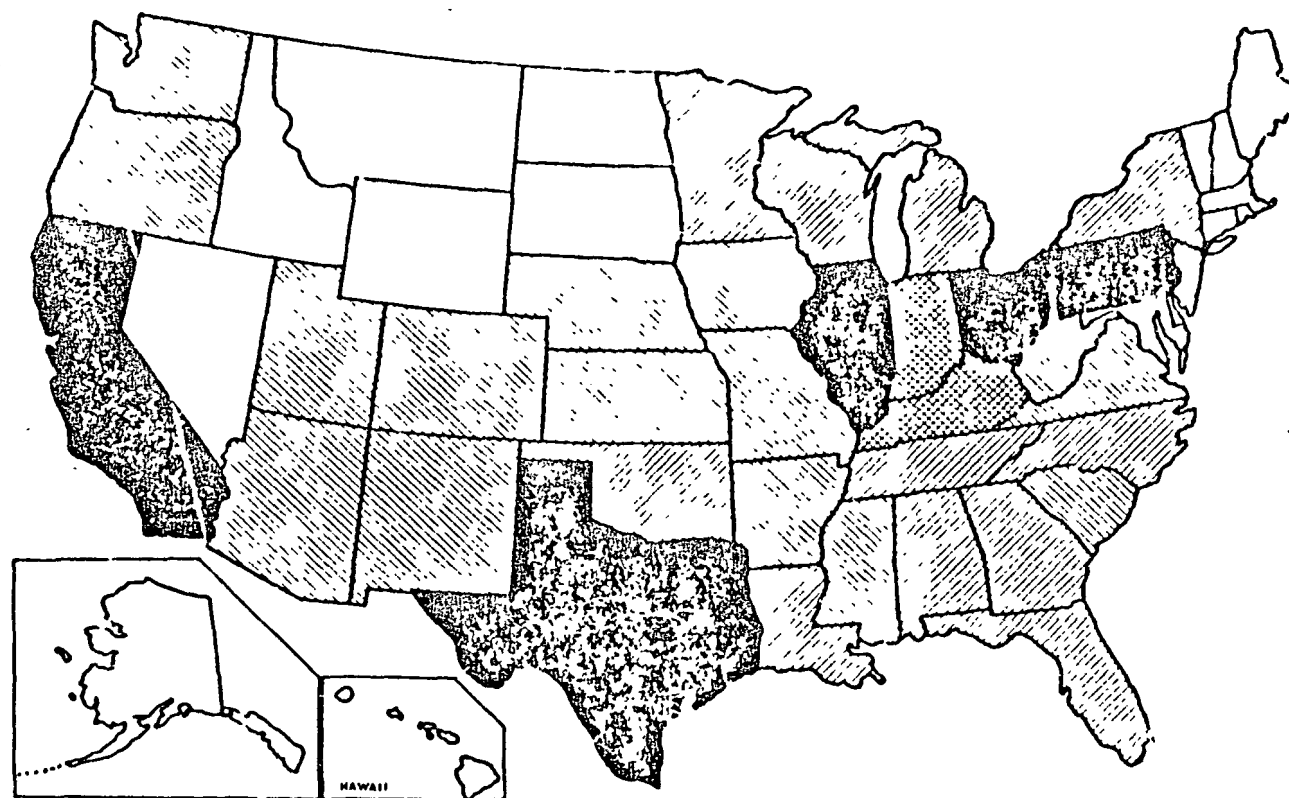
##### 4.3.1 Industry Size

Based on manufacturer surveys and plant visits, the segment of the metal finishing industry performing solvent cleaning-degreasing operations as an integral part of product manufacture is estimated to be 49-51 percent of all industrial manufacturing plants having 20 or more employees [1,3]. The average total amount of organic solvents consumed per year in metal cleaning is estimated at 670 million kilograms (1,500 million lb) [3].

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[6] Sales of lubricating and industrial oils and greases. Current industrial reports series. Washington, DC; U.S. Department of Commerce; Bureau of the Census. 1978 November. 16 p.

[7] Hoogheem, T. J.; Horn, D. A.; Hughes, T. W.; and Marn, P. J. Source assessment: solvent evaporation - degreasing operation. Cincinnati, OH; U.S. Environmental Protection Agency, 1979 August. 133 p. EPA-600/2-79-019f. PB 80-128812.



OILS (1,000 gallons)

- 150,001 - ABOVE
- ▨ 40,001 - 150,000
- ▤ 10,001 - 40,000
- 10,000 - BELOW

Figure 3. Sales of lubricating and industrial oils, by state: 1977 [6].



#### 4.3.2 Growth Trends

The amount of solvent used for industrial cleaning is projected to reach 1,043 million kg/yr (2,300 million lb/yr) by 1985 [3]. Table 6 presents the amounts of degreasing solvents consumed per year in the United States categorized by type of cleaning process and solvent type [7].

TABLE 6. ANNUAL DEGREASING SOLVENT CONSUMPTION,  
BY SOLVENT TYPE [7]

Degreaser type Solvent used	Average solvent consumption, kg/yr
Cold cleaning:	
Butanol	53.6
Acetone	126.3
Methyl ethyl ketone	177.6
Hexane	420.6
Naphthas	454.7
Mineral spirits	420.6
Toluene	256.6
Xylenes	420.6
Cyclohexane	420.6
Benzene	420.6
Ethers	3,410.2
Carbon tetrachloride	68.2
Fluorocarbons	89.7
Methylene chloride	2,187.8
Perchloroethylene	249.2
Trichloroethylene	292.8
Trichloroethane	568.2
Open top vapor degreasing:	
Fluorocarbons	3,806
Methylene chloride	24,518
Perchloroethylene	10,070
Trichloroethylene	7,165
Trichloroethane	16,394
Conveyorized vapor degreasing:	
Fluorocarbons	9,403
Methylene chloride	60,053
Perchloroethylene	24,883
Trichloroethylene	17,780
Trichloroethane	40,468

#### 4.3.3 SIC Code Description

Eight SIC Codes (numbers 25 and 33-39) describe the industrial categories utilizing metal degreasing operations. The number of degreasing operations for each SIC industrial code for 1972 was estimated using percentages calculated from information presented in Reference [1] and the information is presented in Table 7.

TABLE 7. SOLVENT DEGREASING OPERATIONS<sup>a</sup> [7]

Industrial product category	SIC	Number of plants	Estimated number of vapor degreasing operations	Estimated number of cold cleaning operations
Metal furniture	25	9,233	492	23,869
Primary metals	33	6,792	1,547	17,558
Fabricated products	34	29,525	5,140	76,329
Nonelectric machinery	35	40,792	5,302	105,456
Electric equipment	36	12,270	6,302	31,720
Transportation equipment	37	8,802	1,917	22,756
Instruments and clocks	38	5,983	2,559	15,467
Miscellaneous	39	15,187	886	39,262
Subtotal		128,584	24,145	332,417

<sup>a</sup>1972 data.

#### 4.3.4 Geographic Distribution

##### 4.3.4.1 Cold Cleaning--

In 1972 more than half (54 percent) of cold cleaning operations were located in nine states: California, Florida, Illinois, Michigan, New Jersey, New York, Ohio, Pennsylvania, and Texas; Figure 4 illustrates the geographic distribution of the locations of these cold cleaning operations [7]. The remaining plants are distributed throughout all the other states [7].

##### 4.3.4.2 Vapor Degreasing--

In 1972 more than 63 percent of vapor degreasing operations were found in nine states: California, Illinois, Massachusetts, Michigan, New Jersey, New York, Ohio, Pennsylvania, and Texas. The balance of the plants were located in 40 of the remaining 41 states [7]. Figure 5 represents the geographic distribution of vapor degreasing operations [7].

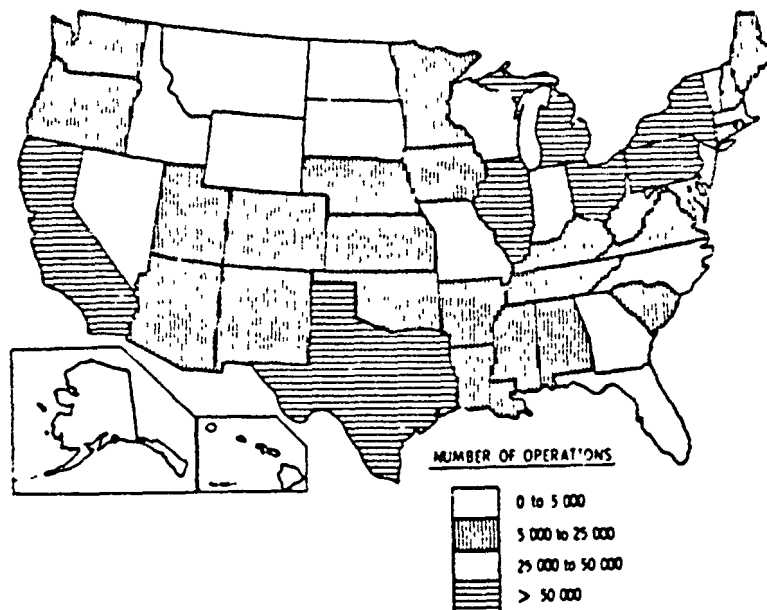


Figure 4. Geographic distribution of cold cleaning operations [7].

#### 4.4 SURFACE COATING INDUSTRY DESCRIPTION

The two categories of products manufactured by the U.S. coatings industry are: (1) architectural coatings, such as exterior and interior house paints, and (2) industrial finishes, including product coatings formulated specifically for original equipment manufacture and applied as part of the manufacturing process, and special purpose coatings such as aerosol paints, roof coatings, and refinish coatings. Figure 6 illustrates the types of coatings produced by the paint and allied products industry [8].

##### 4.4.1 Industry Size

In 1980 the estimated U.S. production of industrial product coatings for original equipment manufacture was over 1.7 billion liters (450 million gallons) [9]. Of this total amount of paint

[8] Hughes, T. W.; Horn, D. A.; Sandy, C. W.; and Serth, R. W. Source assessment: prioritization of air pollution from industrial surface coating operations. Research Triangle Park, NC; U.S. Environmental Protection Agency; 1975 February. EPA-650/2-75-109a.

[9] Dean, J. C. The U.S. coatings industry strategy for survival in the '80s. Chemical Week. 1981 October 21.

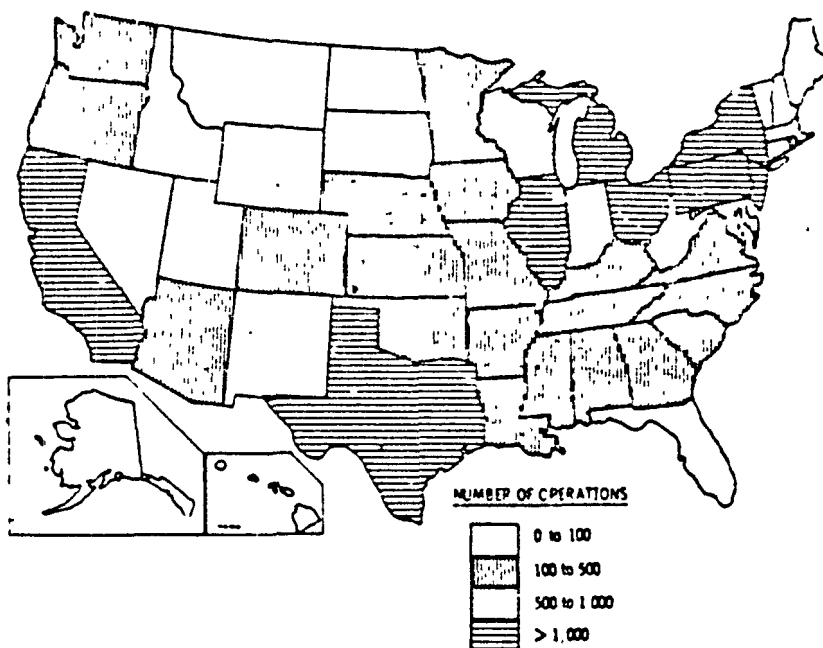


Figure 5. Geographic distribution of vapor degreasing operations [7].

and allied products, an estimated 60 percent consists of volatile compounds such as organic solvents and water. If the volatile portion of the product coatings is disregarded for comparison purposes, the 1980 production can be stated as 680 million dry liters (180 million dry gallons) (40 percent of the preceeding total quantities) [9].

#### 4.4.2 Growth Trends

The production of these products is expected to increase at an average annual rate of 1-1.5 percent for an estimated annual production of 738 million dry liters (195 million dry gallons) by 1990 [9]. Air pollution regulations limiting volatile emissions into the atmosphere will cause an increasing shift from conventional solvent-based coating systems to water-based and high-solids systems. The volatile content of product coatings in 1990 will average 40 percent, down from the present 60 percent [9]. The net result of this shift in product composition will be a decrease in the total volume of product coatings produced in 1990, as indicated in Table 8 [9]. The distribution of product coatings by product category is provided in Table 9 [9].

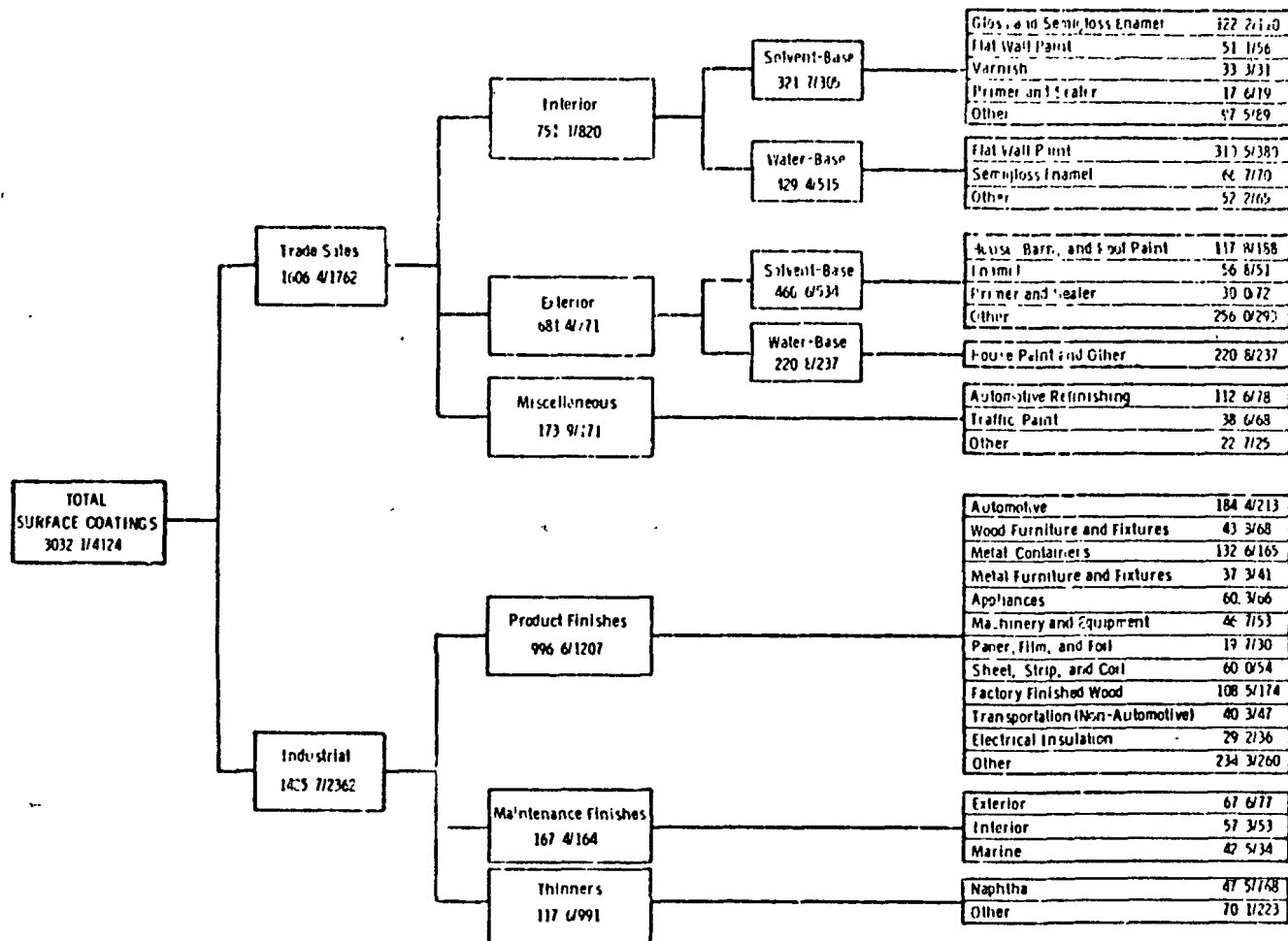


Figure 6. Paints and allied products [8].

TABLE 8. COMPARISON OF ESTIMATED PRODUCTION OF PRODUCT COATING FOR ORIGINAL EQUIPMENT MANUFACTURE IN THE U.S., 1980 AND 1990

	Year	
	1980	1990
Total production, million liters	1,700	1,230
Total production, (nonvolatile ingredients), million dry liters	680	738
Volatile fraction (organic solvents and water), percent	60	40
Nonvolatile fraction (pigments, resins, etc.), percent	40	60

TABLE 9. U.S. PRODUCTION OF PRODUCT COATING FOR ORIGINAL EQUIPMENT MANUFACTURE BY END USE [9]

Product category	Production, millions of dry liters		
	Year		
	1980	1985	1990
Metal coating			
Auto, truck, and bus	114	110	102
Containers, closures, metal deco	83	83	80
Machinery, equipment	72	76	80
Coil, sheet, strip (prefinished)	42	53	68
Appliances	38	38	38
Metal furniture, fixtures	34	34	38
Nonmetal			
Wood furniture, fixtures	117	117	121
Special substances, paper, plastic	72	80	95
Wood and composition flat stock	38	34	34
Other	72	76	83
Total metal coating	382	394	405
Total nonmetal coating	299	307	333
Total production	681	700	738

#### 4.4.3 SIC Code Distribution

Organic product coatings are used in the metal finishing industry in the manufacture of prefinished metal (coil coatings) and for finishing fabricated ferrous and nonferrous metal products such as transportation equipment (auto, truck, and bus), metal containers, electric equipment and nonelectric machinery, metal furniture and household appliances and miscellaneous metal products in SIC Codes 25 and 34-39, as described in Table 1 in Section 4.1. Geographic

distribution by state of metal finishing industries in SIC Codes 25 and 33-39 is presented in Table 2 in Section 4.1.

#### 4.4.4 Geographic Distribution

##### 4.4.4.1 Automobile Coatings--

The automobile<sup>a</sup> industry is the largest manufacturing industry in the United States. Motor vehicle and allied industries account for one-sixth of the Gross National Product. Surface coating is the final and most important automobile finishing process.

At the beginning of 1978, passenger cars and light-duty trucks<sup>b</sup> were being assembled at 45 and 24 locations, respectively, in the United States. Total reported outputs from these plants in 1977 and 1975, respectively, were over 9.1 million passenger cars and over 1.7 million light-duty trucks [10].

Automobile assembly plants are located in 19 states and 43 cities, as shown in Tables 10 and 11. However, over 32 percent of all automobiles and light-duty trucks produced in the United States are manufactured in Michigan [10].

##### 4.4.4.2 Automotive Coatings--

In 1972, according to the Thomas Register of American Manufacturers, there were approximately 8,700 nonautomobile, product-type surface coating plants in the United States each having a total sales volume of \$500,000 per year or more. More than 85 percent of the plants were located in 19 states. These states were: Minnesota, Wisconsin, Iowa, Missouri, Illinois, Indiana, Michigan, Ohio, Pennsylvania, New York, Massachusetts, Connecticut, California, Oregon, Washington, Tennessee, North Carolina, Texas, and New Jersey. The other 15 percent of the plants were located in the remaining 31 states. Only two of the states did not have product-type surface coating plants; these were Alaska and Wyoming [8].

Figure 7 is a graphical presentation of the geographic distribution of these nonautomotive, product surface coating plants, based on 1972 data [8].

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<sup>a</sup>The term "automobile industry" as used here includes both automobile and truck production.

<sup>b</sup>The term "light-duty truck" is defined as "all vehicles with ratings of 8,500 pounds or less GVW." Included in this classification are pickup trucks, vans, panel trucks, station wagons built on pickup truck chassis, multistop trucks, and off-road vehicles.

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[10] Automobile and light-duty truck surface coating operations background information document. Research Triangle Park, NC: U.S. Environmental Protection Agency; 1979 October. 301 p. EPA-450/3-79-030. PB 80-123540.

TABLE 10. GEOGRAPHIC DISTRIBUTION OF U.S. AUTOMOBILE  
ASSEMBLY PLANT PRODUCTION [10]  
(Model Year 1977)

State	City	Percentage	Units
California	(Total)	8.1	740,492
	Fremont	1.8	164,216
	Los Angeles	1.4	128,143
	San Jose	0.7	59,744
	Souch Gate	1.4	131,233
	Van Nuys	2.8	257,156
Delaware	(Total)	4.0	363,202
	Newark	2.5	226,435
	Wilmington	1.5	136,767
Florida	(Total)		-
	Sebring		-
Georgia	(Total)	6.6	595,926
	Atlanta	2.0	186,130
	Doraville	2.7	241,423
	Lakewood	1.9	158,373
Illinois	(Total)	4.5	409,062
	Belvidere	1.9	173,178
	Chicago	2.6	235,884
Kansas	(Total)	2.9	267,110
	Fairfax	2.9	267,110
Kentucky	(Total)	1.1	101,057
	Louisville	1.1	101,057
Maryland	(Total)	2.7	241,171
	Baltimore	2.7	241,171
Massachusetts	(Total)	1.5	135,776
	Framingham	1.5	135,776
Michigan	(Total)	32.3	2,948,759
	Dearborn	1.4	131,016
	Detroit	6.4	587,342
	Flint	4.6	416,459
	Hamtranck	4.2	379,562
	Kalamazoo		-
	Lansing	4.4	404,000
	Pontiac	3.6	326,231
	Wayne	3.0	273,150
	Willow Run	2.8	255,078
	Wixom	1.9	175,921

(continued)



TABLE 10 (continued)

State	City	Percentage	Units
Minnesota	(Total)	1.3	115,464
	Twin Cities	1.3	115,464
Missouri	(Total)	11.1	1,010,786
	Kansas City	1.0	93,946
	Leeds	2.8	252,119
	St. Louis	7.3	664,721
New Jersey	(Total)	6.6	596,791
	Linden	2.7	243,455
	Mahwah	2.9	260,560
	Metuchen	1.0	92,776
New York	(Total)	2.5	230,894
	Tarrytown	2.5	230,894
Ohio	(Total)	7.3	660,101
	Avon Lake	0.4	36,136
	Lorain	2.7	241,017
	Lordstown	1.8	162,029
	Norwood	2.4	220,919
Texas	(Total)	2.5	230,371
	Arlington	2.5	230,371
Wisconsin	(Total)	5.0	457,581
	Janesville	3.0	275,576
	Kenosha	2.0	182,005
United States	TOTAL	100.0	9,104,543

TABLE 11. GEOGRAPHICAL DISTRIBUTION OF U.S. LIGHT-DUTY  
TRUCK ASSEMBLY PLANT PRODUCTION  
(Model Year 1975)

State	City	Percentage	Units
California	(Total)	8	130,829
	Fremont	3	53,000
	San Jose	5	77,829
Georgia	(Total)	4	61,925
	Atlanta	1	13,228
	Doraville		
	Lakewood	3	48,697
Indiana	Fort Wayne		
	South Bend		
Kentucky	(Total)	9	153,404
	Louisville	9	153,404
Maryland	(Total)	4	72,175
	Baltimore	4	72,175
Michigan	(Total)	35	601,456
	Detroit	1	10,543
	Flint	14	250,050
	Warren	12	212,033
	Wayne	8	128,830
Missouri	(Total)	10	181,377
	Kansas City	4	67,946
	Leeds		
	St. Louis	6	113,431
New Jersey	(Total)	3	42,925
	Mahwah	3	42,925
Ohio	(Total)	20	357,502
	Avon Lake	9	143,895
	Lorain		
	Lordstown	6	102,763
	Toledo	3	110,844
Texas	Arlington		
Virginia	(Total)	3	54,777
	Norfolk	3	54,777
Wisconsin	(Total)	4	62,153
	Janesville	4	62,153
United States	TOTAL	100	1,718,523

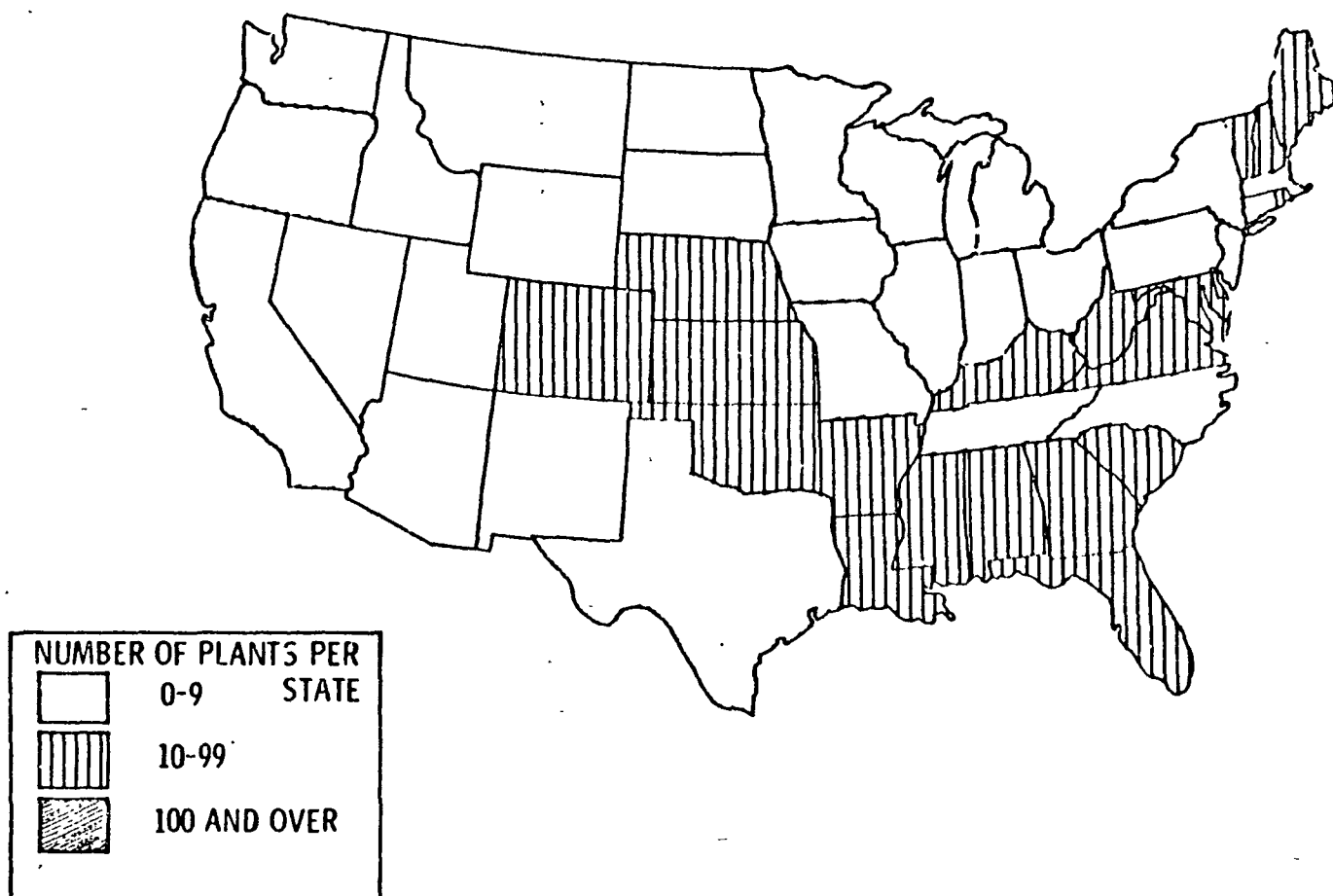


Figure 7. Geographic distribution of nonautomotive product surface coating plants by state<sup>a</sup> [8].

<sup>a</sup>Based on distribution of 8,700 nonautomotive surface coating operations in 1972. For geographic distribution of automotive assembly plants see Table 10.

SECTION 5  
DESCRIPTION OF PROCESS OPERATIONS,  
RAW MATERIALS, AND WASTES

This section describes metal finishing operations including metal working, solvent cleaning, and surface coating, the raw materials used, and the wastes generated.

5.1 METALWORKING

This section describes various metalworking operations, metalworking oils, and the waste oils generated.

5.1.1 Process Descriptions

The metalworking processes utilizing oils include metal forming, metal removal, heat treating, and corrosion-preventive coating processes.

5.1.1.1 Metal Forming--

Metal forming processes are of three major types: (1) casting and molding, (2) hot rolling and cold rolling, and (3) press forming, drawing, and extrusion. All three types of forming operations are conducted on a large scale in metal foundries. Foundries in the United States annually produce 17 million Mg (19 million tons) of cast iron [11], 124 million Mg (137 million tons) of steel [12], and 45 million Mg (50 million tons) of aluminum [13].

Examination of the basic iron casting and steel working processes will illustrate forming, rolling, casting, and molding operations commonly utilized in the production of other metals as well.

- 
- [11] Baldwin, V. H. Environmental assessment of iron casting. Research Triangle Park, NC; U.S. Environmental Protection Agency; 1980 January. 171 p. EPA-600/2-80-021. PB 80-187545.
  - [12] Draft development document for the iron and steel manufacturing point source category. Vol. I, Draft document. Washington, DC; U.S. Environmental Protection Agency; 1979 October. EPA-440/1-79-024a. PB 81-184392.
  - [13] Hotlen, B. W. Bidentate oxygen compounds as boundary lubricants for aluminum. Lubrication Engineering. 398-403, 1974 August.

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Newer technologies for metal forming will be discussed after consideration of the most common processes.

Casting and Molding--Metal castings are produced from iron, steel, alloys of aluminum, copper, brass, nickel, magnesium, or zinc. The technologies for ferrous and nonferrous casting operations are similar, therefore, the discussion will concentrate on iron and steel casting.

Figure 8 is the process flow chart for typical iron foundry casting operations [11]. Figure 9 gives a simplified version of the flow chart, indicating the types of waste expected in casting operations.

In preparation for casting, iron is melted in cupolas, electric arc furnaces, or electric induction furnaces [11]. Various types of processes are used for producing metal castings.

The basic method for casting metal involves pouring the molten metal into a sand mold. A metal casting is produced by filling the cavity in a sand mold with the molten metal, allowing the metal to cool and solidify, then breaking the mold, discarding the sand, and removing the cast metal.

The sand mold is formed by placing a model of wood, metal, or plastic in an appropriately sized container and packing with sand, either by hand or hydraulic press. Clay or other chemical substances are added to increase the shape-retaining ability of the sand. In the next step of the operation, the model is removed and the shaped cavity filled with the molten metal. After the castings are cooled and removed from the molds, excess metal imperfections must be broken or ground off. If the separate parts of the mold did not mate perfectly, there may be a "flash" or sharp edge to be removed [11].

In pressure casting, molds are rectangular blocks of graphite enclosing a cavity of the desired size. A ladle of molten metal is placed in a pressure chamber, which is then sealed. Pressurized air is then directed into the pressure chamber and the molten metal is forced into the graphite chamber through a ceramic pouring tube. The pressure is released from the chamber and the filled mold is removed and allowed to cool [14].

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[14] Proposed development document for effluent limitations guidelines and standards for the iron and steel manufacturing point source category. Volume III - Steel making, vacuum degassing and continuous casting subcategories. Washington, DC; U.S. Environmental Protection Agency; 1980 December. 513 p. EPA-440/1-80-024b. PB 81-184418.

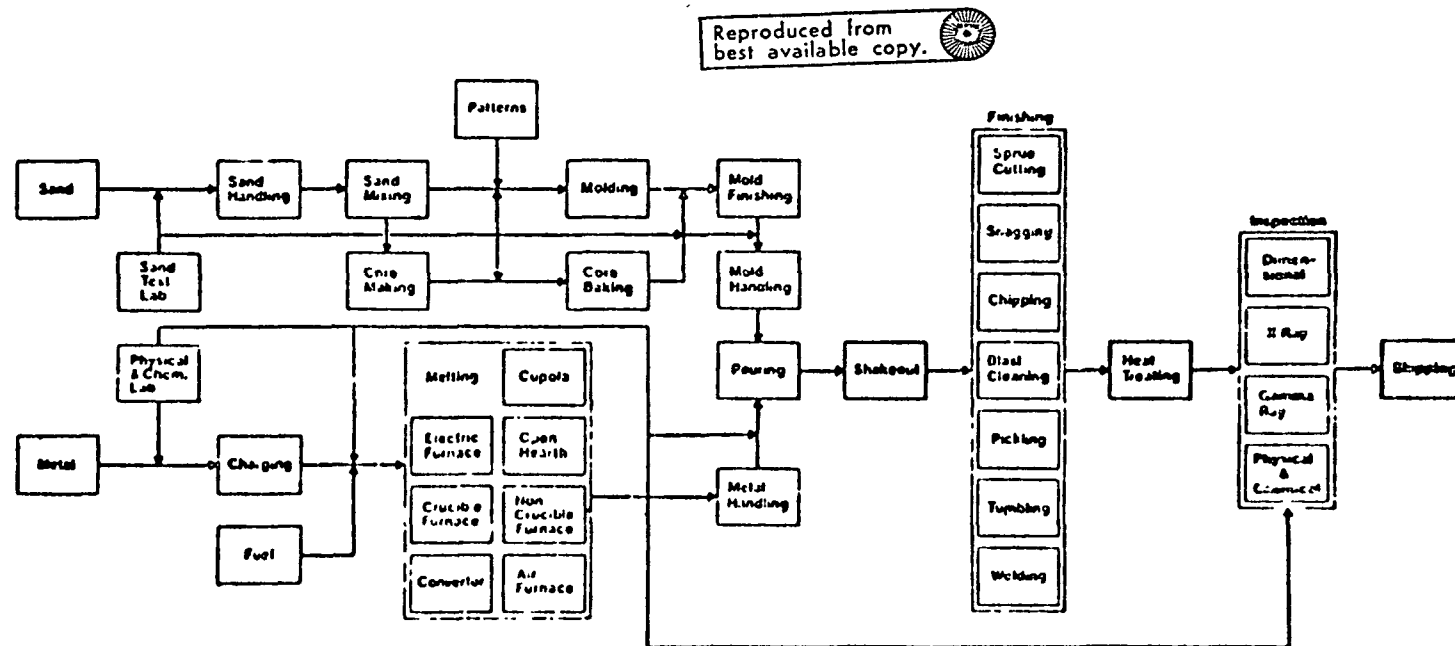


Figure 8. Typical foundry production flow chart [11].

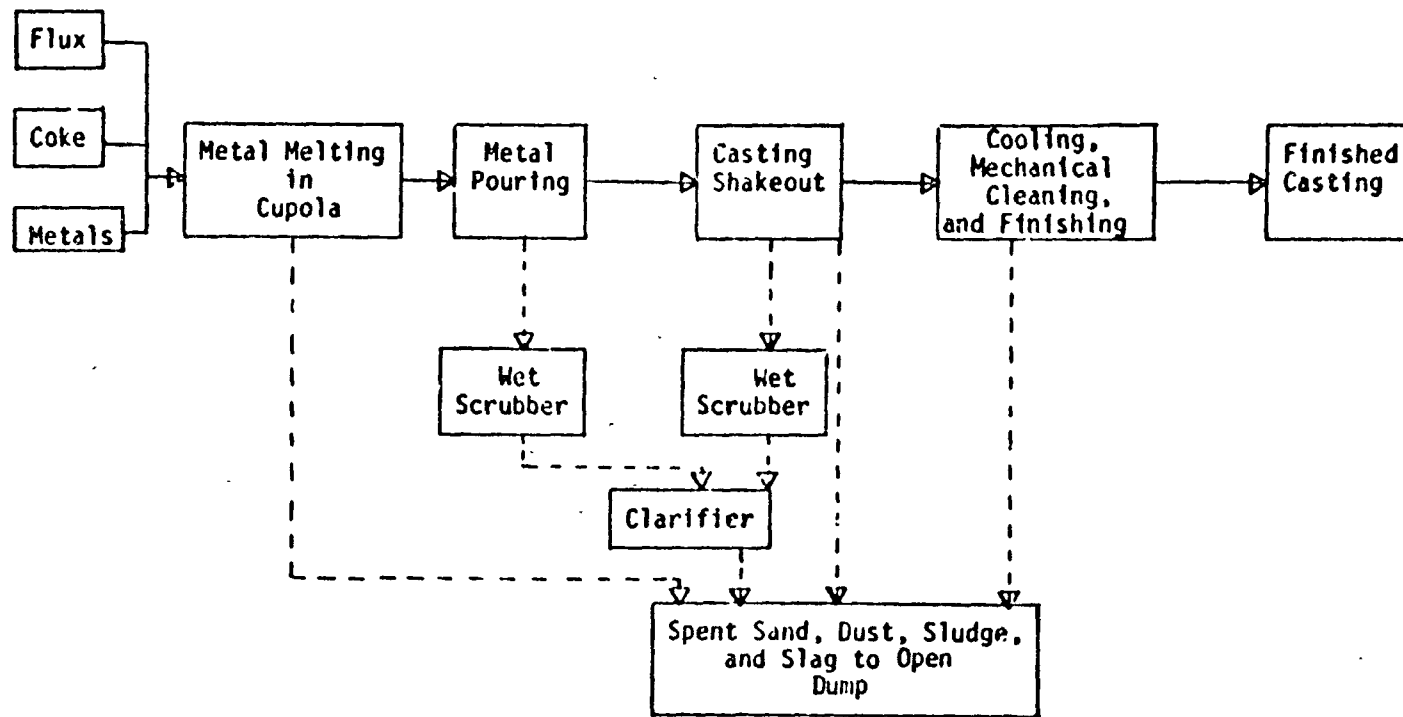


Figure 9. Simplified typical foundry operation [14].



In the continuous casting process, molten steel from the furnace is forced through a water-cooled copper mold to produce a semi-finished product. As the semi-solidified (liquid center) steel emerges from the molds, it is sprayed with water to further cool and solidify the cast product. The semi-finished product then passes into the cut-off zone, where the product is cut to the desired length, as bloom, billet, or slab. One of three configurations is used for continuous casting: vertical casting, vertical casting with bending rolls, or a curved mold design with straightening mechanism. The latter design needs the smallest area for production [14].

Shell molding using a two-piece plastic shell supported by iron shot is employed for the production of high precision castings. Permanent molds of steel, cast iron, or ceramic may be used, although they are more expensive and time-consuming. Physically bonded molding is the newest technology for casting metal using non-chemically-bound sand or powdered iron. Applications of air pressure, magnetic or vacuum molding processes are expected to increase because of their lower potential for environmental pollution [11].

Steelmaking--Basic raw materials for steelmaking are hot metal or pig iron, steel scrap, limestone, dolomite, fluorspar and iron ores. Iron is converted into steel ingots in either an open hearth, basic oxygen, or electric-arc furnace. Use of the slow process open hearth furnace is widespread but declining. The basic oxygen furnace can handle a greater variety of raw materials, and the electric-arc furnace is best suited for production of high quality stainless steels [12].

The molten steel either is cast continuously into products of the desired shape or is cast into ingots for subsequent forming. In conventional casting, the molten steel is tapped into a refractory-lined steel ladle. The ladle is moved by an overhead crane to a pouring platform where the steel is then poured into a series of molds of the desired dimensions. Alloying materials and deoxidizers may be added during the tapping of the charge or in the molds. The steel solidifies in each of the molds to form a casting called an ingot. In the continuous casting process, a ladle of steel is brought and positioned over the tundish which is over the water-cooled copper mold. The ladle nozzle is opened and the tundish is filled with molten steel to the desired depth. Then the tundish nozzles are opened to permit molten steel to enter the molds. The casting then passes through a cooling chamber, straightening mechanism, and cutting device where it is cut into the desired lengths [15].

- [15] Parsons, T., ed. Industry profiles for environmental use: the iron and steel industry. Research Triangle Park, NC; U.S. Environmental Protection Agency; 1977 February. 209 p. EPA-600/2-77-023x. PB 266 226.

Figure 10 presents the flow diagram for the basic steel manufacturing process [12].

Hot Rolling [12]--The temperature of steel ingots is raised in a soaking pit furnace to prepare the steel for hot working (rolling). In the furnace, the steel is heated until it is plastic enough for rolling to the desired shape.

In the rolling of steel to reduce thickness, metal is deformed but not cut. In the rolling process, the same volume of metal leaves the rolls as enters it and therefore the speed of exit of the metal from the rolls is greater than the speed of entry. Some slippage therefore occurs as the metal passes between the rolls. The main properties desired of a rolling fluid are to control the amount of slippage, withstand the high roll pressures, cool the rolls and produce a good quality surface finish on the rolled strip.

The basic operation in a primary mill is the gradual compression of the steel ingot between the surfaces of two rotating rolls and the progression of the ingot through the space between the rolls. The physical properties of the ingot prohibit making the total required deformation of the steel in one pass through the rolls, so a number of passes in sequence are always necessary. As the ingot enters the rolls, high pressure water jets remove surface scale. The ingot is passed back and forth between the horizontal and vertical rolls while manipulators turn the ingot from time to time so that it is well worked on all sides. When the desired shape has been achieved in the rolling operation, the end pieces or crops are removed by electric or hydraulic shears. The semi-finished pieces are stored or sent to reheating furnaces for subsequent rolling into sheets, coils, or other shapes.

Ever increasing attention is being devoted to the conditioning of semi-finished products as the requirements for high quality steel products increases. Major elements in this area involve the need for removing surface defects from blooms, billets, and slabs prior to shaping, as by rolling into a product for the market. Such defects as rolled seams, light scabs, checks, etc., generally retain their identity during subsequent forming processes and result in products of inferior quality. These surface defects may be removed by hand chipping, machine chipping, grinding, milling, and scarfing. Scarfing removes defects with an oxyacetylene torch, either by a manual process or with a production machine.

Merchant-bar, rod, and wire mills produce a wide variety of products in continuous operations ranging from shapes of small size through bars and rods. The designations of the various mills as well as the classification of their products are not very well defined within the industry; in general, a small cross-sectional area and a very long length distinguish the products of these mills. Raw materials for these mills are reheated billets. Many older mills use hand looping operations in which the material is

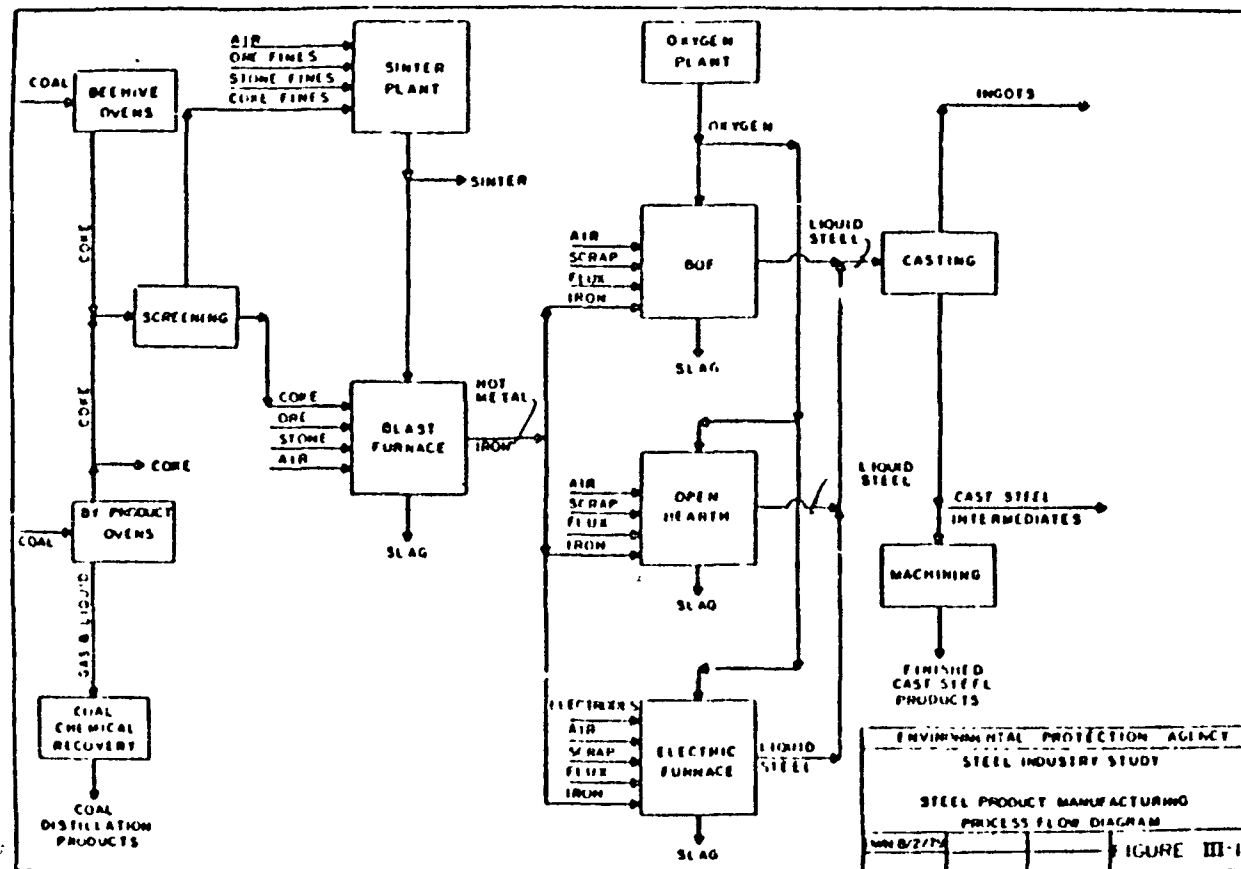


Figure 10. Steel manufacturing process flow diagram [12].

passed from mill stand to mill stand. As with other rolling operations, the billet is progressively squeezed and shaped to the desired product dimensions in a series of rolls. Water sprays are used throughout the operation to remove scale.

The continuous hot strip mill utilizes slabs which are brought to rolling temperatures in continuous reheating furnaces; the conditioned slabs pass through scale breakers and high pressure water sprays which dislodge the loosened scale. A series of roughing stands and a rotary crop shear produce a section that can be finished to a coil of the proper weight and gauge. The second scale breaker and high pressure water sprays precede the finishing stand train in which the final size reductions are made. Cooling water is applied through sprays on the run-out table, and the finished strip is coiled. Such a mill can turn a 6-foot thick slab of steel into a thin strip or sheet a quarter of a mile long in three minutes or less. The product of the modern hot strip mill may be sold as produced, or used within the mill for further processing in cold reduction mills, and for plated or coated products.

Welded tubular products are made from hot-rolled skelp with square or slightly beveled edges, the width and thickness of the skelp being selected to suit the various sizes and wall thicknesses to be made. The coiled skelp is uncoiled, heated, and fed through forming and welding rolls where the edges are pressed together at high temperature to form a weld. Welded pipe or tube can also be made by the electric weld process, where the weld is made by either fusion or resistance welding.

Seamless tubular products are made by rotary piercing of a solid round bar or billet, followed by various forming operations to produce the required size and wall thickness.

The product flow of typical steel mill operations is illustrated in Figure 11.

Cold Rolling [16]--Cold rolling is that operation where unheated metal is passed through a pair of rolls to reduce its thickness, to produce a smooth dense surface, and to develop controlled mechanical properties of the metal.

Direct application, recirculation, or combination systems are used for oil application at cold rolling mills. A general process diagram of the recirculation system is shown in Figure 12.

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[16] Proposed development document for effluent limitation guidelines and standards for the iron and steel manufacturing point source category. Volume VI. Cold forming, alkaline cleaning. Washington, DC; U.S. Environmental Protection Agency; 1980 December. 604 p. EPA-440/1-80-024b. PB 81-184442.

FIGURE III-2

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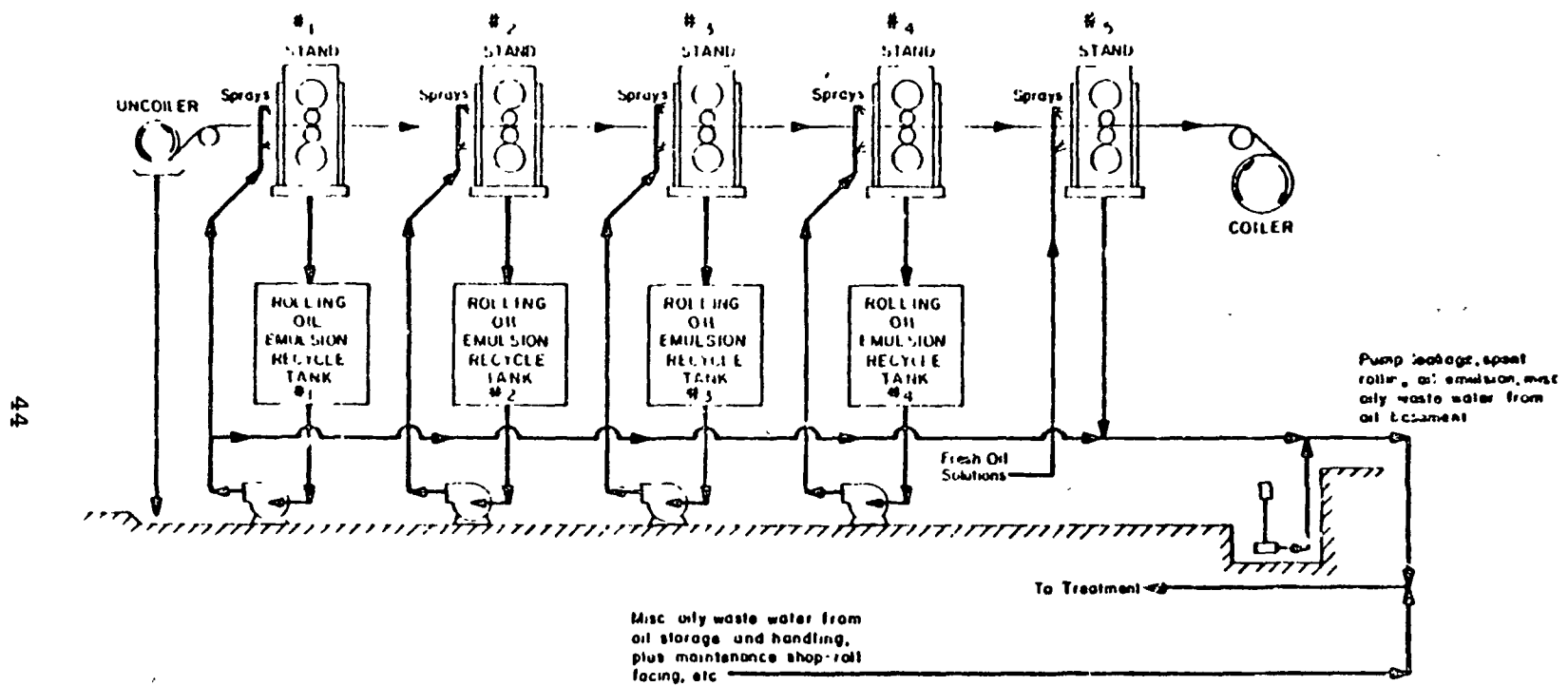


Figure 12. Process diagram for cold rolling oil application recirculation system [16].

There are various types of cold rolling processes. Cold reduction is a special form of cold rolling in which the thickness of the product is reduced by relatively large amounts in each pass through the rolls. In the production of most cold rolled materials, the cold reduction process is used to reduce the thickness of the hot rolled breakdown between 25 percent and 90 percent.

Cold rolled strip, cold rolled sheet, and cold rolled flat bar are the principal cold reduced flat products. Carbon, alloy or stainless steels are used, depending on the end use of the products.

Most rolled products are carbon steel in sheet form and are used as base material for such coated products as long terne sheets, galvanized sheets, aluminum coated sheets, tin-plate, or tin-free steel. Hot rolled coils called "breakdowns" are the base material used in the cold rolling operation. Prior to rolling, however, they must be descaled and pickled, usually in a continuous pickling operation.

There are several types of cold reduction mills which vary in design from single stand reversing mills to continuous mills with up to six stands in tandem (in series). In the single stand reversing mill, the product is rolled back and forth between the work rolls until the desired thickness and mechanical and surface characteristics are achieved. In the single stand nonreversing mill, the material makes a single pass through the rolls and is recoiled. If additional rolling is required, the coil is returned to the head of the mill and reworked. The single stand nonreversing mill is generally used for tempering operations.

Most cold reduced flat steel is rolled on continuous three, four, or five stand tandem mills. In these mills, the material continually passes from roll to roll until the desired thickness is attained. The continuous rolling mills represent modern technology and is the type of equipment installed in new mills.

A typical modern cold rolling shop contains a continuous pickling operation (sulfuric or hydrochloric acid) to remove scale and rust from the hot rolled breakdown coil. As it leaves the pickler the strip is oiled to prevent rusting and to act as a lubricant in the cold rolling mill. The coil is then fed into a continuous cold rolling reducing mill that can contain up to six rolling stands in tandem. Each stand contributing to the reduction in thickness of the material, the first contributes the greatest reduction while the last stand acts as a straightening, finishing, and gauging roll. Unlike hot forming, no scale is formed during this operation.

The properties of hot rolled seamless pipe can be improved by cold working the product. Cold working the pipe increases its yield strength and generally improves the product. One method of cold working is the seamless pipe method, in which the hot rolled

pipe is dropped into an expander trough and clamped with one end held firmly against a backstop. A long ram is positioned at the opposite end of the pipe, and an expander plug is forced through the pipe by extreme pressure. The plug is lubricated through the ram head with a water soluble oil. After cold expansion, the seamless pipe enters a rotary straightener and then is hydrostatically tested [16].

Drawing--While most quality requirements for seamless pipe and tubing products can be met by the hot rolling processes, some pipe and tube specifications require closer tolerance, enhanced physical and surface properties, thinner walls, and smaller diameters than can be met by cold drawing the hot rolled tubes in a finishing operation.

The process consists of pulling a cold tube through a die, the hole of which is smaller than the outside diameter of the tube being drawn. At the same time, the inside surface of the tube is supported by a mandrel anchored on the end of a rod, so that the mandrel remains in the plane of the die during the drawing operation. Another method involves using an internal bar rather than a stationary mandrel. This bar travels along with the tube, as it is drawn through the die. The hot rolled tubes are crimped and pointed on one end, so that the pipe section can pass through the die and permit the jaws of the puller mechanism to grip the end of the tube. Some tubes of certain steel grades are annealed prior to the cold drawing operation. All tubes are pickled to remove scale and oxides, rinsed, and then dipped into a lubricant tub (flour, tallow and water, or a special oil emulsion for a bright finish) prior to the cold drawing operation [16].

Wire Drawing--Wire drawing bears some similarity to cold rolling, in that the same volume of metal leaves the die as enters it and metal deformation takes place with some slippage in the die. The speed of exit of the metal from the die is greater than the speed of entry, because the wire drawing operation reduces the cross-sectional area of the wire. The exit speed may be several hundred feet per minute, many times the entry speed into the initial die. In a wire drawing train, the wire is pulled through a series of dies so that the diameter of the wire is progressively reduced. Between each die, the wire is passed around rollers to obtain the desired tension. The art of wire drawing is a complex phenomenon and much depends upon the skill of the operators. The lubrication of the wire during its passage through the die plays an important role, particularly with regard to lessening the amount of die wear [17]. Figure 13 presents a representation of the process for wire drawing.

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[17] Billett, M. Industrial lubrication. New York, Pergamon Press, 1979. 136 p.



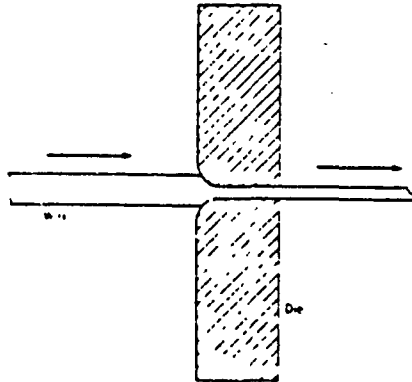


Figure 13. Wire drawing [17].

Press Forming and Extrusion--The term press work is used by the metals industry to embrace almost all press operations including stamping, blanking, forming, and related processes. Blanking is a process accomplished with dies in presses in which desired shapes are cut from flat or preformed stock. A blank is usually the workpiece for subsequent forming or machining, but may constitute a finished product in some cases. A number of processes are used in press forming, the choice depending on the type of shape needed. These include drawing, bending, stamping, and coining. Although cold forming is most common, hot forming is used for very heavy stock. Some forming operations are dry and in others a lubricant is used [18]. For hot forging on a hydraulic press, adequate lubrication of dies is essential, due to longer contact times in this type of forging. Although a lower sliding friction is desirable at the die-workpiece interface, one of the main functions of the die lubricant is to act as an intermediate layer between the die and the workpiece. This prevents seizing on the die and reduces die wear. Further, the axial motion of the dies causes radial flow of metal on the die surface. This tends to wipe the lubricant off the die surface. Thus, hot-forging lubricants should withstand high temperatures under high pressures and sliding contact [19].

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- [18] Levin, J.; Beeland, G.; Greenberg, J.; and Peters, G. Assessment of industrial hazardous waste practices special machinery manufacturing industries. Washington, DC; U.S. Environmental Protection Agency; 1977 March. 328 p. EPA-530/SW-141c. PB 265 981.
  - [19] Lahoti, G. D.; Nagpal, V.; and Altan, T. Selection of lubricants in hot forging and extrusion. First international conference on lubrication challenges in metalworking and processing. Chicago, ITT Research Institute, 1978, 52-59.

Extrusion--There are two alternative methods, forward or direct extrusion and backward or indirect extrusion. In the process of forward extrusion, the metal is pushed through a die, when it is required to form it into a desired component shape (Figure 14). It thus differs from wire drawing, where metal is continuously being pulled through a die. However, as with wire drawing, the pressures involved in the cold extrusion process are extremely high as are the resulting temperatures. Most attempts to avoid the necessity to phosphate the metal surface of the component to be extruded and to use only a lubricant, without an underlying key, have not been successful. A similar lubrication situation exists with backward extrusion, in which a punch is used to cause metal flow back over the punch tool surface to form the component shape. In contrast to forward extrusion, the metal is not pushed forward through a die (Figure 14) [17].

Titanium alloys, alloy steels, stainless steels, and tool steels are extruded on a commercial basis using a variety of graphite and glass base lubricants. In the patented Sejournet process, the heated billet is commonly rolled over a bed of ground glass, or it is sprinkled with glass powder which supplies a layer of low-melting glass to the billet surface. Prior to insertion of the billet into the container, a suitable die glass lubricating system is positioned immediately ahead of the die. This may consist of a compacted glass pad, glass wool, or both. The prelubricated billet is quickly inserted into the container followed by appropriate followers or a dummy block, and the extrusion cycle is started. The unique features of glass as a lubricant are its ability to soften selectively during contact with the hot billet and, at the same time, to insulate the hot-billet material from the tooling, which is usually maintained at a temperature considerably lower than that of the billet [20].

#### 5.1.1.2 Metal Removal--

Metal removal or machining processes are of four major types: (1) cutting, (2) grinding, (3) polishing and buffing, and (4) mass finishing and barrel tumbling.

Machining, according to the definition of the metalworking industry, is the removal of material in the form of chips from metal parts, usually through the use of a machine tool. The factors involved in machining are the workpiece, machine tool, cutting tool, and cutting fluid. Grinding is a form of cutting in which abrasive grains in a grinding wheel act as the cutters.

The machine shop equipment used in plants for metalworking includes: engine and turret lathes, milling machines, drill presses and electric drills, grinders of several types, boring mills,

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[20] Cook, C. R. Lubricants for high temperature extrusion. 28:199-218, 1971 June.

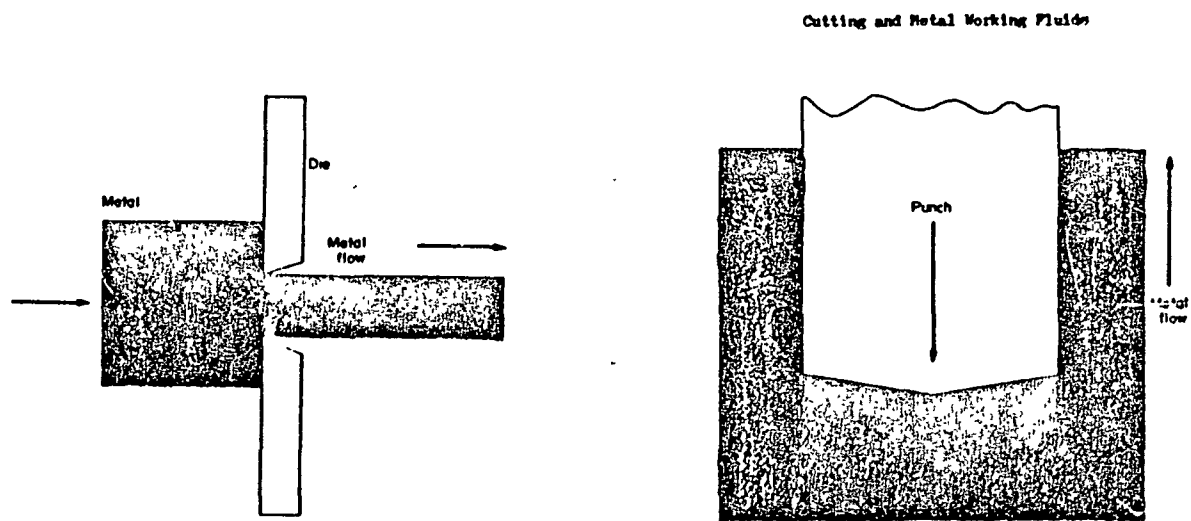


Figure 14. Forward extrusion/backward extrusion [17].

planers and hand and cut-off saws. These tools are capable of functions with a wide variety of nomenclature but they all fall within the general category of cutting and shaping. Several machining operations are often carried out in conjunction with each other and many pieces of equipment are capable of performing more than one machining function. A typical machining process is shown schematically in Figure 15 [18].

Examples of the machining operations which are common to many metalworking establishments include: milling, facing, turning, grinding, boring, drilling, reaming, sawing, and planing. All of them remove metal which may be in the form of chips, turnings, grindings, borings, etc.

When metal is cut by any of the above methods, heat is generated. Continuous cooling and lubrication are usually necessary to protect both the tool and the workpiece from damage and to facilitate cutting action. These functions are accomplished by the use of cutting fluids, or coolants, which also flush away metal chips, reduce strain hardening of the metal, and prevent rust. Cast iron and some nonferrous materials do not require the use of cutting fluids [18].

Cutting [17]--In a metal cutting operation, a tool shears the metal and the sheared metal removed from the workpiece forms into either continuous or discontinuous chips (Figure 16). The energy resulting from the shearing of the metal is dissipated through the workpiece and tool, in the form of heat. Additional frictional heat is also produced by the flow and rubbing of the metal chips, as they are formed, over the surface of the cutting tool. The total heat released may cause the building up of some sheared metal on the tool surface, a phenomenon known as a built-up edge. This welding of tool to workpiece can be avoided by the rapid removal of the heat evolved and also by decreasing the total amount produced, by reducing the frictional heat component.

A copious, well-directed supply of cutting fluid can remove sufficient heat by metal surface cooling, as the fluid can penetrate fairly well into the region where the formed chip is rubbing over the tool, producing the frictional heat. The fluid can also lubricate the passage of the chip over the tool. The two main requirements for cutting fluids are, therefore, the ability to maintain the tool and workpiece at acceptable temperature levels and to reduce the frictional heat formed during the cutting operation.

In all cutting oil applications, whether with neat or water-based fluids, it is important to maintain a copious supply of fluid to the cutting zone. This is especially important when ceramic or cemented carbide tools are used. An interruption in fluid flow will allow large temperature variations in the tool, with the possibility of cracking of the tool tip and its early breakdown.

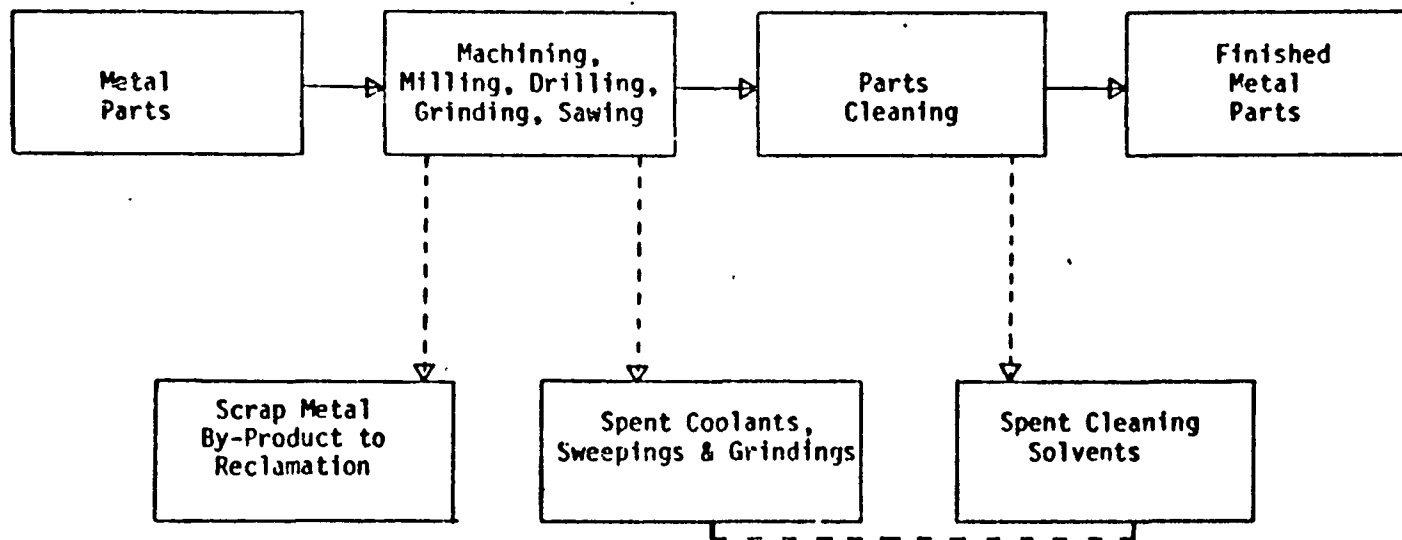


Figure 15. Simplified typical machining operation [18].

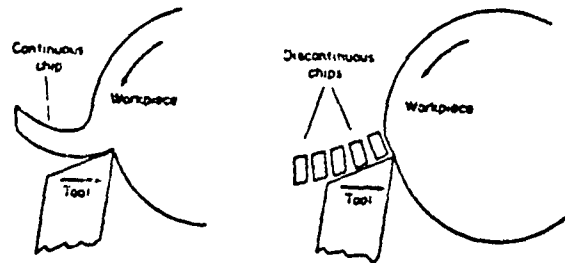


Figure 16. Cutting tool chip formation [17].

The correct use of cutting fluids allows increased rates of production to be achieved in workshops. This is due to the increase of tool life obtained by reducing the tool wear, improving the stock removal rate, making power savings and obtaining better component surface finish, with more accurate dimensional tolerances. A further advantage of using a cutting fluid is that with ferrous components, the residual fluid remaining on the surfaces after the machining operation prevents rusting occurring.

Grinding--Grinding is the application of abrasives to a workpiece to effect the removal of surface material. In metal finishing shops, grinding may be performed to achieve a desired surface finish, to remove undesirable material from the surface, to remove burrs or sharp edges, or to achieve close dimensional tolerance.

Grinding equipment includes belts, disks, or wheels consisting of or covered with various abrasives; e.g., silica, alumina, silicon carbide, garnet, alundum, or emery. Grinding equipment may be portable or stationary. Grinding may be with or without the use of lubricants or coolants such as water or water-based mixtures, solutions, or emulsions containing cutting oils, soaps, detergents, wetting agents, or proprietary compounds. Auxiliary equipment associated with grinding operations includes hoods, vents, ducts, and dust collectors, and in the case of wet grinding, tanks, pumps, and pipes for the supply, collection, and recycle of lubricants or coolants [21].

Polishing and Buffing--Polishing operations are performed for the purpose of achieving an intermediate surface which can be refined further, normally by buffing, prior to plating or surface coating. The purpose of buffing is to smooth and brighten the surface without much metal removal.

- [21] Hollowell, J. B.; Valter, L. E.; Gurlis, J. A.; and Layer, C. H. Assessment of industrial hazardous waste practices - electroplating and metal finishing industries - job shops. Washington, DC; U.S. Environmental Protection Agency; 1976 September. 516 p. PB 264 349.

Polishing is carried out on hard-faced wheels varying in diameter, thickness, and material depending upon the part that is being processed, the finish, and the material-removal rate desired. Wheels are constructed of woven cotton fabrics, canvas, felt, or leather discs glued or sewn together, or a combination of glued and sewn discs. Felt wheels are used where true surfaces are required or where a contoured shape is being finished. Leather wheels produce a finer finish, and wood wheels covered with leather are normally used for flat surfaces.

Abrasives are generally applied to these belts or wheels with synthetic adhesives or cements which have generally replaced the hide glue formerly used. The ratio of abrasive to glue used in the facing of the wheels changes with grit size [21].

The power is generally transmitted to the coated abrasive belt through a contact wheel, which is a multi-purpose component and plays a crucial role in stock removed per time interval, finish generated and belt life, hence, cost of operation.

Figure 17 illustrates a typical design for an abrasive-coated polishing belt [22].

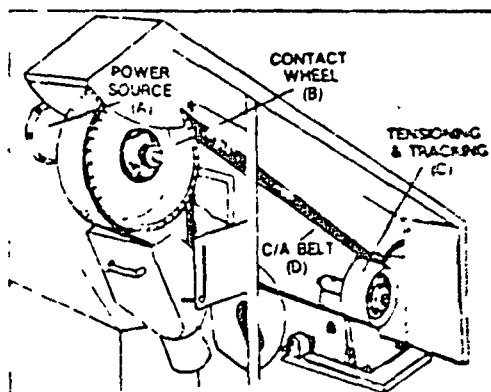


Figure 17. The abrasive coated belt for polishing and buffing [22].

Table 12 provides a listing of typical specifications for polishing and grinding various metals with an abrasive-coated belt [22].

Mass Finishing and Barrel Tumbling--Mass finishing is a process of deburring, edge and corner radiusing, and surface finishing a quantity of components in bulk by mechanical means. Improvement of surface includes removal of rust and scale, reduction of surface

[22] Leggett, R. The coated belt: a production tool. Metal Finishing. 75(12):9-15, 1977 December.

TABLE 12. POLISHING AND GRINDING WITH AN ABRASIVE-COATED BELT [22]

Material	Operation	Abrasive	Grits	Belt speed	Lubricant	Contact wheel type	Durometer/hardness
Hot and cold rolled steel	Grinding	ZA or A/O	24-60	4000-7000	Dry	Cog tooth or serrated	70-95
	Polishing	ZA or A/O	80-150	4000-7000	Dry or light grease	Plain face rubber, canvas	40-79 Medium
	Fine Polishing	A/O	180-320	1000-7000	Heavy grease or polishing oil	Plain face rubber, canvas, cloth	Soft
Stainless steel	Grinding	ZA or A/O	36-60	3000-5000	Dry	Cog tooth or serrated	70-95
	Polishing	ZA or A/O	80-150	3000-5000	Dry or light grease	Plain face rubber	40-70
	Fine Polishing	A/O or S/C	180-240	3000-5000	Heavy grease or polishing oil	Plain face rubber, canvas, cloth	Soft
Aluminum	Grinding	ZA or A/O	24-80	4000-7000	Light grease	Cog tooth or serrated	70-95
	Polishing	A/O or S/C	100-180	4000-7000	Light grease	Plain face rubber	40-70 Medium
	Fine polishing	A/O or S/C	220-320	4000-7000	Light grease or heavy grease	Plain face rubber, canvas, cloth	Soft
Copper and copper alloys	Grinding	A/O or S/C	36-80	3000-7000	Light grease	Cog tooth or serrated	70-95
	Polishing	A/O or S/C	100-150	3000-7000	Light grease	Plain face rubber, canvas, cloth	40-70 Medium
	Fine polishing	A/O or S/C	180-320	3000-7000	Light grease or heavy grease	Plain face rubber, canvas, cloth	Soft
Nonferrous die castings	Grinding	ZA or A/O	24-80	5000-7000	Light grease	Serrated or plain	70-95
	Polishing	A/O or S/C	100-180	5000-7000	Light grease	Plain face rubber, canvas, cloth	40-70 Medium
	Fine polishing	A/O or S/C	220-320	5000-7000	Light grease or heavy grease	Plain face rubber, canvas, cloth	Soft
Cast iron	Grinding	ZA or A/O	24-60	2000-5000	Dry	Cog tooth or serrated	70-95
	Polishing	ZA or A/O	80-150	2000-5000	Dry	Serrated or plain	40-70
	Fine polishing	ZA or A/O	150-240	2000-5000	Light grease	Plain rubber	30-50
Titanium	Grinding	ZA or S/C	36-60	1000-2500	Dry	Cog tooth or serrated	70-95
	Polishing	S/C	80-120	1000-2500	Light grease	Serrated or plain	40-70
	Fine polishing	S/C	150-240	1000-2500	Light grease	Plain face rubber, canvas, cloth	Soft



profile and generating suitable surface textures for decorative reasons or subsequent paint or chemical coatings. All mass finishing techniques are based on the principle of loading components to be finished into a container together with media, the media being natural stones, manufactured nuggets, or abrasives bonded into various ceramic and plastic shapes. Media can also include steel shapes, wood pegs, leather pieces and, on occasion, the components themselves can act as their own media for what is commonly called, "part on part" processing. Generally, water and some form of compound are also added to the container during operation. Some form of action is applied to the container to cause the media to rub against component surfaces, edges, and corners [22].

The basic limitations of mass finishing are that, generally, action will be effective on all the surface edges and corners of the part, and it is not normally possible to give preferential treatment to one area compared with another. Action will be greater on corners than on similarly exposed surfaces. Action in holes and recesses is significantly less than on exposed areas and, in small deep recesses, it is unusual to be able to do any significant work at all [23].

In rotating barrel finishing the drum is loaded approximately 60 percent full with the mixture of parts and media. For normal operations, loading higher than 60 percent slows down the action, and lesser loading is wasting space. For most operations, water is added about level to the top of the load. Increasing amounts of water provide gentle action but slow down the process, reducing the water level can increase the action, but can also produce problems with maintenance of cleanliness and consistency. Compounds are usually added as a means of increasing abrading or polishing action, and to keep components and media clean, inhibit corrosion, soften the water, etc.

The finishing action within a tumbling barrel results from parts and media sliding down the slope formed by barrel rotation and, hence, rubbing against each other. It is possible to automate barrel tumbling equipment. This process incorporates its own material handling system. The drum rotates in a clockwise direction for finishing the parts. Then, at the end of the process, the drum's rotation is reversed and parts are fed out through a screener [23].

Centrifugal barrel finishing, like tumbling, uses abrasive media, compound and water to deburr and surface finish a variety of components, but the centrifugal action results in very fast, highly controllable deburring, radius, and finishing operations, together

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[23] Hignett, B. Mass finishing. Metal Finishing. 76(7):17-21, 1978 July.

with the capability of imparting very high compressive stresses in the surface of components.

In the operation of centrifugal barrel finishing, a number of drums are mounted on the periphery of a turret. The turret rotates at a high speed in one direction while the drums are rotated in a slower speed in the direction opposite to that of the turret. Drums are generally loaded in a manner similar to that for normal tumbling or vibratory operations, that is, with parts, media, water, and some form of compound. Turret rotation creates a high centrifugal force, up to as much as 50 gravities, compacting the load within the drums into a tight mass. Rotation of the drums causes the media to slide against the work load, removing burrs and refining the surfaces [23].

Vibratory deburring equipment is faster and more convenient than tumbling barrels. It also has the capability of getting more action in recesses of components. In addition, vibratory machines can process larger components than those that can be handled in normal barrels, without fixtures and with less likelihood of damage. Modern tub type vibrators are made long enough to process components up to about 9 meters (30 feet) long, such as wing spars. With the long tub-type vibrators, it is possible to have fully automated, continuous processing of small parts loading at one end of the tub, with unloading at the far end through a separator where media can be returned to the load end on a conveyor.

Round style or donut vibrators are driven by a vibratory motor mounted directly under the center of the tub with a vertical shaft. Parts and media move around the donut-shaped barrel as they are vibrated against one another. Most donut-type vibrators have simple integral separating systems. Of somewhat more gentle action, donut style machines are easier and more economical to handle than tub-type units for most smaller-sized components [23].

Spindle machines comprise a circular, rotating tub which holds loose abrasive media, and a rotary spindle to which the part is fixed. The workpiece mounted on the spindle is immersed into the rapidly moving abrasive slurry, causing the abrasive to flow swiftly over rough edges and over the surface of components. Process cycles in spindle equipment rarely exceed 5 minutes and are frequently less than 30 seconds. This equipment is clearly very well suited for parts such as gears, sprockets, and bearing cages where fixturing is straightforward and action of the abrasive will be absolutely uniform over all significant areas. Equipment can deburr, edge radius, and produce very fine surface finishes and, because parts are fixtured, there is no possibility of part-on-part impingement during the process or at reload time. The limitations result primarily from the need to fixture the workpieces. Where parts can be handled entirely satisfactorily in bulk in vibrators, centrifugal barrel machines or conventional barrels, then probably those machines will be more economical [23].

#### 5.1.1.3 Heat Treating

Heat treatment of metals is defined as the process of heating and cooling of a solid metal or alloy in such a way as to obtain desired conditions or properties. Heat treating processes include annealing and normalizing, used to reduce or control hardness in hot or cold worked metals; hardening by heating and quenching of certain metals, principally steels; carburizing, in which carbon is introduced into the surface of low carbon steels by heating them in carbon-rich media followed by quenching; and tempering or drawing in which metals are heated at low temperatures for stress relieving or to modify the hardness of quenched steels. Although steel is the principal metal which is heat treated, the process is also applied to some grades of cast iron, aluminum alloys, copper alloys, and magnesium alloys.

Heat treating operations always involve heating of metals under controlled conditions to a prescribed temperature, followed by cooling at a rate required to result in the desired physical property in the part being heat treated. Heating operations are performed in a variety of batch or continuous furnaces in which reducing or oxidizing atmospheres may be present to control the rate of carbon introduction or elimination from the metallic surfaces; or they may be performed in liquid heating media such as molten salts or lead. The type of heat treating process used depends on the type of metal involved and the specific properties to be rendered. Quenching media include such liquids as water, brine, oil, molten salt, and molten lead. For some operations, cooling is done in still air, or in the furnace by reducing the temperature at a controlled rate. Parts to be heat treated are often cleaned by washing in alkaline solutions before heating, and are generally cleaned after heat treatment by washing, shot blasting, or pickling in acids [18].

Quenching--In a typical quenching operation, baskets of hot metal parts are dipped into an oil bath or quench oil is sprayed on metal parts too large for smaller batch operations. In this application, the oil acts as a cooling medium rather than as a lubricant [24].

Annealing [16]--During cold rolling, the steel becomes quite hard and unsuitable for most uses. As a result, the strip must usually undergo annealing to return its ductility and to effect other changes in mechanical properties. This is done in either a batch or continuous annealing operation.

In batch or box annealing, a large stationary mass of steel is subjected to a long heat treating cycle and allowed to cool slowly. In continuous annealing, a single strip of cold reduced product

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[24] Bigda, R. J. Review of all lubricants used in the U.S. and their re-refining potential. Bartlesville, OK; U.S. Department of Energy; 1980 June. 86 p. DOE/BC/30227-1.

passes through a furnace in a relatively short period of time. The heat treating and cooling cycle in the furnace is determined by the temperature gradient within the furnace as well as the dimensions and rate of travel of the steel. To prevent oxidation and the formation of scale, inert atmospheres are maintained in these furnaces at all times. Prior to annealing, the material must be cleaned of all dirt and oil from the pickling operation to prevent surface blemishes. In the case of the continuous annealing furnaces, the material is uncoiled and passes through a continuous cleaning operation prior to entering the furnace. Upon leaving the furnace, the material is oiled and recoiled and is then ready to be tempered.

Tempering [16]--After cleaning and annealing, a considerable amount of product is tempered. In tempering, the thickness of the material is reduced only a few percent to impart desired mechanical properties and surface characteristics.

The temper mill is a single stand cold rolling mill designed to produce a slight reduction in thickness of the steel. This reduction develops the proper stiffness or temper by cold working the steel at a controlled rate. The end use of the material dictates the degree of tempering to be performed.

An oil-water emulsion lubricant is sprayed on the material before it enters the rolls of a cold rolling mill and the material is coated with oil prior to recoiling. This oil prevents rust while the material is in transit or in storage and must be removed before the material can be further processed or formed.

#### 5.1.1.4 Corrosion Prevention [17]--

The role of temporary corrosion preventive coatings in the industrial oil field is to give short-term protection to metallic components or equipment. This protection may be during storage, or transportation, or between manufacturing processes. The word temporary implies the products are easily removable, when required, from the metallic surfaces. This is usually done by solvent or alkali degreasing. The products are therefore not designed for the same duties as the permanent protectives, such as paints and metal coatings, which are not intended to be removable after application.

The chief destructive mechanism is the atmospheric rusting of iron. Rusting is an electrochemical process and proceeds in the presence of air - providing oxygen - and water. Small differences in electrochemical potential are usually present on iron surfaces and these set up local anodes and cathodes. In the presence of air and water, which acts as an electrolyte, the cathodic reaction which takes place on the surface produces rust. Rust consists of oxides, and hydroxides of iron, and its hygroscopic nature allows moisture to be trapped, encouraging further rusting.

Mechanisms other than rusting can also cause the corrosive destruction of unprotected iron and steel surfaces. The presence of sulfur dioxide and pollutants in the atmosphere can lead to the formation of acidic corrosion. Wood acids, exuding from wooden packing cases in contact with metal, can also cause a similar form of attack. Even mineral oils, used as a protective, can be oxidized when in thin films to form organic corrosive acids. Bacterial colonies present on the metallic surface can also set up a corrosive mechanism by the formation of oxygen concentration cells. The metal under the colony exists under anaerobic conditions and locally corrodes when it becomes anodic with respect to the colony edges. The edges have a higher concentration of oxygen and are cathodic. These forms of acidic corrosion are normally combated by the inclusion of basic inhibitors in the protective, to neutralize the acids as they form.

The temporary corrosion preventives are predominantly designed for the protection of ferrous materials under indoor or outdoor short-term sheltered storage. They may be classified into three main types: soft film, hard film, and oil protectives.

Soft Film--The soft film types frequently contain a solvent for ease of application of the protective film. When the solvent evaporates, the soft film is left evenly distributed on the metal surface. The film often consists of hydrocarbon material and natural products such as lanolin. Sometimes, these solvent-deposited products possess dewatering properties in addition, so that metal components do not have to be dried before being dipped into the product. The dewatering grades have surface-active agents incorporated in them, so that any water on the metal surface is displaced and the surface becomes preferentially wetted by the hydrocarbon material. The displaced water falls to the bottom of the dipping bath where it is drained away at intervals.

In addition to the solvent-deposited grades, there are also the non-solvent-deposited soft film grades, such as the petrolatums and greases. Sometimes, the petrolatums have corrosion inhibitors incorporated in them to neutralize acidic corrosion. The petrolatums are normally heated before the components to be protected are dipped in them. The type of film formed is soft, thick, and malleable. The exact thickness will depend upon the dipping temperature.

The thick film petrolatums can be used for the long-term storage of components, under indoor conditions. They can also be utilized for storage under outdoor conditions, as long as a further protective wrapping layer is employed. This is ideally a grease-proof paper. The additional wrapping protects the film from contamination and reduces the risk of mechanical damage. Roller and ball bearings are frequently protected during storage by the use of petrolatums. The thick film can easily be removed, when required,

from the protected component. Besides wiping and solvent degreasing, a dip in a hot oil bath can also be used to remove the protective film.

Hard Film--The hard film protectives are the second type of temporary corrosion preventives. They are solvent deposited grades which yield, as the name implies, a hard rather than a soft film, after application. These products are frequently based on hard-film-forming ingredients, such as bitumen, contained in a solvent. They protect metal surfaces for much longer periods than the soft film types, because the hard film is tougher and more resilient. They are used in such applications as car underbody sealants and for the protection of certain deck areas of ships.

Oils--The third type of temporary corrosion preventives are the oil protectives. These do not contain solvents and consist of mineral oil with corrosion inhibitors to combat acidic corrosion. They are used mainly for the protection of small components. Due to the relatively low viscosity of mineral oil, the films formed tend to be of a thin nature because of the oil drainage which occurs from a component after dipping. They give, therefore, less protection than the soft and hard film protectives. A special class of temporary oil protective is used for the filling or gear boxes and crankcases of internal combustion engines. These oils are used for protection during transportation of the units, and are designed also for the units to be run for a short time on the oils, before filling with the service oil.

In the field of steel rolling, special sheet coating oils are used for the protection of the rolled strip after tempering. These oils are used to protect the coiled strip during its transportation from the steel mill to the customer. These types of oils are usually formulated to suit the specified requirements of the customer. A motor manufacturer may require special degreasing properties for the oil, so that it can readily be removed by the established process used at the factory. Ease of removal of the coating oil is of prime importance in this case, so that the process of metal phosphating and the application of permanent protective paint coats can be readily carried out when desired. Before the transportation of the oiled coils of strip from the steelworks, it is normal practice to treat the exposed edges of the coils with additional protective. Edges are particularly prone to corrosion and are subject to rubbing during handling and transit. As in extra precaution during transportation, the coils of strip may also be protected with a wrapping of waxed paper.

#### 5.1.2 Raw Materials

Each segment of the metalfinishing industry demands oils specifically formulated for its requirements. The following widely used oils illustrate the variety of products needed by the industry: rolling oils, cutting oils, quenching oils, and rust preventative

oils. The following section describes the purposes of metalworking fluids, the classification of metalworking fluids, metalworking oil descriptions, and process applications for specific types of fluids.

5.1.2.1 Requirements--The basic functions of metalworking fluids are lubrication and/or cooling.

#### Lubrication

Three types of lubrication, differentiated on the basis of lubricating film thickness, are hydrodynamic lubrication (bulk or thick film), boundary or extreme pressure lubrication (thickness of molecular level), and thin film lubrication (an intermediate thickness film) [25]. When moving parts are separated by a film of fluid greater than 0.25 micrometer ( $1 \times 10^{-6}$  in.), the surface load is supported entirely by the hydrostatic pressure built up in the film [25]. In this type of lubrication, friction and temperature rise are due entirely to the viscosity of the fluid and are not affected by the chemical composition of the fluid or the metal surfaces with which it comes in contact [25].

As long as hydrodynamic lubrication is maintained, metal surfaces do not come in contact and surface wear is negligible. When the load on the surface increases or the viscosity of the fluid decreases, the film decreases to a thickness measured in molecules, and the lubricant film is characterized as boundary or extreme pressure lubrication. Boundary lubricant films are formed by a surface chemical reaction or physical absorption of a component of the fluid. In boundary lubrication, moving surfaces may come into contact, causing surface wear or metal transfer [25].

Thin film lubrication is intermediate between the first two types. In this type of lubrication, both viscosity of the fluid and chemical composition are important to metalworking fluid performance [25]. The type of metalworking operation, and the type of lubrication will determine the choice of metalworking fluid.

Cooling--In metalworking operations such as cutting and quenching the cooling properties of a fluid are more important than the lubricating properties. A good coolant must have a high specific heat, a high thermal conductivity, and a high heat of vaporization. The cooling ability of a fluid is also influenced by its ability to penetrate to the work zone and effectively wet the tool, die, and/or workpiece [25]. Oil-based fluids have good wetting and penetrating properties, while water-based systems vary from poor to good. The specific heat and thermal conductivity of oil is approximately

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[25] Ackerman, A. W. The properties and classification of metalworking fluids. Lubrication Engineering. 7:285-291, 1969 July.

one-third that of water. Therefore, oil-based systems generally cool less effectively than water-based coolants [25]. In addition, all metalworking fluids must fulfill one or more of the following requirements [26]:

Friction Reduction - The most common purpose of metalworking lubricants is the reduction of friction by the maintenance of a film separating metallic surfaces, thus reducing force and power requirements.

Heat Removal - In many instances, especially if the metalworking operation is of the continuous type, the lubricant is required to cool the dies and/or the workpiece material. The lubricant must remove both heat generated during the plastic deformation of the workpiece material, and heat generated at the interface of tool and workpiece.

Thermal-Insulation - Lubricants employed in hot working operations must provide thermal insulation between die and workpiece surfaces, partly to reduce heat loss from the hot stock and partly to protect the die from excessive heat.

Wear Reduction - Effective metalworking lubrication reduces the surface erosion wear on dies and rolls by forming a film to minimize metal-to-metal contact. Wear may also be decreased through removing suspended metal fines and debris in recirculating lubrication systems.

Metal Pick-up Prevention - A metalworking lubricant prevents metal pick-up on the tool surface by preventing the metal-to-metal contact that can result in spot welding of tool and workpiece. Lubrication failure can cause rapid scoring of the softer material or gradual surface deterioration.

Improving Surface Finish - Elimination or reduction of surface defects by proper lubrication in metalworking operations results in an improved surface on finished metal products.

Corrosion Prevention - In ferrous and nonferrous metalworking, the oxidation and corrosion preventive properties of the metalworking oils are extremely important. The metalworking fluid must protect the surface against oxidation and scale formation.

In addition, the metalworking fluid must remain stable in use, be unaffected by temperature or bacteriological attack, and protect against formation of corrosive breakdown products.

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[26] Schey, J. A. Purposes and attributes of metalworking lubricants. Lubrication Engineering. 23:193-198, 1967 May.



5.1.2.2 Classification--The ASTM has adopted a standard classification of metalworking fluids which divides fluids into five groups. Table 13 provides the current ASTM standard classification of metalworking fluids and related materials [27].

For the purposes of this report, metalworking fluids are classified into three groups and will be discussed in the following order:

- (1) straight oils (mineral and fatty),
- (2) emulsified oils,
- (3) synthetic fluids.

A fourth section discusses metalworking fluid additives. Table 14 presents the classification scheme for metalworking fluids used in this report, based on information in Reference 24.

5.1.2.3 Description--This section describes the three main types of metalworking fluids and the additive utilized therein.

Straight oils with no water phase (neat oils) are of two types, mineral oils and fatty oils. Approximately forty-five percent of all metalworking oils are straight mineral oils [24]. The neat cutting oils are used for the slower and more difficult machining operations, such as gear cutting, screwing and broaching. The main ability required is lubrication to reduce frictional heat and thus decrease tool wear. Complicated tool form regrinding can be an expensive operation and therefore reduced tool wear can be a key factor in the economy of the machining operations. The neat oils fall into two main classes, straight mineral oils and mineral oils blended with fatty oils [17].

Straight Mineral Oils--Mineral oils used as metalworking fluids are produced from petroleum base stocks. After the lower boiling components have been removed by distillation from the crude oil, the remaining complex mixture of hydrocarbons is fractionated under vacuum conditions to prevent the cracking or decomposition of the higher molecular weight hydrocarbons. In the vacuum fractionation process, lubricating oils are separated and collected in fractions of various boiling ranges. The separated fractions are refined and may then be blended together to make a long series of viscosity grades for use as industrial mineral oils.

Mineral oils are mixtures of vast numbers of hydrocarbons, although small amounts of sulfur and traces of nitrogen and oxygen compounds may also be present. The composition of the hydrocarbon

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[27] Standard classification of metalworking fluids and related materials. In: 1976 Annual Book of ASTM Standards. Part 24. Philadelphia, PA, American Society for Testing and Materials. 1976. ANSI/ASTM D 2281-73.

TABLE 13. CLASSIFICATION OF METALWORKING FLUIDS  
AND RELATED MATERIALS [27]

- 
- I. Oils and oil base fluids
    - A. Minerals oils - uncompounded
    - B. Fatty oils
      - 1. Uncompounded
      - 2. Fatty oils containing chlorinated compounds
      - 3. Fatty oils containing sulfurized compounds
      - 4. Fatty oils made by combining B2 and B3
    - C. Mineral oils - compounded
      - 1. Blends of mineral oil and fatty oil
      - 2. Sulfurized and/or chlorinated mineral oil
      - 3. Mineral oils containing sulfurized fatty compounds and/or sulfurized nonfatty compounds
      - 4. Mineral oils containing chlorinated fatty compounds and/or chlorinated nonfatty compounds
      - 5. Mineral oils containing sulfo-chlorinated fats or sulfo-chlorinated nonfatty compounds
      - 6. Mineral oils made by combining C3 and C4
      - 7. Mineral oils and/or fatty oils containing nitrogen or phosphorus compounds or solid lubricants, etc., in addition to compounds from the groups described in C1 through C6
  - II. Aqueous emulsions and dispersions
    - A. Oil-in-water emulsions (soluble oils)
      - 1. Mineral oil - emulsions of Class I-A
      - 2. Blends of mineral oil and fatty oil - emulsions of Class I-B1 or I-C1
      - 3. Heavy duty or extreme pressure - emulsions of Class I-C2 through I-C7
    - B. Water-in-oil emulsions
      - 1. Mineral oil - emulsions of Class I-A
      - 2. Blends of mineral oil and fatty oil - emulsions of Class I-B1 or I-C1
      - 3. Heavy duty or extreme pressure - emulsions of Class I-C2 through I-C7
    - C. Colloidal emulsions
      - 1. Regular - emulsions of Class I-A
      - 2. Fatty - emulsions of Class I-B1 and I-C1
      - 3. Heavy duty or extreme pressure - emulsions of Class I-C2 through I-C7
    - D. Dispersions
      - 1. Physical dispersions of liquid (Class I) materials
      - 2. Physical dispersions of solid (Class IV) materials

TABLE 13 (continued)

- 
- 
- III. Chemical solutions (true and colloidal solutions)
    - A. Organic - water-soluble organic systems giving clear, transparent solutions of low surface tension
    - B. Inorganic
    - C. Mixtures - blends of organic and inorganic solutions
      - 1. High surface tension (45 dynes or over)
      - 2. Intermediate surface tension (36 to 44 dynes)
      - 3. Low surface tension (35 dynes and under)
  - IV. Solid lubricants
    - A. Powders
      - 1. Crystalline, such as graphite, lead sulfide, mica, molybdenum disulfide, talc, calcium oxide, calcium carbonate, zinc oxide, and zinc sulfide
      - 2. Polymeric, such as polyethylene and PTFE (polytetrafluoroethylene)
      - 3. Amorphous, such as soaps and waxes
      - 4. Mixtures of Classes IV-A1, IV-A2, and IV-A3
    - B. Vitreous materials
      - 1. Borates
      - 2. Glasses
      - 3. Phosphates
    - C. Greases and pastes
    - D. Dry films
      - 1. Particle bonded
      - 2. Resin bonded
      - 3. Vitreous bonded
        - a. Salts
        - b. Glasses
    - E. Chemical conversion coatings
      - 1. Phosphate
      - 2. Oxalate
  - V. Miscellaneous
    - A. Chlorinated nonoil type materials, neat
    - B. Sulfurized nonoil type materials, neat
    - C. Combinations of Classes V-A and V-B
    - D. Organic materials not otherwise specified, such as alcohols, glycols, polyols, esters, phosphorus compounds, etc.; and dispersion of solid lubricants (Class IV) in such organic materials
- 
-

TABLE 14. REPORT CLASSIFICATION SCHEME  
FOR METALWORKING FLUIDS [24]

Type of fluid	Usage, %	Base stock	Additives	
			Percent	Type
Straight oils	45			
Mineral oils		Naphthenic petroleum Paraffinic petroleum	2-10	Extreme pressure (EP)
			2-15	Friction reducing animal fats
			<18	Chlorine
			<22	Sulfur Corrosion inhibitors detergent/dispersant Biocide
Fatty oils		Animal or fish oils Vegetable oils		Used to formulate mineral oil additives
Emulsified oils	50	High viscosity petroleum		Emulsifiers Corrosion inhibitors Biocide
Synthetic oils	5	Nonpetroleum chemical fluids		Used to formulate mineral oil additives

mixture depends largely upon which part of the world the crude oil originated. However, most oils are mixtures of paraffins, naphthenes and aromatics. The paraffinic oils are more resistant to oxidation than the aromatic oils, but when oxidation is not a problem, the unsaturated ring-type structures of the aromatics allows them to absorb greater quantities of energy before breakdown occurs. This specific advantage of aromatic oils is exploited in the field of high temperature heat transfer where the better thermal stability of the aromatic-type oils becomes advantageous. However, when the oxidation stability of the oil is more important than its thermal stability, for example, in a quenching oil bath, then the paraffin-type oils are preferred to the aromatics [17].

An especially important characteristic for the straight mineral oil class is the viscosity level chosen for a particular application. Although the oil must be able to lubricate effectively, the use of a low viscosity oil will improve the cooling ability which, of course, is advantageous. On the other hand, higher viscosity

oils would have better retentive properties on the tool and work-piece in the region of the cutting zone. This is an important advantage in the slow speed cutting of the tougher metals.

Mineral oils, blended with fatty oils, are sometimes used when additional lubrication characteristics are desired. The fatty component has good friction reduction properties, due to the tenacious films it forms on metal surfaces. The compounded oils are also useful in the machining of metals, where staining by the cutting fluid may be a problem. Examples are the yellow metals (copper alloys) and aluminum alloys, which can be machined with compounded oils to give excellent surface finishes and minimal tool wear. The main disadvantage of compounded oils is that the fatty component is prone to oxidation, with the result that the viscosity and acidity of the oil may increase [17].

Fatty Oils--The sources of the fatty acids are frequently vegetable, animal, or fish oils. These naturally derived oils provide the vast majority of the fatty compounds used in the general compounding of mineral oils for many industrial purposes. We have already mentioned their use in modifying the frictional characteristics of mineral oils. They are also employed in mineral oils which have to operate in wet environments. The fatty oil, in the same case, acts as a surface active agent. It tends to take the water into the body of the oil, in the form of a water-in-oil emulsion, thus preventing the lubricant film from being washed off the surface to be lubricated.

Selected fatty oils such as rape seed, lard, tallow, arachis, sperm, olive, palm oil, castor have been frequently used for many industrial lubrication purposes. Some have also been utilized for the manufacture of fatty additives which have incorporated in them extreme pressure agents such as sulfur and chlorine.

The various fatty oils possess different compositions. They are a source of both saturated fatty acids, such as palmitic and stearic, in admixture with unsaturated fatty acids, such as oleic and linoleic acids. Castor oil is rather unique, in the fact that it contains an appreciable quantity of ricinoleic acid and hardly any saturated fatty acids. Ricinoleic acid is an unsaturated hydroxyoleic acid which has practically no action on rubber, unlike the other fatty oils and also, for that matter, mineral oil. This makes the use of castor oil especially advantageous in industrial applications, where it may come into contact with rubber components. However, one of the great disadvantages of castor oil is that it possesses a very high viscosity at low temperatures. This considerably reduces its potential field of activity.

The various fatty oils have different solubility characteristics in mineral oils. Castor oil has only a limited solubility of about 2 percent. Other fatty oils are much more soluble and are

frequently used in the 10 to 20 percent weight range for the compounding of mineral oils. The solubility is affected by the hydrocarbon types present in the mineral oil and, of course, the temperature.

The main disadvantages of fatty oils, for industrial lubrication, are lack of stability and high price. They tend to decompose and form gummy deposits at elevated temperatures. They possess, therefore, short working lives in comparison to mineral oils. On lengthy exposure to air at room temperature, there is a tendency for the fatty oils to become sticky and rancid. They are also relatively expensive and many are in short supply. For example, sperm oil supplies have been drastically affected by the international restrictions imposed on the hunting of sperm whales to conserve the species.

However, despite these disadvantages, fatty oils have played and will continue to play an important role in industrial lubrication. This role is not only in the compounding of mineral oil lubricants. In specific applications, fatty oils are utilized in their own rights as lubricants, without admixture with mineral oil. An example is the use of palm oil in the steel industry for the rolling of thin gauge strip, a process for which no mineral oil product can give the same performance.

Emulsified Oils--Approximately fifty percent of metalworking oils are used as emulsified oils [24]. Emulsified oil concentrates are derived from high viscosity petroleum feedstocks. These oils contain additives such as emulsifiers and biocides so that they may be diluted with water 10:1-20:1 for metalworking service, the degree of dilution depending on the severity and type of operation [24].

The soluble oils are used as emulsions of oil in water and are the most widely used cutting fluids. Emulsions of soluble oil, when prepared in water, are of a milky or clear appearance. This will depend upon the degree of dispersion, or the size of the oil particles, present in the continuous phase of the emulsion. In general terms, the greater the amount of emulsifying agent present in the soluble oil, the more clear and transparent will be the emulsion prepared from it. Emulsion stability is of great importance in service and the selection of the optimum emulsifier system for the particular oil used is a prime consideration. Also, the oil must be able to produce stable emulsions in the waters of various degrees of hardness met in industry [17].

Soluble oil emulsions, because of their cooling power, are ideally suited for use in rapid and light machining operations, such as turning, drilling, and grinding. However, it is possible to include extreme pressure additives in soluble oils to increase their range of application. The presence of the dispersed oil in the emulsion has some lubricating power but the primary characteristic of the soluble oil emulsion is its cooling ability. The

concentration of the soluble oil dispersed in the water will depend upon the individual application. It may range from 1 part of oil to 10 parts of water for turning, to 1 part of oil to 50 parts of water for grinding. For operations, such as grinding, it is important that the machinist can have a clear view of his work as it progresses. It is therefore common practice to use transparent soluble oil emulsions for this application.

Water-based fluids are subject to bacteriological attack. The presence of hydrocarbons, water, and often nitrogen, sulfur, and phosphorus compounds, makes an excellent diet for bacterial growth. Initially, bacterial infection of the aqueous cutting fluid is usually caused by airborne dust, or the water used to prepare the emulsion. Once established, bacterial growth rates can be very rapid. Sometimes the machine tool may not have been cleaned effectively before the introduction of the cutting fluid. Stagnant pockets of a previously infected emulsion may be left behind. The bacterial attack may be of the aerobic type when air is present, or the anaerobic type in the absence of air. Aerobic bacteria frequently produce acidic components which can cause corrosion of the machine tool and workpiece. The anaerobic type can attack the emulsifying agent used in the soluble oil, with the result that emulsion breakdown can take place [17].

Synthetic Fluids--Many synthetically produced hydrocarbons find specialized applications in metalworking. Unlike the conventional mineral oil products which contain a multitude of mixed hydrocarbons, the synthetic hydrocarbons are relatively pure and possess relatively narrow boiling ranges. They may be paraffinic or aromatic in nature. The aromatic synthetic-type oils find outlets in such applications as high temperature heat transfer. The synthetic paraffinic types may prove useful in the metal rolling field, or in other applications where narrow boiling liquids of good oxidation stability are advantageous [17].

The synthetic lubricants are classified as silicone polymers, polyoxyalkanes, polyesters, fluorocarbons, chlorocarbons, and phosphorus derivatives. These products are first manufactured chemically and then refined and compounded for use as lubricants.

Because of their poor solvent properties, silicones have proved difficult to use as lubricants for steel, and additives are needed to increase their lubricity. They have found their primary lubrication application in the form of greases [24].

Liquid polyoxyalkanes are generally polymers of polyethylene glycols or polypropylene glycols or copolymers of ethylene or propylene oxide. They have been successfully used as metal forming lubricants. They can be tailored to various degrees of oil solubility. Lubricants made from these products have high enough viscosity indexes and low enough pour points to be used as all-weather engine oils.

Polyester-type lubricants have been synthesized with trimethylolpropane reacted with various fractions of mixed fatty acids, adipic acid reacted with various fractions of mixed branched alcohols; esters of adipic acid and branched nonyl alcohols; and esters of methyl adipic acid and mixtures of branched alcohols. There also are many commercially available esters suitable for lubricating oils which are prepared from oxo process branched chain alcohols reacted with adipic, azelaic, and sebacic acids or other polycarboxylic acids. These ester lubricants are widely used in military and commercial aircraft as engine oils and as instrument oils and greases.

The phosphate ester oils are probably the most commonly used synthetic oils in the United States today. Most turbine powered aircraft utilize diester lubricants. These ester oils show excellent response to many types of lubricant additives such as antioxidants, rust inhibitors, viscosity index improvers, detergents, and antiwear agents. They are available in a variety of viscosity grades. Further, they have the advantage that their hydrolysis or oxidation products are mild wear additives and rust inhibitors. Because of the good solvent properties, the esters behave like good detergent oils [24].

For more general lubrication applications, outside the field of fire-resistant lubricants, the synthetic esters are sometimes utilized in certain circumstances, such as in compressors and gear boxes, when the operating conditions are severe enough to warrant them. The synthetic organic esters can be manufactured with higher stabilities than mineral oil based products. The use of special additives allows the esters to be utilized at much higher temperatures.

The synthetic esters were originally developed for the lubrication of high speed aircraft and aviation gas turbines. The diesters, utilized as base oils for these applications, are based on products derived from such materials as sebacates, azelates, and adipates. The diester lubricants were originally designed for aviation purposes. In the high temperature region, it is essential that the synthetic lubricants be able to lubricate not only under high speed conditions, but also under high bearing loads. The ester fluids have excellent thermal stabilities but special high temperature anti-oxidants are utilized to increase the oxidation stabilities, and also additives are incorporated for the improvement of the load carrying properties [17].

These synthetic base stocks, though each possess special properties, must be formulated in much the same manner as the hydrocarbon base stocks; that is, with antioxidants, rust inhibitors, wear additives and other materials to improve the lubricating properties of the oils. All of the synthetics are inherently more costly than hydrocarbon-based oils because they must first be synthesized in a complex chemical operation.



Additives--In many industrial metalworking applications, the selection of a certain hydrocarbon-type oil may not be enough to cope with the working conditions imposed upon it. Additives are then incorporated into the oil to enhance its properties [17].

Table 15 summarizes the types of lubricant additives most frequently used in metalworking fluids [28]. The following paragraphs describe the purposes and types of additives used in metalworking oils.

Oxidation Inhibitors--The rate at which the oxidative process proceeds depends predominantly upon the quality of the oil. When severe oxidation conditions are present in an industrial application, it is common to use oxidation inhibitors to reinforce the inherent stability of the oil. These oxidation inhibitor additives normally function by prolonging the induction period which precedes the main oxidation reaction. The additives may be of the oxidation chain breaker type that interrupt the initial stage of the reaction before it can proceed catastrophically. Alternatively, they may be of the metal deactivator type which minimize the catalytic effect of the metals present in the system by adsorption onto their surfaces, thereby passivating them. In certain applications, it may be necessary to employ both types of oxidation inhibitor in the oil [17].

Rust Preventatives--Oils prevent rusting by wetting the metal surfaces, thereby preventing air and water coming into contact with them. The use of rust inhibitors as additives can assist the oil in this respect, by making the oil film become more strongly adsorbed onto the metal surface.

In certain application, it is necessary to incorporate vapor phase corrosion inhibitors into oils to prevent corrosive attack occurring in spaces above the oil level in the system. These types of inhibitors function by possessing relatively high vapor pressures, which allows them to migrate from the oil solution into the air spaces where they are adsorbed onto the metal surfaces to be protected [17].

Anti-Foamants--Oils dissolve air, the amount depending predominantly on the air pressure and also to a lesser extent on the temperature. When the air remains in solution, there is no problem. However, if the air pressure above the oil is suddenly reduced, then the air will tend to come out of solution and form small bubbles which may become trapped in the oil. It is possible to break such foams by the incorporation of anti-foam agents into the oil. However, care must be taken that the use of such agents does not

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[28] Weinstein, J. J. Waste oil recycling and disposal. Cincinnati, OH; U.S. Environmental Protection Agency; 1974 August. 327 p. EPA-670/2-74-052. PB 236 148.

TABLE 15. LUBRICANT ADDITIVES [28]

Type	Reason for use	How they work	Adverse effects	Limits of activity	Typical compounds	Other possible compounds
Oxidation Inhibitor	Prevent or control formation of varnish, sludge and corrosive compounds. Limit viscosity increase.	Decomposes peroxides inhibit free-radical formation, and passivate metal surfaces	Can increase oil vapor pressure, promote (in the case of zinc organics) corrosion and cause heavy oil sludging and darkening (in some nitrogen compounds)	Most additives have an optimum temperature range and are not uniformly effective at preventing all forms of catalytic oxidation	Mindered phenols, bisphenols, metal (especially zinc) dialkyl dithiophosphates, compounds of nitrogen and sulfur.	Berium dialkyl dithiophosphates, phosphites, amines.
Rust Preventive, (Liquid Phase)	Prevent formation of rust in areas under the oil especially during equipment shutdown.	Polar type compounds react with or are adsorbed on metal surfaces.	Reduce oil oxidation resistance and promote formation of emulsions	Only effective in the oil-wetted parts of the system.	Sulfonates, soaps, fatty acids, phosphates, mono- and difunctional organic acids and esters	Alkyl amines, amine phosphates, acid phosphate esters
(Vapor Phase)	Prevent rust formation in areas above the oil level.	Volatile basic compounds are vaporized with water and keep condensate basic.	Reduce oil oxidation resistance and promote formation of emulsions	Re-inhibition required in systems volatilizing large volumes of water.	Low-molecular-weight amines having a wide boiling range.	
Anti-Foamants	Ensure rapid collapse of large air bubbles, prevent excessive oil oxidation.	Attracted to oil/air interface, they lower the surface tension of air bubbles, causing the formation of quick-breaking large bubbles	Silicone types tend to promote air entrainment (the formation of tiny, long-lasting bubbles). Other types may promote emulsion formation	Some lubricant additives or contaminants may render anti-foamants ineffective	Silicone polymers, methacrylate polymers	Waxes.
Viscosity Index Improvers	Reduce the rate of viscosity change with temperature	These polymers are tightly coiled (and relatively insoluble) in oil at low temperatures and uncoiled (and quite soluble) in oil at high temperatures. VI improvers contribute to oil viscosity at higher temperatures preventing "thinning"	Polymers shear in service, thus causing the compounded oil to suffer both "temporary" and "permanent" viscosity loss. When high VI finished oils are desired, the base oils must have low viscosities, hence, low flash points	Many polymers exhibit "VI humps" (e.g., concentration ranges beyond which further additive addition will not increase VI)	Polyisobutylene (such as STP), methacrylate polymers, some copolymers	Succinimide-acrylic acid reaction products, ethylene-propylene polymer derivatives

(continued)

TABLE 15 (continued)

Type	Reason for use	How they work	Adverse effects	Limits of activity	Typical compounds	Other possible compounds
Pour Depressants	Lower the pour point (or "freezing point") of paraffinic oils. Most pourpoint depressants are less than 40°F (say from 20 to 20°F) and are achieved with less than 2% additive.	Prevent wax crystal-growth or oil adsorption at low temperatures.	None	The pour-point depression effect of any single polymer is limited and often specific, so combinations of pour depressants are often used.	Methacrylate polymers, alkylated naphthalene or phenols	Polyacrylamides
Extreme Pressure (EP) Oiliness and Antiwear	Modify friction properties, reduce wear, prevent galling and seizing	Form physical or chemical bonds with rubbing surfaces that provide supplemental "wearing surfaces." The key is friction and wear control, rather than elimination.	Promote oil oxidation, foaming, emulsification and corrosive tendencies. Thermal stability is weakened.	EP agents require heat (generated by metal-to-metal contact) to be effective. Not all desired oiliness properties are contributed by one set of additives.	Oiliness-fatty acids and soaps. Antiwear-impure tricresyl phosphates. EP-organic phosphates, lead and chlorine compounds.	Organic compounds with barium, antimony, bismuth, silicon, molybdenum, sulfur, phosphorus, nitrogen, halogens, carbonyl or carboxylate salts, silicones, polyphenyls.
Emulsifiers	Hold oil and water together in emulsion-type cutting fluids, coolants and hydraulic fluids.	Polar-type (both ionic or nonionic) compounds line up at oil/water interfaces, and thus they provide solubility bridges between the oil and water.	Reduces oil oxidation resistance. Fights activity of antiwear, EP, oiliness, antirust, and anti-foam agents. May cause seal swelling.	Different emulsifiers must be used for every oil, every concentration of water and, often, every service temperature.	Metal sulfonates, glycols, ethoxylated phenols, alcohols or acids, naphthonic acids.	Fatty acid soaps.
Other Additives	Perfumes and formaldehyde compounds as antiodorants with EP additives; alcohols, phenols, chlorine compounds as antiseptics for emulsion lubricants, amine compounds as color stabilizers, polyacrylates and polybutenes as tackiness agents for gear oils.					

aggravate the trapped air problem by retarding the rate of escape of the small air bubbles from the body of the oil.

Certain silicone polymers are added as anti-foam agents to many industrial mineral oils in concentrations of a few parts per million. The presence of such traces of silicone has a dramatic effect in accelerating the rate of collapse of a mineral oil foam. The action is possibly caused by the silicone polymer altering the interfacial tension force existing between the gas and liquid interfaces of the foam [17].

Extreme Pressure (EP)--Extreme pressure (load carrying) additives are included in oils when the load, temperature, or velocity between two surfaces does not allow a hydrodynamic oil film to build up. There is then nothing to prevent metal surfaces from coming into contact, with resulting wear, unless a load-carrying additive is present in the oil.

This type of additive functions by chemical reaction with the metallic surfaces but only when the conditions of temperature or pressure prevailing in the contact zone are severe enough. This means that at lower temperatures and pressures the additives remain inert. The main chemical elements used for extreme pressure conditions are sulfur, chlorine, phosphorus, and lead. They are normally present in the form of oil-soluble organic compounds, but sometimes sulfur may also be present in its elemental form. The additives are controlled chemical release agents which, on reaction, yield metallic films such as chlorides and sulfides. These films prevent welding and metallic pick-up between the surfaces under heavy duty conditions.

Selected fatty oils such as rape seed, lard, tallow, arachis, sperm, olive, palm and castor have been utilized for the manufacture of fatty additives which have extreme pressure agents such as sulfur and chlorine incorporated in them.

Fatty acids function by forming a strongly adsorbed polar film on the metallic surface, which reduces the frictional value. The polar type films formed have relatively low melting points compared, for example, to sulphide films. The polar films break down under extreme pressure conditions and are used as friction reduction agents and not as anti-weld agents [17].

Viscosity Index Improvers--In the majority of applications, the most important characteristic of a lubricating oil is its dynamic viscosity value; i.e., the stress required to shear unit thickness of the oil at unit velocity. This is because under hydrodynamic lubrication conditions, when two moving surfaces are completely separated by an oil film, the only friction source is the oil viscosity. The values of viscosity vary with temperature. However, determinations at various temperatures allow a calculation to be made of the viscosity index. This index can be used to compare

different oils, since the higher its value, the lower the change in oil viscosity with temperature. The types of hydrocarbons present in the crude oil and the refining process given to it determine the viscosity index level. For example, paraffinic oils have generally higher index values than naphthenic oils and solvent-refined oil [17].

Pour Point Depressants--Certain applications for industrial oils demand that they remain fluid at low temperatures. In general, naphthenic oils have lower pour points than the paraffinic oils. The pour point gives an indication of low temperature fluidity. However, pour point depressant additives can be incorporated into paraffinic oils in order to increase their fluidity at low temperatures. The additives are thought to function by inhibiting the honeycombing of the wax separating out from the oil at low temperatures [17].

Emulsifiers--Outside the main field of additive-treated industrial oils which are used in the neat oil form, it will be found that in several specialized applications, industrial oils are employed in admixture with water to form stable emulsions. Typical examples are soluble cutting fluids. Mineral oils and water are not mutually soluble. A very large quantity of energy has to be expended to shear a mineral oil down to colloidal dimensions so that it can be dispersed in water to form a stable emulsion. On an industrial scale, this mechanical method is not usually practicable so additives are dissolved in the oil to facilitate the task.

The additives used are called emulsifiers, or surface active agents, and they work chiefly by lowering the interfacial tension between the oil and the water. This allows an emulsion to be readily formed. Afterwards, the surface active agent has the additional task of making the emulsion stable and preventing coalescence back into separate oil and water layers. There are two main types of emulsion, the oil in water and the water in oil. In the former type, the water forms the continuous phase and the oil the dispersed phase. In the latter type, the reverse is true, and the oil forms the continuous phase and the water the dispersed phase. Primarily, the type of emulsifier selected will determine the type of emulsion formed. Emulsifiers normally contain components, or groups, which are soluble in both water and oil to varying extents. The ratio and relative influences of these components, or the so-called hydrophilic and lipophilic balance, will normally determine the type of emulsion formed when an emulsifier is present in an oil and water mixture.

The two main types of emulsifier used for the preparation of industrial oil emulsions are petroleum sulfonates and nonionic surface active agents. The former type are very commonly utilized for the preparation of soluble cutting fluids, which are always used in the form of oil-in-water emulsions. The petroleum sulfonates are ionic materials, which means they form electrically

charged ions in solution. This phenomenon is advantageous when it becomes necessary to dispose of an emulsion after service, because it allows the emulsion to be split readily into separate oil and water phases by the addition of a salt solution or acid. Such materials upset the electric charge stabilization of the emulsion. This process cannot be done with an emulsion based on a so-called nonionic emulsifier, and the disposal problem after service is therefore not quite so easy [17].

Preservatives--Water-based fluids, emulsified oils, and synthetic fluids are subject to bacteriological attack and require bactericide additives to extend operating life. Selected commercially available cutting fluid preservatives are listed in Table 16 [29].

TABLE 16. CHEMICAL CATEGORIES OF CUTTING FLUID PRESERVATIVES [29]

Chemical Compound	Category	Trade name	Company
<i>o</i> -Phenylphenol	Phenolic	Dowicide 1	Dow Chemical
Sodium salt of <i>o</i> -phenyl phenol	Phenolic	Dowicide A	Dow chemical
2,3,4,6-Tetrachlorophenol	Phenolic	Dowicide 6	Dow Chemical
<i>o</i> -Benzyl- <i>p</i> -chlorophenol	Phenolic	Santophen-1	Monsanto
Sodium salt of <i>o</i> -phenyl-phenol and sodium mercurio salicylate	Phenolic/salicylate combination	Elicide 75	Eli Lilly
2-Hydroxymethyl-2-nitro-1,3-propanediol	Formaldehyde "donor"	Tris Nitro Cimcool Wafers	Commercial Solvents Cincinnati Milling
Hexahydro-1,3,5-tris-2-hydroxyethyl-(s)-triazine	Formaldehyde "donor" (?)	Grotan	Hallemitte (Sterling Drug)
Hexahydro-1,3,5-tri-ethyl-(s)-triazine	Formaldehyde "donor" (?)	Vancide TH	Vanderbilt
1-(3-chloro ally)-3,5,7-Triaza-1-azonia-adamantane	"Quat" Formaldehyde "donor"	Dowicil 100	Dow Chemical
3,4',5-Tribromosalicyl anilide (76-88%) and 3,5-dibromosalicylanilide (12-24%)	Salicylanilide	Tuasal 85	Dow Chemical Fine Organics
3,4,5-Tribromosalicyl-anilide (98-100%)	Salicylanilide	Tuasal 100 TBS 95	Dow Chemical Maumee Chemical

[29] Smith, T. H. Toxicological and microbiological aspects of cutting fluid preservatives. Lubrication Engineering. 25:313-319, 1969 August.

### 5.1.3 Waste Description

Metalworking operations produce wastes in either liquid, solid, or sludge form. These wastes are primarily composed of the materials being processed and the materials used to achieve a desired finish. The types of waste generated by various operations are primarily classified into the following three categories: straight oils, emulsified oils, and synthetic fluids. Table 17 lists the types of waste generated by various metalworking operations.

TABLE 17. WASTE TYPES GENERATED BY METALWORKING OPERATIONS

Operation	Straight oil	Emulsified oil	Synthetic fluid
<u>Metal forming</u>			
Rolling	X	X	X
Drawing	X	X	X
Stamping and extrusion	X	X	
Casting and molding	X		X
<u>Metal removal</u>			
Cutting	X	X	X
Grinding	X	X	X
Machining	X	X	X
Polishing and buffing	X	X	
Barrel tumbling and abrasive machining	X		X
<u>Heat treating</u>			
Tempering and quenching	X	X	X
<u>Rust prevention</u>			
Oil coating	X	X	

The following subsections describe the three waste types. For each type of waste potential contaminants, their sources, and factors affecting their concentrations are described.

#### 5.1.3.1 Straight Oils--

The contaminants of neat or straight oils are of various kinds, depending on initial composition, the type of usage, and the surrounding atmosphere. So, waste oil characteristics will vary from plant to plant within a company, and also from company to company. Waste neat oils may contain water, sulfur, chlorine, fluorides, nitrogen, phosphates, metal chips and fines, sediment, PCBs, oxidation products, and phenolic compounds. These contaminants may be present separately or in various combinations depending on the

initial composition of neat oil, its application, and surrounding atmosphere.

Waste neat oils often have a high water content due to water leakages from other parts of machinery, mixing with water soluble oil from other parts of machinery, or because of water held in suspension by detergent/dispersant additives [24]. The chlorine content of waste neat oils may be high. The chlorine is derived from the additive package added to the oils to improve their performance. To improve their performance under pressure, straight oils are mixed with pressure additives which may contain as much as 18% chlorine [30]. Waste oils may contain phenolic compounds as they are added as preservatives or for odor control [30]. PCBs can enter metalworking oil through PCB-contaminated tramp oil accumulations. Tramp oil is oil (usually hydraulic oil) from other parts of the machine that leaks or drips into metalworking oil. Hydraulic oil is likely to be contaminated with PCBs, and it can accumulate in metalworking oil. Until 1972, PCB-based hydraulic fluids were commonly used. When manufacture of these fluids was discontinued, it was not recommended that hydraulic systems be drained, flushed, or refilled. Rather the public was advised to merely replace these fluids (without PCBs) as leaks and spills occurred. Also the extreme complexity of hydraulic systems makes it very difficult to eradicate all PCB contamination from these systems. As a result, PCB levels in hydraulic systems range from 60 to 500,000 mg/L [30].

Atmospheric dust and metal chips and fines also become incorporated into waste neat oils [31]. There are three basic variables which determine the metallic particulate characteristics. They are as follows [32]:

1. The first variable is the metal being worked. Obviously, if cast iron is the metal being worked, cast iron particulate will be generated.
2. The type of operation is the second variable. The operation may be grinding, machining, broaching, gun drilling, honing, boring, hobbing, lapping, or whatever, and each will produce characteristic metallic particulate. Because of variations in feed rates, speeds, size of work-piece, etc., no two specific operations will produce identically sized particulate.

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[30] Listing waste oil as a hazardous waste. Washington, DC; U.S. Environmental Protection Agency; 1981. SW-909.

[31] Sargent, L. B., Jr. Lubricant conservation in industry. Alcoa Center, A; Aluminum Company of America.

[32] Nehls, B. L. Particulate contamination in metalworking fluids. Lubrication Engineering. 33(4):179-183, 1977 April.



3. The type of metalworking fluid is the third variable. Field studies and laboratory research indicate that different types of fluids will cause generation of different sized metallic particulate under identical operational parameters.

Waste neat oils may also contain zinc, sulfur, phosphates, lead, nitrogen, amine compounds, sulfates, barium, calcium, magnesium, and fluorides from various additives added to the metalworking oils.

Depending on the ambient conditions, lubricants and additives may undergo oxidation and other types of chemical changes. Petroleum oils are a complex mixture of three primary types of hydrocarbons, all of which will react with oxygen (oxidation) at high operating temperatures. The reaction of mineral oils causes several unsatisfactory results. Paraffin-based oils tend to form corrosive acids, aromatic oils form sludges and varnish, and naphthenic oils generally yield a combination of both acids and sludges. These materials may be further oxidized or they may react with each other to form high molecular weight polymers. Some of these are oil soluble and result in an increase in oil viscosity, while the insoluble polymers create sludge and eventually hard deposits. In nearly all cases, the oil begins to thicken during oxidation, and may eventually become too thick for proper equipment functionings, and may affect product quality [33].

Tallow oil, lard oil, palm oil, 50/50 mixtures of tallow oil and mineral oil, and straight mineral oils are used in the metal forming operations of rolling and stamping. Rolling oils from the steel industry are usually recovered from the mill's wastewater treatment plant. This results in a number of oils being mixed together, along with the animal fats, greases, etc., which accumulate on top of the skimming tanks.

Tempering and quenching of metals generate waste quench oils. They are often very black in appearance. They have a low additive content, and are usually made from paraffinic base stocks. These oils are found at heat treating and metalworking shops. While these shops do not generate large volumes of oil, when a bath is changed (typically every six to nine months), several drums of waste are generated. While some oil is lost to evaporation and by clinging to the dripped parts, a higher percentage (approximately 50 percent of total quench oil purchased) is collected relative to other metalworking oils [24].

Rust preventive oil coating operations normally do not generate any waste [24]. Oil that drips after coating is usually collected and reused.

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[33] Increase fluid life with oxidation/corrosion inhibitors. Fluid and Lubricant Ideas. 24-25, 1979 Spring.

Raw waste straight oil composition data obtained from the state environmental regulatory agencies are presented in Appendix A by the type of the metal finishing operation. Examination of data indicates that waste oils have water, heavy metals, phenols, organic solvents, sulfur, and chlorine as major contaminants present separately or in various combinations. Because of increasingly restrictive regulations concerning disposal of waste oils into environment, the disposal problem is becoming serious, and it is affecting economics of metalworking oils use. It may be possible to economically refine the waste oils for reuse or to use the waste oil in other applications. These aspects are discussed in detail in Section 6.

#### 5.1.3.2 Emulsified Oils--

Characteristics of waste emulsified oil tend to be plant specific and depend on the uses to which the oil has been put. Waste emulsified oils often contain contaminants such as metal particles, biodegradation products, tramp oil, nitrosamines, and residues from oil additives, including sulfur, phosphorus, chlorine, zinc, lead, copper, and phenolic compounds.

Emulsified oil systems are affected by accumulation of tramp oil. If an emulsified oil starts at a 1:20 oil-to-water ratio, or about 5 percent oil, accumulation of tramp oil may raise the oil content to 10 percent by the time the oil is changed. This accumulation of tramp oil reduces the effectiveness of the emulsified oil to the point it must be changed.

Waste emulsified oils may contain residues from oil additives and metal fines and chips similar to those described for straight oils in Section 5.1.3.1. Also, recent studies indicate that emulsified oils may contain nitrosamines, either as contaminants in amines, or as products from reactions between amines and nitrites. The nitrosamine content of emulsified oils is attributed to the additive package, specifically to the antiwear/extreme pressure, corrosion and rust inhibitors; friction modifiers; antioxidants; and metal deactivator additives [30]. According to NIOSH, a recent study showed concentrations of 1,000 mg/L of diethanol nitrosamine in cutting oil before use and 384 mg/L after use [34]. This means 616 mg/L of nitrosamine was emitted into the surrounding atmosphere.

Bacteria growth is the most common cause of emulsified oil spoilage. Once the emulsified oil is placed in operation, bacteria and fungi can enter the oil from five sources: air in the plant, water used to prepare the emulsified oil, the metal or other material being processed, a contaminated holding tank, or the operator himself. Once the microorganisms enter the emulsified oil, they

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[34] Concentrates - industry/business. Chemical and Engineering News. p. 12, 1976 October 18.

encounter excellent conditions for growth: moisture, warmth, and food in the form of the emulsified oil. Bacteria growth can occur to the extent that organisms may plug nozzles, pipes, and filters, thus restricting emulsified oil flow and decreasing tool life. Most problems, however, relate to emulsified oil life expectancy and stability. The microorganisms will attack the emulsifiers, corrosion inhibitors, and other additives in the emulsified oil and reduce their effectiveness. Since the emulsifiers are critical to the stability of the oil/water emulsion, this can lead to complete destruction of the emulsified oil. Lower pH will cause increased corrosion of cutting tools, machinery and work pieces, leading to poor workmanship and reduced equipment life. Perhaps the most widely known effect is the creation of a foul, rotten-egg smell known as "Monday morning odor." This is caused by attack of sulfur-reducing microorganisms on sulfur-containing additives, and is particularly noticeable after a weekend shut-down during which time these microorganisms have an opportunity to come to the surface. Circulating the fluid over the weekend will eliminate the smell, but will do nothing to get rid of the organisms. Most manufacturers recommend keeping the pH between 8.5 and 9.2, but the rapid growth of some bacteria can lower the pH below 7.0, and cause metal corrosion. Use of a buffering agent rather than a biocide can reduce the corrosion effects but will not reduce the level of growth [35]. The oil-water ratio has a significant effect upon the magnitude of microbial growth in emulsified oil. Table 18 shows that a 1:5 ratio is inhibitory, and normally there is very little growth. The 1:10 ratio is partially inhibitory, but in several days the organisms begin to proliferate. The 1:25 to 1:50 ratios are almost invariably ideal for maximum growth. In ratios greater than 1:50, the inhibitory components are diluted out, and

TABLE 18. EFFECT OF OIL-WATER RATIO ON GROWTH OF BACTERIA IN AN OIL EMULSION [36]  
(Results are expressed as number of cells  $\times 10^6$ /mL)

Oil-water ratio	Days					
	0	2	6	12	16	20
1:5	0.0	0.0	0.0	0.0	0.0	0.0
1:10	0.0	0.0	0.003	8.0	19.0	8.5
1:15	0.1	5.6	20.5	24.0	36.0	25.0
1:50	0.1	6.3	20.5	24.0	42.0	33.5
1:100	0.2	2.9	8.5	12.8	10.0	7.0

[35] How to improve metalworking operations by organizing a biocide treatment program. Fluid and Lubricant Ideas. 22-25, 1980 September-October.

[36] Bennett, E. O. Biology of metalworking fluids. Journal of American Society of Lubrication Engineers. 28(6):237-247, 1972 July.

the concentration of oxidizable materials seems to be the major limiting factor [36].

Table 19 presents data on pollutant concentrations found in waste emulsified oils from metal finishing plants. This table was compiled by EPA by actual sampling and analysis of waste emulsified oils from various metal finishing plants during preparation of the development document for effluent limitations guidelines and standards for the metal finishing industry [2]. Raw waste emulsified oil composition data obtained from the state environmental regulatory agencies are presented in Appendix A by the type of metal finishing operation. Examination of state and U.S. EPA data indicates that waste emulsified oils have heavy metals, sulfur, chlorine, various organic compounds, and solvents as major contaminants present separately or in various combinations. They have high BOD<sub>5</sub>, COD, and oil levels. Generally, environmental regulations do not allow discharge of untreated emulsified oil into surface waters because of its contaminants. Various treatment, recycle, reuse alternatives and economic aspects of waste emulsified oil are discussed in detail in Section 6.

#### 5.1.3.3 Synthetic Fluids--

Characteristics of waste synthetic fluid tend to be plant specific and depend on the uses to which the fluid has been put. Waste synthetic fluids may contain contaminants such as metal fines and chips, biodegradation products, tramp oil, nitrosamines, and residues from additives similar to those described for waste emulsified oils in Section 5.1.3.2.

Since synthetic fluid formulations are generally proprietary, very little information is available about their composition. A study was conducted at the University of Houston to develop data pertaining to the COD and BOD<sub>5</sub> values of synthetic fluids. The data are presented in Table 20 [37]. These data show that waste synthetic fluids have very high BOD<sub>5</sub> and COD values.

Waste synthetic fluid composition data obtained from state environmental regulatory agencies are presented in Appendix A. Owing to limited usage and formulation confidentiality, only limited data were available at state offices. Nevertheless, examination of data presented in Table 20 and Appendix A indicates that waste synthetic fluids have high BOD<sub>5</sub>, COD, and metal contaminants. Generally, untreated waste synthetic fluids may not be allowed to discharge into surface waters, since they are organic or inorganic compounds with contaminants. Waste synthetic fluids treatment,

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[37] Adams, M. C.; et al. BOD and COD studies of synthetic and semisynthetic cutting fluids. Water, Air, and Soil Pollutant. 11:105-113, 1979.

TABLE 19. POLLUTANT CONCENTRATIONS FOUND IN EMULSIFIED OILS FROM METAL FINISHING PLANTS (2)

Compound	Average daily values, #/L				Number of points	Number of zeros
	Minimum	Maximum	Mean	Median		
1. Acenaphthene	0.057	5.70	2.88	2.88	2	35
2. Benzene	0.001	0.110	0.012	0.008	18	19
3. Carbon tetrachloride	0.001	10.0	2.60	0.097	5	32
4. Chlorobenzene	0.011	0.610	0.310	0.110	2	34
5. 1,2-Dichloroethane	0.009	2.10	1.12	1.35	6	31
6. 1,1,1-Trichloroethane	0.001	1.300	74.8	0.265	18	19
7. 1,1-Dichloroethane	0.002	1.10	456	0.603	11	26
8. 1,1,2-Trichloroethane	0.006	1.30	0.331	0.010	4	33
9. 1,1,2,2-Tetrachloroethane	0.006	0.570	0.288	0.288	2	35
10. Bis-chloromethyl ether	0.009	0.009	0.009	0.009	1	36
11. Bis(2-chloroethyl) ether	0.004	0.010	0.007	0.007	2	35
12. 2-Chloronaphthalene	0.130	0.130	0.130	0.130	1	36
13. 2,4,5-Trichlorophenol	0.010	1.80	0.613	0.030	3	34
14. p-Chloro-m-cresol	0.004	800	104	2.33	8	29
15. Chloroform	0.002	0.691	0.058	0.010	19	18
16. 2-Chlorophenol	0.076	0.620	0.348	0.348	2	35
17. 1,1-Dichloroethylene	0.002	10	1.51	0.195	12	25
18. 1,2-Trans-dichloroethylene	0.008	1.70	0.507	0.008	9	34
19. 2,4-Dichlorophenol	0.010	0.068	0.039	0.039	2	35
20. 2,4-Dimethylphenol	0.001	31	5.21	0.010	6	31
21. 1,2-Diphenylhydrazine	0.005	0.012	0.008	0.008	2	35
22. Ethylbenzene	0.001	5.50	0.380	0.012	16	21
23. Fluoranthene	0.001	55	8.26	0.108	8	29
24. Bis(2-chloroisopropyl) ether	0.004	0.004	0.004	0.004	1	36
25. Bis(2-chloroethoxy)-methane	0.003	0.003	0.003	0.003	1	36
26. Methylene chloride	0.005	7.60	0.604	0.092	29	8
27. Methyl Chloride	0.001	4.70	1.18	0.009	4	35
28. Bromoform	0.010	0.010	0.010	0.010	1	36
29. Dichlorobromomethane	0.001	0.010	0.005	0.005	2	35
30. Trichlorofluoromethane	260	290	275	275	2	35
31. Chlorodibromomethane	0.001	0.010	0.004	0.002	3	34
32. Naphthalene	0.011	260	36.3	0.104	10	27
33. Nitrobenzene	0.001	0.010	0.005	0.005	2	35
34. 2-Nitrophenol	0.010	0.320	0.122	0.035	1	34
35. 4-Nitrophenol	0.010	0.010	0.010	0.010	1	36
36. 2,3-Dinitrophenol	0.010	10	3.34	0.013	3	34
37. 4,6-Dinitro-o-cresol	0.010	5.70	2.85	2.85	2	35
38. N-nitrosodiphenylamine	0.004	0.000	0.488	0.750	5	32
39. Pentachlorophenol	0.016	.0	18.4	5.20	3	34
40. Phenol	0.003	6.51	1.72	0.440	1	24
41. Bis(2-ethylhexyl) phthalate	0.002	9.10	0.818	0.073	20	17

(continued)

TABLE 19 (continued)

Compound	Average daily values, mg/L			Number of points	Number of zeros
	Minimum	Maximum	Mean		
42. Butyl benzyl phthalate	0.001	10.3	1.63	9	28
43. Di-n-butyl phthalate	0.001	3.10	0.269	15	22
44. Di-n-octyl phthalate	0.004	0.120	0.062	2	35
45. Diethyl phthalate	0.001	1.90	0.415	9	28
46. Dimethyl phthalate	0.001	1.20	0.401	3	34
47. 1,2-Benzanthracene	0.002	0.170	0.047	4	23
48. Benzo(a)pyrene	0.010	0.010	0.010	1	36
49. Chrysene	0.001	0.073	0.025	3	34
50. Acenaphthylene	0.077	1	0.406	3	34
51. Anthracene	0.003	2	0.360	7	36
52. Fluorene	0.001	0.760	0.176	7	30
53. Phenanthrene	0.002	2	0.393	8	29
54. Pyrene	0.031	0.150	0.079	5	32
55. Tetrachloroethylene	0.001	110	8.91	18	19
56. Toluene	0.001	37	1.77	25	12
57. Trichloroethylene	0.001	130	23.2	11	26
58. Aldrin	0.004	0.011	0.007	2	35
59. Dieldrin	0.003	0.003	0.003	1	36
60. Chlordane	0.001	0.013	0.007	2	35
61. 4,4'-DDT	0.002	0.010	0.006	2	35
62. 4,4'-DDE(P,P-DDX)	<0.001	0.053	0.014	4	33
63. 4,4'-DDD(P,P-TDE)	0.001	0.010	0.005	3	34
64. $\alpha$ -Endosulfan	0.008	0.028	0.018	2	35
65. $\beta$ -Endosulfan	<0.001	0.006	0.003	2	35
66. Endosulfan sulfate	0.001	0.016	0.010	4	33
67. Endrin	0.007	0.010	0.008	2	35
68. Endrin aldehyde	0.010	0.014	0.012	2	35
69. Heptachlor	<0.001	<0.001	<0.001	1	36
70. Heptachlor epoxide	<0.001	<0.001	<0.001	1	36
71. $\alpha$ -BHC	0.004	0.018	0.012	3	34
72. $\gamma$ -BHC (lindane)	0.001	0.009	0.006	3	34
73. $\gamma$ -BHC	0.004	0.011	0.007	2	35
74. PCB-1254	0.076	1.10	0.588	2	35
75. PCB-1248	0.160	1.80	0.980	2	35
Ammonia	0.460	270	46.6	10	27
BOD <sub>5</sub>	10	17,000	3,240	21	16
COD	312	1,520,000	117,000	16	21
Oil and grease	65	802,000	40,700	37	0
Total phenols	0.002	49	2.50	34	3
TDS	246	4,930	1,960	9	28
TOC	3	560,000	27,600	37	0
TSS	34.8	18,100	2,720	35	2
Total priority organics	0.053	1,920	112	37	0

TABLE 20. BOD AND COD VALUES FOR  
SYNTHETIC CUTTING FLUIDS

Fluid	BOD <sub>5</sub>	COD
	mg/L x 10 <sup>5</sup>	mg/L x 10 <sup>5</sup>
A	2.00	6.46
B	2.37	10.40
C	1.18	6.28
D	1.55	8.38
E	0.97	5.95
F	1.88	11.60
G	2.05	15.80
H	0.49	4.10
I	1.97	18.30
J	1.02	11.90
K	0.87	11.30
L	0.20	2.88
M	1.15	17.50
N	0.17	5.45
O	0.52	18.50
P	0.00	20.90

recycle, reuse alternatives along with economic aspects are discussed in detail in Section 6.

#### 5.1.3.4 Geographic Distribution--

It is reported that approximately 1,890 million liters per year (500 million gallons per year) of used oils are generated by metalworking operations [31]. Also, approximately 878 million liters per year (232 million gallons per year) of new metalworking oils are sold [31]. Since metalworking operations do not consume any oil except for evaporation and drag-out losses, it is estimated that of the 1,890 million liters per year (500 million gallons per year) generated, 1,012 million liters per year (268 million gallons per year) are recycled, and 878 million liters per year (232 million gallons per year) are disposed of.

Since sufficient data are not available to determine accurately the waste volume produced by each state, the total estimated waste volume generated was proportionately distributed among states based on the total number of metal finishing plants (with more than twenty employees) in each state. The estimated geographic distribution of waste generation is presented in Table 21, and Figure 18. Seven industrial states (California, Illinois, Texas, Michigan, New York, Ohio, and Pennsylvania) generate approximately 53 percent of the total industry waste.

The total waste will consist of approximately 50 percent straight oils, 45 percent emulsified oils, and 5 percent synthetic fluids.

TABLE 21. GEOGRAPHIC DISTRIBUTION OF WASTE OILS  
GENERATED BY METAL FINISHING INDUSTRY

State	Million liters/year
1. Alabama	11.3
2. Alaska	0
3. Arizona	5.5
4. Arkansas	6.2
5. California	110.9
6. Colorado	7.4
7. Connecticut	24.7
8. Delaware	0.9
9. District of Columbia	0.2
10. Florida	19.4
11. Georgia	12.2
12. Hawaii	0.6
13. Idaho	1.2
14. Illinois	66.5
15. Indiana	31.0
16. Iowa	9.4
17. Kansas	8.2
18. Kentucky	9.2
19. Louisiana	6.6
20. Maine	2.3
21. Maryland	7.9
22. Massachusetts	32.6
23. Michigan	61.3
24. Minnesota	17.3
25. Mississippi	6.4
26. Missouri	16.4
27. Montana	0.7
28. Nebraska	3.9
29. Nevada	1.0
30. New Hampshire	4.4
31. New Jersey	39.3
32. New Mexico	1.3
33. New York	65.4
34. North Carolina	19.1
35. North Dakota	0.7
36. Ohio	64.5
37. Oklahoma	9.5
38. Oregon	8.1
39. Pennsylvania	53.4
40. Rhode Island	10.2

(continued)



TABLE 21 (continued)

State	Million liters/year
41. South Carolina	6.4
42. South Dakota	0.9
43. Tennessee	15.5
44. Texas	43.2
45. Utah	3.6
46. Vermont	1.7
47. Virginia	9.6
48. Washington	9.6
49. West Virginia	3.6
50. Wisconsin	26.3
51. Wyoming	0.2

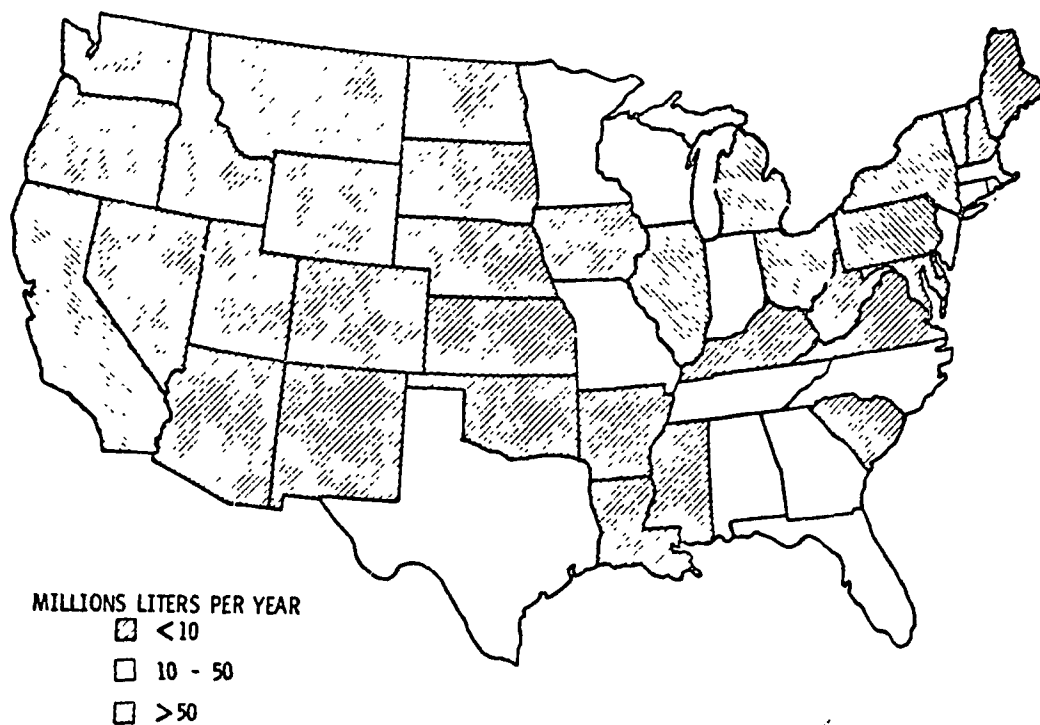


Figure 18. Geographic distribution of waste oils generated by metal finishing plants in the United States.

## 5.2 SOLVENT CLEANING

This section describes solvent cleaning operations, including solvents used and waste solvents generated.

### 5.2.1 Process Description

#### 5.2.1.1 Cold Cleaning [38]--

Cold cleaning is the simplest, least expensive, and most common type of degreasing. It is most often used for the removal of oil-base impurities from fabricated metal parts in a batch-load procedure. The cleaning solvent is generally at room temperature, although it may be heated slightly to well below its boiling point.

The solvent dissolves the greasy dirt on the part to be cleaned as it is immersed. The part is usually lowered into the solvent bath in a metal basket. The cleaning action is often enhanced by spraying solvent on the part and by agitation of the solvent by pumps, compressed air, mechanical motion, or sound. After cleaning, the part is dried by allowing evaporation and drainage of the solvent on drying racks which are located inside the cleaner or on external racks which route the drainage back into the cleaner.

Figure 19 illustrates the simple design of a typical cold cleaner [39].

#### 5.2.1.2 Emulsion Cleaning [38]--

According to current estimates, approximately 15 percent of the metal cleaning processes used in this country use emulsion cleaning. Generally, emulsion cleaning is a process for removing soils from metal surfaces by the use of common organic solvents dispersed in an aqueous medium with the aid of an emulsifying agent. The stability of the emulsion may be accentuated by such additives as surface-active agents, finely-divided solids, etc. Depending on the solvent used, cleaning is done at temperatures from room temperature to 60°C to 80°C. Dilution of solvent with water is generally over 95 percent.

A vast increase in interfacial surface results from emulsification. Because of the large solvent surface provided in the emulsion,

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[38] Peter, R.; Tanton, T.; and Leung, S.; et al. Alternatives to organic solvent degreasing. Sacramento, CA; California Air Resources Board; 1978 May. 232 p. ARB-A6-2-6-30. PB 282 466.

[39] Suprenant, K. S.; and Richards, E. W. Study to support new source performance standards for solvent metal cleaning operations. U.S. Environmental Protection Agency. 1976 April. EPA Contract 68-02-1329.

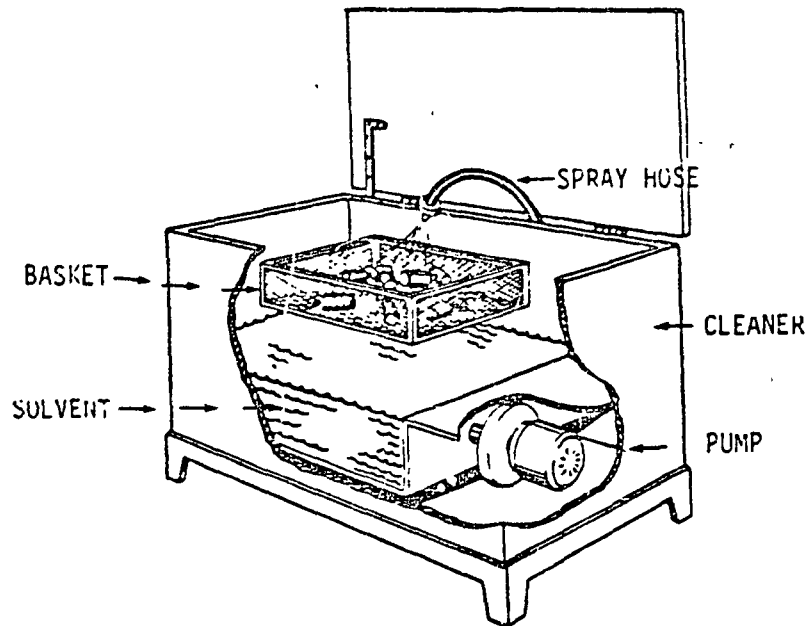


Figure 19. Cold cleaner [39].

less solvent is required to achieve the same cleaning efficiency. Surface-active materials added to the solution are attracted to the surface of the droplet, and they provide a mechanical barrier between the solvent droplets to keep them dispersed in water rather than to permit them to coalesce.

Emulsifiable solvent mixtures can be applied without prior dispersion in water. In this way, the advantage of solvent cleaning (greater soil removal) is coupled with the ability to rinse with water. This results in less solvent usage than with straight solvent usage.

Factors affecting the degree of cleaning include agitation, operating temperature, contact time, concentration of cleaner, and degree of rinsing.

The size and configuration of the part and the nature of the soil are the main considerations that influence the selection of type of cleaning method.

Two types of cleaning methods are commonly used in emulsion metal cleaning. Immersion cleaning is preferred for small parts that must be placed in baskets. Spray cleaning is often used to clean large parts with surfaces exposed for impinging. Hard-to-remove soils are generally removed with this method. In this type of application the cleaner in a concentrated form is sprayed on the

work surface and then rinsed with a pressure spray. Combination cycles of immersion, spray washing, and pressure-spray rinsing are often used to clean intricate parts. Agitation is usually provided to help in removing soil.

Compared to conventional solvent degreasing, emulsion cleaning has the following advantages [38]:

- Emulsion cleaning is an effective means of removing a wide variety of soils from metal surfaces, especially when rapid superficial cleaning is required. This is mainly because a mixture of solvent and water is used.
- It is usually less costly than solvent cleaning because a large amount of water is added to a relatively small amount of solvent.
- Since it can be operated at room or slightly elevated temperatures, hazards from fire and toxic fumes are not great. Much less hydrocarbon is emitted to the ambient air.
- Emulsion cleaning leaves a thin film of oil on the work; this thin film provides some protection against rusting.

#### 5.2.1.3 Ultrasonic Degreasing--

Ultrasonic cleaning is a special application of solvent metal cleaning, employed most frequently in the manufacture of electric and electronic equipment and aircraft parts [38].

Ultrasonic degreasing combines a precleaning cycle, such as vapor degreasing or immersion cleaning, with subsequent treatment by immersion in a ultrasonically agitated liquid bath of the degreasing solvent. Transducers which convert electrical energy to mechanical energy are placed in the bath either at the bottom or on the sides to supply the power for agitation. Solvent filtration for particle size down to 2  $\mu\text{m}$ , 5  $\mu\text{m}$ , or 10  $\mu\text{m}$ , depending on the type of soil, is provided. The frequency and intensity of the ultrasonic energy are selected on the basis of tests. An application example is the removal of residual oil from roller bearing cones. The cones are ultrasonically cleaned in trichloroethylene at 60°C, with the immersed transducers operating at a frequency of 400 kHz (400 kilocycles). The average power intensity at the transducer is  $2.5 \times 10^4 \text{ W/m}^2$  [7].

Capacity of ultrasonic cleaning tanks may be as little as 0.6 liter and generally are designed to be appropriate to the size of the parts to be cleaned [38].

#### 5.2.1.4 Vapor Degreasing--

Vapor degreasing provides an efficient and economical method for preparing clean, dry articles for subsequent finishing or fabricating. Vapor degreasing makes use of a convenient difference

between the soils removed in solvent metal cleaning and the solvents used to remove them. The solvents boil at a much lower temperature than the oils. Consequently, a mixture of solvent and metalworking oils can be boiled, and the vapors produced will be essentially pure solvent. These pure solvent vapors will condense on metal parts until the temperature of the parts approaches the boiling point of the pure solvent. The condensed solvent dissolves the oils present on the parts and drains from them as new solvent condenses [39]. Vapor degreasers are satisfactory for removing oils and greases that are partially or completely soluble in the degreasing solvent.

The two types of vapor degreasers used for industrial solvent metal cleaning are: (1) open top vapor degreasers, and (2) conveyorized vapor degreasers.

The open top vapor degreaser cleans by condensing vaporized solvent on the surface of the metal parts. The condensing solvent dissolves oil and grease, washing the parts as it drips down into the tank. To condense rinsing vapors and prevent solvent loss, the air layer or freeboard above the vapor zone is cooled by a series of condensing coils which ring the internal wall of the unit. Most vapor degreasers also have an external water jacket which cools the freeboard to prevent convection up hot degreaser walls [38]. The freeboard is usually 50 to 60 percent of one width of the degreaser [39]. Steam, electricity, or gas is used to boil the solvent. Nonflammable solvents are usually used.

Figure 20 illustrates a basic open top vapor degreaser.

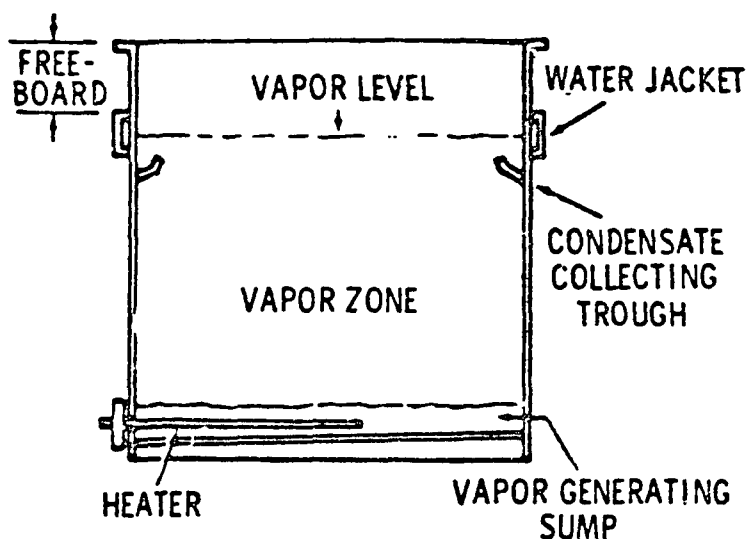


Figure 20. Basic open top vapor degreaser [7].

Open top degreasers represent a compromise between the extreme low capital investment of cold cleaning and the more capital intensive conveyorized systems discussed next. As such, they are often located in one or more convenient sites in the plant. Open-top degreasers process parts manually and are frequently used for only a small portion of the workday or shift. In contrast, conveyorized vapor degreasers tend to be central cleaning stations where the parts to be cleaned are transported to the machine [39].

Conveyor-operated solvent degreasers provide an efficient and economical method for preparing clean, dry articles for subsequent finishing of fabricating [40]. There are several types of conveyorized degreasers and each can operate with either cold or vaporized solvents. The basic steps found in the typical conveyorized vapor degreaser include a vapor rinse upon entry to the degreaser vapor space section, liquid immersion, liquid spray, vapor rinse, and finally, a slow withdrawal through a cold air space drying area. Conveyorized vapor degreasers employ the same process techniques as do open-top degreasers; the only significant difference is material handling.

There are several basic designs which are termed conveyorized degreasers: gyro, vibra, monorail, cross-rod, mesh belt, and strip cleaners. Figures 21 through 25 present sketches of the ferris wheel, vibra, monorail, cross-rod, and mesh belt degreasers [7]. Conveyorized degreasers are generally large, automatic units designed to handle a high volume of work in either a straight-through process or a return type process in which the work pieces enter and leave the degreaser unit from the same end. Their use minimizes the human element and produces consistently high quality cleaning with minimum solvent losses.

### 5.2.2 Raw Materials

#### 5.2.2.1 Requirements

Ten characteristics are required of solvents used in degreasing processes [7]. Solvents must:

- Either dissolve or attack oils, greases, and other contaminants.
- Have a low latent heat of vaporization and a low specific heat so that a maximum amount of solvent will condense on a given weight of metal and keep heat requirements to a minimum.

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[40] Allen, R. D. Inspection source test manual for solvent metal cleaning (degreasers). Washington, DC; U.S. Environmental Protection Agency; 1979 June. 150 p. EPA-430/1-79-008. PB 80-125743.

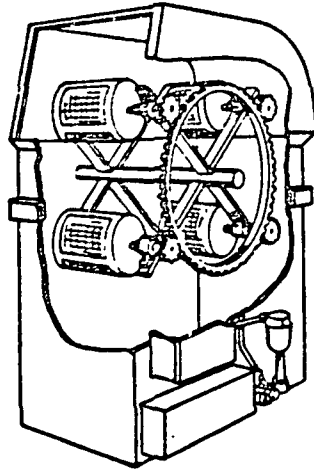


Figure 21. Ferris wheel degreaser [7].

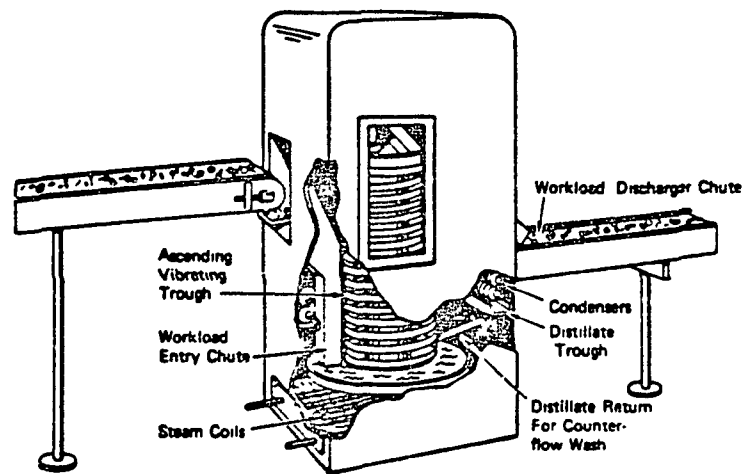


Figure 22. Vibra degreaser [7].

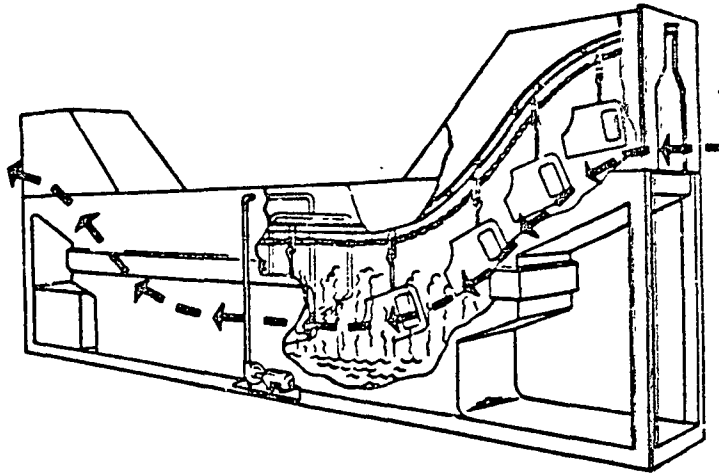


Figure 23. Monorail degreaser [7].

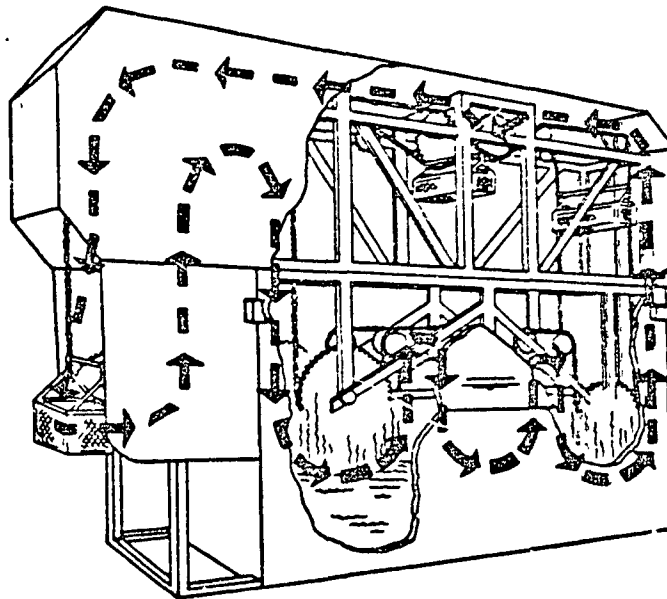


Figure 24. Cross-rod degreaser [7].



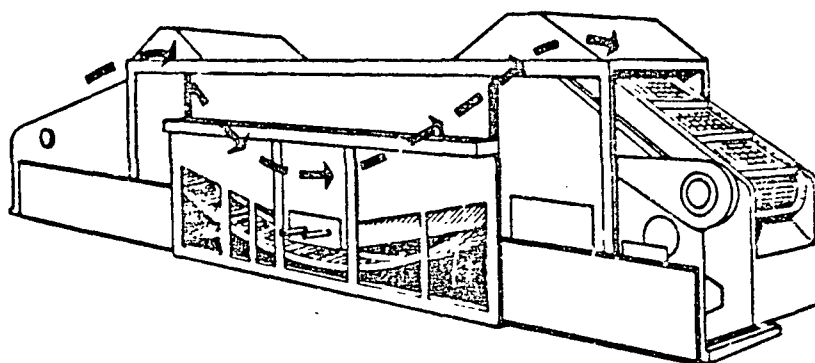


Figure 25. Mesh belt conveyorized degreaser [7].

- Have a high vapor density relative to air and a low rate of diffusion into the air to minimize solvent losses.
- Be chemically stable under conditions of use.
- Be essentially noncorrosive to common materials of construction.
- Have a boiling point low enough to permit the solvent to be easily separated from oil, grease, and other contaminants by simple distillation.
- Not form azeotropes with liquid contaminants or with other solvents.
- Have a boiling point high enough so that sufficient solvent vapors will be condensed on the work to ensure adequate cleaning.
- Be available at reasonable cost.
- Remain nonexplosive under the operating conditions of vapor degreasing.

Table 22 [41] lists typical applications for vapor degreasing solvents. Table 23 [7] lists the physical properties of commercially available solvents. Table 24 [7] gives the estimated consumption of solvents used in degreasing operations.

#### 5.2.2.2 Solvent Description [38]--

Four main types of organic solvents are used in industries with solvent-degreasing operations: alcohols, halogenated solvents,

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[41] Metal finishing guidebook and directory, 1974 Edition.  
Hackensack, NJ; Metals and Plastics Publishing, Inc.

TABLE 22. TYPICAL APPLICATIONS FOR VAPOR-DEGREASING SOLVENTS [41]

Application	Solvent	Approximate vapor temperature, °C	Factors affecting selection
Removal of soils from parts	Trichloroethylene	87	Most commonly used degreasing solvent.
Removal of slightly soluble (high melting) soils	Perchloroethylene	121	Used where higher operating temperature is desirable.
Removal of water films from metals	Perchloroethylene	121	Rapid and complete drying in one operation.
Cleaning coils and components for electric motors	Methyl chloroform	74	Solvent must not damage wire coating or sealing agents. Requires special equipment design. Selection should be based on preliminary trials
	Trichlorotrifluoroethylene	48	
Cleaning temperature-sensitive materials	Methylene chloride	40	Used where parts must not be exposed to higher vapor temperatures during cleaning. Special corrosion resistant equipment is required.
	Trichlorotrifluoroethylene	48	
Cleaning components for rockets or missiles	Trichloroethylene	87	Cleaned parts must be free of soils or residues which might react with oxidizers.
Cleaning with ultrasonics	Trichloroethylene	87	For cleaning efficiency beyond that obtained from standard vapor degreasing Solvent must be kept clean by continuous distillation and filtration during use. Selection should be based on preliminary trials.
	Perchloroethylene	121	
	Methylene chloride	40	
	Fluorinated hydrocarbon	48	

[42] Payne, H. F. Organic coating technology. Vol. II. New York; John Wiley & Sons, Inc. 1961. pp. 1019-1020.

[43] Heat exchanger tube manual. Waterbury, MA; Scovill Manufacturing Co. 1957. 171 p.

TABLE 23. PROPERTIES OF COMMERCIALY AVAILABLE SOLVENTS [7] <sup>a</sup>

Solvent	Boiling point °C	Latent heat of vaporization J/g	Specific heat, J/g°C	Specific gravity		Evaporation rate (CCl <sub>4</sub> = 100) <sup>b</sup>	Water solubility in solvent, (@ 20°C, g/100 g)
				Liquid (water = 1)	Vapor (air = 1)		
Nonhalogenated							
Toluene	110.6	363.4	1.76	0.87	3.14	12	0.05
Methyl ethyl ketone	79.6	443.8	2.30	0.81	2.41	45	13.4
Acetone	56.7	521.3	2.22	0.79	2.00	91	Complete
n-Butanol	117.2	591.6	2.34	0.81	2.55	3.5	25.8
sec-Butanol	107.2	578.2	2.34	0.81	2.55	9.4	57.0
Naphtha, coal tar	150 to 200	326	1.30	0.90 <sup>c</sup>	4.3 <sup>c</sup>	1.5 to 12	<0.05
Naphtha, safety (Stoddard)	150 to 200	301.5	1.34	0.86 <sup>c</sup>	4.3 <sup>c</sup>	1.5 to 12	<0.05
Mineral spirits	155 to 175	326.6	1.34	0.87 <sup>c</sup>	4.1 <sup>c</sup>	0.63	<0.05
Ethers (petroleum)	40 to 70	288.9	1.17	0.60 <sup>c</sup>	2.9 <sup>c</sup>	100 <sup>b</sup>	<0.05
Benzene	80.1	394	1.72	0.88	2.77	49	0.05
o-Xylene	143.9	347	1.72	0.88	3.66	5.5	0.04
Cyclohexane	80.7	158.4	1.80	0.78	2.90	2 <sup>b</sup>	<0.01
Hexane	66.7	337.0	1.55	0.66	2.97	113	<0.01
Halogenated.							
Trichlorotrifluoroethane	74.1	146.5	0.80	1.514	6.75	280	0.01 <sup>d</sup>
Methylene chloride	40.0	330.4	1.17	1.326	2.93	147	0.15
Perchloroethylene	121.1	209.4	0.88	1.623	5.73	27	0.01
Trichloroethylene	87.2	239.5	0.96	1.464	4.54	69	0.02
1,1,1-Trichloroethane	74.1	221.1	1.09	1.327	4.50	139	0.05 <sup>e</sup>
Carbon tetrachloride	76.7	218.1	0.84	1.58	5.3 <sup>c</sup>	100	0.08

<sup>a</sup>Specific gravity of vapor phase was calculated using the ideal gas law.

Assuming boiling points for naphtha coal tar, Stoddard, mineral spirits, and ethers of 175°C, 175°C, 165°C, and 55°C, respectively, along with the densities shown, the molecular weights estimated from Reference 42 are 124, 125, 130, and 85, respectively, the density of air is assumed to be 1.293 kg/m<sup>3</sup>.

Latent heats of vaporization were estimated from Reference 43.

Specific heats were estimated from Reference 43 for the temperature range of 0 to 250°C, where applicable.

API gravities were assumed for the various petroleum fractions relative to the list above, to be 25°C, 33°C, 31°C, and 100°API.

<sup>b</sup>Carbon tetrachloride is the basis for evaporation rate comparisons. Its evaporation rate is given a value of 100.

<sup>c</sup>Estimated value.

<sup>d</sup>24°C.

<sup>e</sup>25°C.

TABLE 24. DISTRIBUTION OF U.S. DEGREASING SOLVENT CONSUMPTION [7]

Chemical	1974 Apparent U.S. consumption, 10 <sup>3</sup> metric tons	1974 Apparent solvent/degreasing consumption, 10 <sup>3</sup> metric tons		Percent of total consumption for metal cleaning and degreasing
		Cold	Vapor	
Halogenated hydrocarbons:				
Fluorocarbons	428.6	6	11.1	4
Methylene chloride	235.4	46.2	10	24
Perchloroethylene	330.2	11.4	43	16
Trichloroethylene	173.7	43.8	112.7	90
1,1,1-Tricyloroethane	236.3	78	90	71
Hydrocarbons:				
Hexane	135	7		5
Toluene	3,085	14		0.5
Xylene	2,635	12		0.5
Cyclohexane	1,066.7	1		0.1
Ethers	56.3	6		11
Mineral spirits	210	30		14
Naphthas	4,450	188		4.2
Ketones:				
Acetone	882.5	10		1.1
Methyl ethyl ketone	237.2	7.5		3.1
Alcohols:				
Butyl alcohol	159.6	3.3		2.1

hydrocarbons, and ketones. The maintenance type of cold degreasing and wiping uses mainly hydrocarbons, such as mineral spirits. Manufacturing cold degreasing and conveyorized cold degreasing use a wide variety of solvents. Open-top vapor degreasers and conveyorized vapor degreasers use halogenated solvents exclusively.

Alcohols and ketones are selected for cold degreasing mainly because they evaporate faster than petroleum products and leave cleaner surfaces; they are preferred to halogenated solvents mainly because of their solvency and cost.

The five major halogenated solvents listed in Table 24 are manufactured and sold under a variety of trade names. While they are all certainly suitable to general vapor degreasing processes, each has limitations associated with it.

Trichloroethylene has been the historical favorite for vapor degreasing usage. It is felt that the development of the vapor degreasing process and associated industry was largely based on the particular properties, availabilities, and low cost of this versatile solvent. The boiling point (87°C) allows adequate vapors to condense on the work being cleaned, yet the work is not too hot to handle upon removal from the degreaser. Utility requirements also are easily met with 15 psig steam (or less) and nominal cooling. The other properties of trichloroethylene have created such widespread general usage that many vapor degreasers must be retooled or otherwise modified to allow alternate solvent usage. However, regulations restrict the use of trichloroethylene for vapor degreasing because of its photochemical reactivity and resultant production of atmospheric oxidants.

Another halogenated solvent, 1,1,1-trichloroethane, is second only to trichloroethylene in nationwide usage for vapor degreasing. General behavior is similar to trichloroethylene primarily due to a similar boiling point. However, the chemical stability of 1,1,1-trichloroethane can cause significant problems associated with water contamination and use with "reactive" metals (i.e., aluminum or zinc). The primary advantages to the user of choosing 1,1,1-trichloroethane over trichloroethylene are that parts are lower in temperature on removal from the degreaser (~14°C lower) and are thus easier to handle. An important consideration for air quality is the substantially lower photochemical reactivity of 1,1,1-trichloroethane compared to that of trichloroethylene.

Perchloroethylene is used in about 15 percent of the vapor degreasers nationwide. Perchloroethylene has inherent stability to reactive metals and thus requires less stabilization. Because of its higher boiling point (121°C), significantly more vapor condenses on the work than with either of the other two solvents. Because of the combined effects of higher temperature and increased vapor flushing, better cleaning efficiency is generally obtained with perchloroethylene. Further, because of its significantly higher boiling point, perchloroethylene drives off transient water from the workload more quickly. As with most advantages, the higher boiling point also creates some disadvantages. A minimum of 60 psig steam is required for vapor degreasers using perchloroethylene, usually requiring a larger steam coil (and probably a licensed engineer's presence). If electric or gas heaters are used, significant additional utility costs result. Safety and comfort of employees also suffer as the vapor degreaser is operated at 121°C rather than at 87°C.

Methylene chloride may be used to remove polymer residue because of its high solvency. It is especially useful for cleaning heat-sensitive parts because of its low boiling point. Less heat is required for degreasers using methylene chloride as solvent; however, methylene chloride diffuses more readily because of its low vapor density. Extensive modification of a vapor degreaser

is required to convert from trichloroethylene to methylene chloride. The low boiling point and the low volume of condensate generated may cause low cleaning efficiency.

Fluorocarbon-type solvents, such as Freon-113, have the same advantages as methylene chloride and are suitable to remove polymer residue and heat-sensitive parts, but since the vapor density of Freon-113 is much higher than that of methylene chloride less Freon will diffuse out of the degreaser. A slightly higher boiling point and a larger volume of condensate have made Freon a better solvent than methylene chloride to clean small, delicate parts. The cost of Freon is, however, much higher than that of any other halogenated solvents.

Carbon tetrachloride is not often used for degreasing except in special applications because of problems with toxicity to operators.

Brief descriptions and selected analyses of degreasing solvents and stabilizers are provided in Appendix B.

### 5.2.3 Waste Solvent Description

The degreasing equipment, sump, and stills contain spent solvents along with removed oils, greases, waxes, and metallic particles. These spent solvents are also commonly known as degreasing sludges. The following subsections describe waste solvent characteristics and their geographic distribution.

#### 5.2.3.1 Waste Characteristics--

Waste solvent composition will depend on the solvents used for degreasing and type of soils (oils, greases, waxes, buffing compounds, metallic particles, etc.) to be removed from the material being processed. It is independent of the nature of the plant.

The volume of waste solvent from a vapor degreaser per load is less than that from cold cleaners because the solvent in a vapor degreaser may be used for a longer time. Vapor degreasing wastes can contain from 15 percent to 30 percent oil contamination, whereas cold cleaning waste solvent can only contain about 10 percent oil contamination before it must be replaced [7]. Table 25 presents data for the fraction of solvent consumed that becomes waste solvent by type of degreasing operation [7].

Some criteria have been established to determine when a vapor degreaser should be cleaned. Most commonly, the need for cleaning the degreaser is established when the boiling point of the contaminated solvent is from 5 to 10 degrees above the boiling point of the pure solvent [21]. In most shops, experience shows that this will take place at nearly consistent intervals. Generally, this corresponds to a contaminated solvent with contaminant

TABLE 25. WASTE SOLVENT GENERATION BY TYPE  
OF DEGREASING OPERATION [7]

Degreasing operation	Total solvent consumption, that becomes waste solvent, %	
	Range	Average
<u>Cold cleaners</u>		
Manufacturing (44%)	40 to 60	50.0
Maintenance (56%)	50 to 75	62.5
Open top vapor degreasers	20 to 25	22.5
Conveyorized vapor degreasers	10 to 20	15.0

level approaching 30 percent [7]. Table 26 presents boiling points of clean and contaminated chlorinated solvents [44].

TABLE 26. BOILING POINTS OF CLEAN AND CONTAMINATED SOLVENTS [44]

Solvent	Boiling point, °C	
	Clean	30% Contaminated
Trichloroethylene	87.2	90.5
Perchloroethylene	121.1	126.7
1,1,1-Trichloroethane	74.1	85.0
Methylene chloride	40.0	48.9

Raw waste solvent composition data obtained from the state environmental regulatory agencies are presented in Appendix B, by type of degreasing operation wherever it is known. Examination of data indicates that waste solvents are contaminated with oils, greases, and heavy metals. Since the Resource Conservation and Recovery Act (RCRA) lists waste degreasing solvents as hazardous wastes, they should be disposed of in accordance with the regulations. Waste solvents can be reclaimed and reused. Various waste solvent reclamation technologies along with economic aspects are discussed in Section 6.

#### 5.2.3.2 Geographic Distribution--

It is reported that in 1980 approximately 1.8 million kg/day (4 million lb/day) of waste solvents are generated by the metal finishing industry [2]. This corresponds to 468 million kg/yr

[44] Vapor degreasers. Clarke, NJ; Branson Equipment Co.

(1,040 million lb/day) for a five-day work week. This estimate is based on a random survey conducted by EPA of 900 manufacturers having Standard Industrial Classification (SIC) Codes between 3400 and 3999. Since the manufacturers were selected at random, the survey data are considered representative of the entire population of manufacturers within those SIC Codes.

Since sufficient data are not available to determine accurately the waste volume produced by each state, the total estimated waste volume generated was proportionately distributed between states based on the total number of metal finishing plants (with more than twenty employees) in each state. The estimated geographic distribution of waste generation is presented in Table 27 and in Figure 26. Seven industrial states (California, Illinois, Texas, Michigan, New York, Ohio, and Pennsylvania) generate approximately 53 percent of the total industry waste.

TABLE 27. GEOGRAPHIC DISTRIBUTION OF WASTE DEGREASING SOLVENTS GENERATED BY METAL FINISHING INDUSTRY

State	Million kg/year
1. Alabama	6.0
2. Alaska	0
3. Arizona	2.9
4. Arkansas	3.3
5. California	59.1
6. Colorado	3.9
7. Connecticut	13.2
8. Delaware	0.5
9. District of Columbia	0.1
10. Florida	10.3
11. Georgia	6.5
12. Hawaii	0.3
13. Idaho	0.7
14. Illinois	35.4
15. Indiana	16.5
16. Iowa	5.0
17. Kansas	4.4
18. Kentucky	4.9
19. Louisiana	3.5
20. Maine	1.2
21. Maryland	4.2
22. Massachusetts	17.4
23. Michigan	32.7
24. Minnesota	9.2
25. Mississippi	3.4
26. Missouri	8.8

(continued)



TABLE 27 (continued)

State	Million kg/year
27. Montana	0.4
28. Nebraska	2.1
29. Nevada	0.5
30. New Hampshire	2.4
31. New Jersey	20.9
32. New Mexico	0.7
33. New York	34.9
34. North Carolina	10.2
35. North Dakota	0.4
36. Ohio	34.4
37. Oklahoma	5.1
38. Oregon	4.3
39. Pennsylvania	28.5
40. Rhode Island	5.4
41. South Carolina	3.4
42. South Dakota	0.5
43. Tennessee	8.3
44. Texas	23.0
45. Utah	1.9
46. Vermont	0.9
47. Virginia	5.1
48. Washington	5.1
49. West Virginia	1.9
50. Wisconsin	14.0
51. Wyoming	0.1

### 5.3 SURFACE COATING

This section describes metal product surface coating operations; solvent-based, water-borne, and powder paints; and waste coatings and paint sludges generated in metal coating operations.

#### 5.3.1 Process Description

The six major painting methods used to apply surface coatings in the metal fabricating and finishing industry are: (1) spray painting, (2) dip coating, (3) flow coating, (4) roll coating, (5) electrodeposition, and (6) powder coating. The most commonly used processes and equipment are described in the following sections.

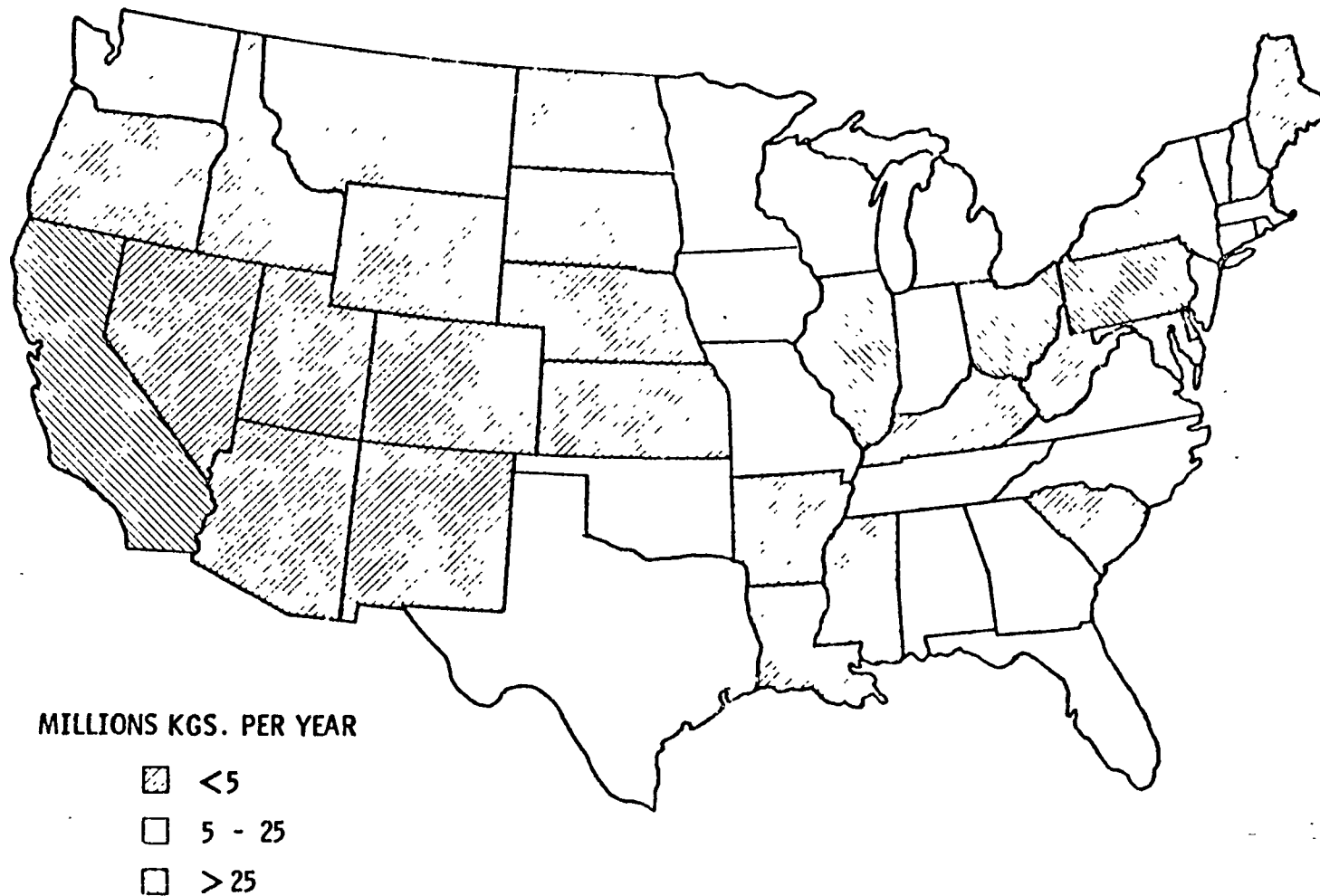


Figure 26. Geographic distribution of waste degreasing solvents generated by metal finishing plants in the United States.

#### 5.3.1.1 Spray Painting [45]--

The principle of spray painting is to break up the liquid paint composition into tiny droplets and propel them through the air onto the surface of the merchandise to be coated. Owing to the airborne solid and semisolid wastes generated by spray painting operations, they must be performed in a confined area. A paint spray booth may simply be an area enclosed on three sides with an exhaust fan and filter in an overhead hood, or it may be a much more elaborate arrangement. There are several methods for atomizing the paint composition, and a variety of spray painting equipment is currently in use.

Air Atomization--In this method, a jet of compressed air impinges on a stream of liquid paint which emerges from an orifice in the tip of the spray gun. The air jet atomizes the paint and propels (transfers) the droplets onto the surface of the merchandise (Figure 27).

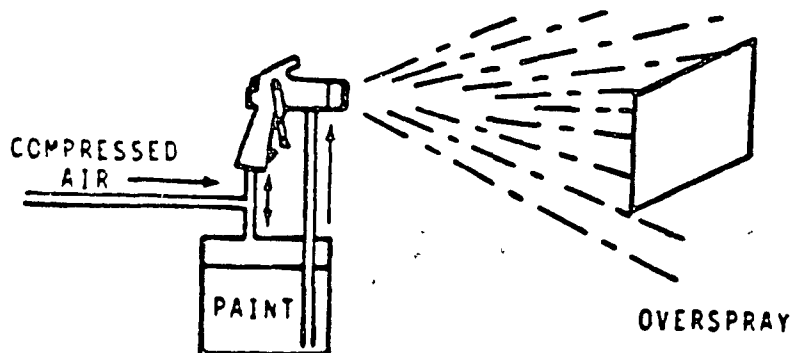


Figure 27. Air atomized spray [45].

Pressure Atomization--In this method, the liquid paint is forced through a small diverging orifice at a relatively high pressure of about 600 psi. The paint emerges from the orifice as a fine spray with sufficiently high kinetic energy to propel (transfer) it through the intervening air onto the surface of the merchandise (Figure 28).

Electrostatic Field Assisted Spray Painting--In this method, the atomized paint is given a polarized high-voltage electrical charge (usually about 100,000 volts) at or near the point where it emerges from the paint gun and the merchandise is electrically grounded to

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[45] Brewer, G. E. F. Calculations of painting wasteloads associated with metal finishing. Cincinnati, OH; U.S. Environmental Protection Agency; 1980 June. 85 p. EPA-600/280-144. PB 80-226731.

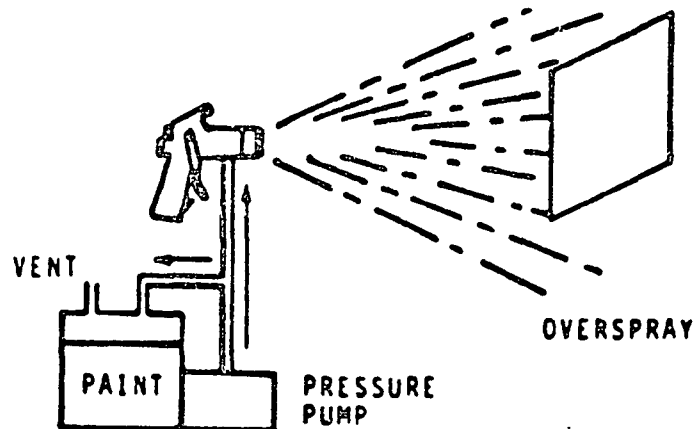


Figure 28. Pressure atomized spray [45].

the opposite polarity of the power source. Thus, the charged paint particles are electrically attracted to the surface of the merchandise (Figure 29).

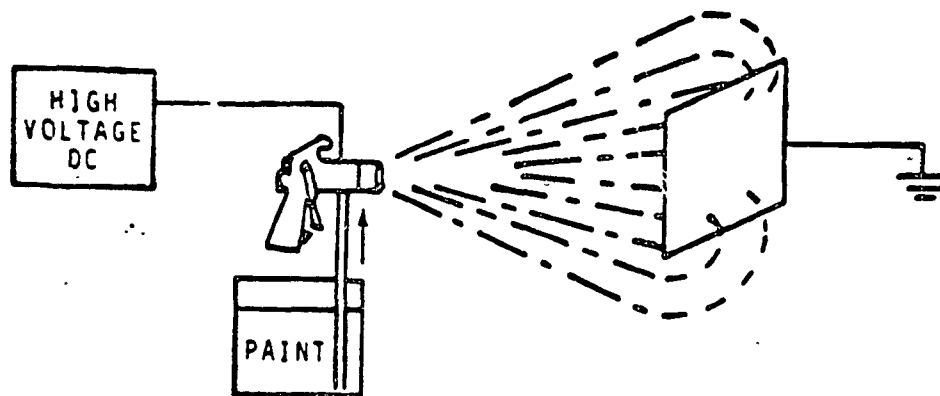


Figure 29. Electrostatic field assisted spraying painting [45].

Centrifugal Atomization--In the most commonly used centrifugal atomization method, liquid paint is gradually coated onto the center inside surface of a rapidly rotating bell. The centrifugal force of the rotating bell moves the paint to the open end where it passes through an electrostatic field and emerges as a charged, atomized spray. As the spray emerges, the electrostatic field directs (transfers) it to the surface of the merchandise (Figure 30).

A common variation of the centrifugal atomization method uses a horizontally rotating disk instead of the bell described above. This variation has about the same transfer efficiency and provides a wider coverage area. In this method, the merchandise is usually carried by a conveyor in a horseshoe-shaped loop around the disk.

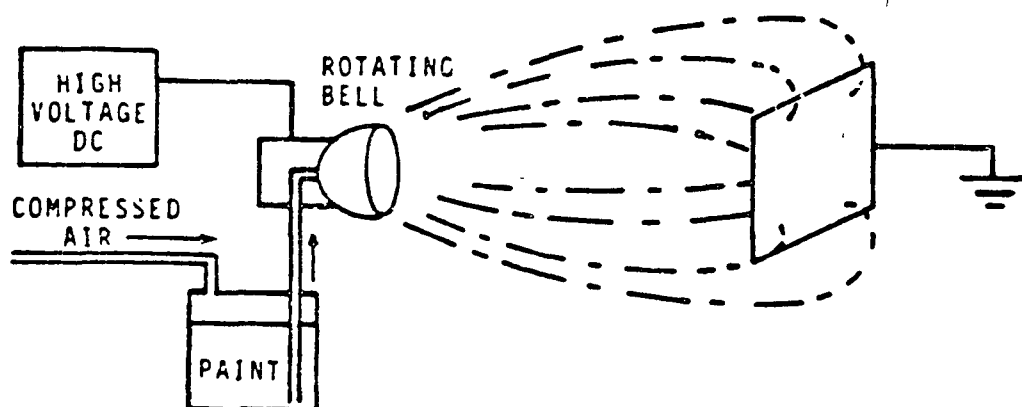


Figure 30. Centrifugal atomized spray [45].

#### 5.3.1.2 Dip Coating [45]--

In the dip coating method, the merchandise is actually submerged in a container of liquid paint and then lifted back out. The excess paint drips off the merchandise either directly back into the paint container or into a drip recovery tray. Dip coating of rigid, profiled merchandise requires that each piece be submerged individually (Figure 31).

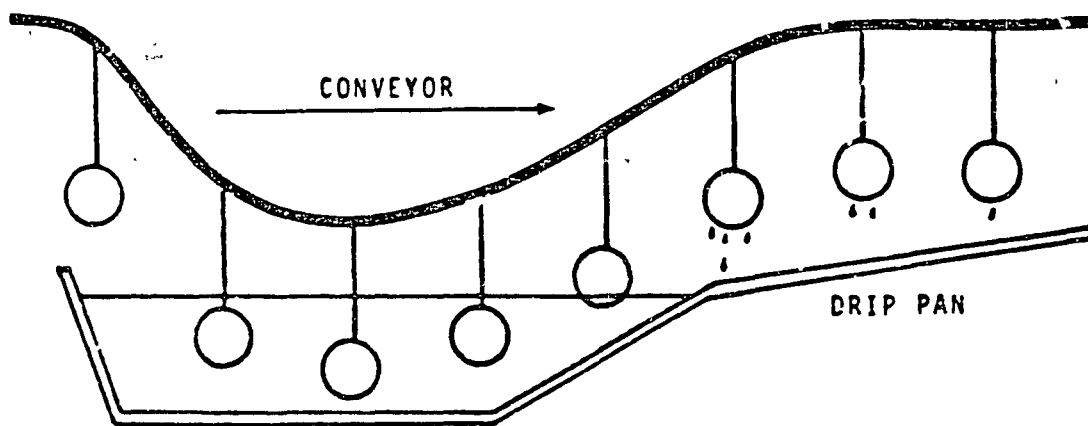


Figure 31. Dip coating rigid, profiled merchandise [45].

The drip-off process is sometimes aided by the use of a high voltage electrostatic field which is effective in eliminating drops of paint that might otherwise form on the bottom of the merchandise.

#### 5.3.1.3 Flow Coating [45]--

In the flow coating method, liquid paint is poured over the top of the merchandise and allowed to drip off the bottom. The merchandise is positioned over a container of paint, part of the paint is pumped to a dispensing head over the merchandise, the paint flows

over the merchandise forming a coating, and the excess drips back into the container (Figure 32).

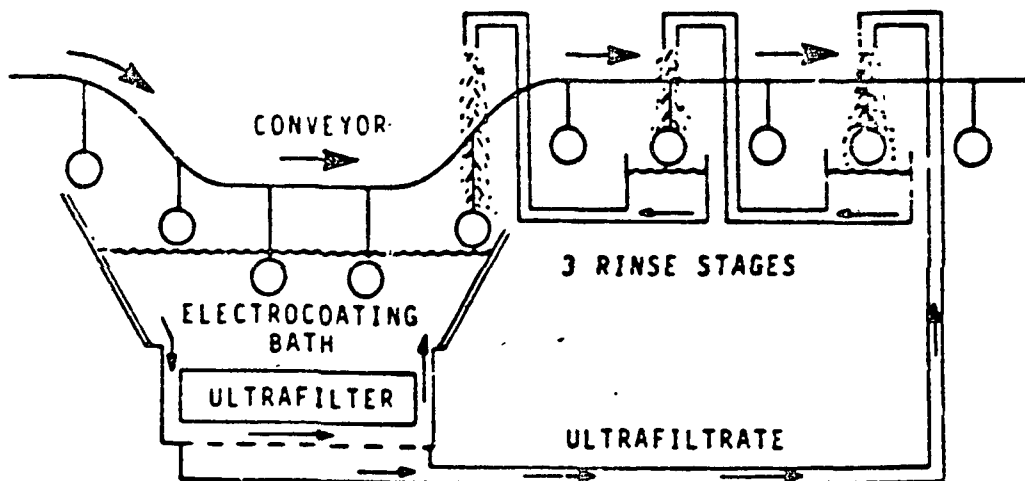


Figure 32. Flow coating [45].

Drip off is sometimes aided by use of a high voltage electrostatic field. The expected transfer efficiency for the flow coating method is about the same as for the dip coating method (75 percent to 90 percent).

#### 5.3.1.4 Roll Coating [45]--

In this method, liquid paint is applied by a transfer roll directly to the surface of the merchandise. This method can be used to paint any flat material, rigid or flexible, individual pieces or continuous sheets, to one side or to both sides simultaneously. The principle of roll coating is to cover the surface of the transfer roll with liquid paint, control the amount of paint on the surface of the transfer roll by means of a metering roll, and then to transfer the paint from the transfer roll directly to the surface of the merchandise by direct contact (Figure 33).

Figure 33 illustrates a typical arrangement for roll coating both sides of a continuous sheet of material simultaneously. In a typical arrangement for coating only one side, the transfer and metering rolls on the opposite side would be replaced by a single roll for the purpose of maintaining pressure between the transfer roll and the material.

There are a number of variations to the typical method of roll coating shown in Figure 33. For example, a better application of the paint to the surface of the merchandise is sometimes achieved by reverse roll coating. In other words, at the point of contact between the transfer roll and the material, the transfer roll is rotating in the opposite direction from the direction of travel of the material. This causes a wiping action at the point of transfer.

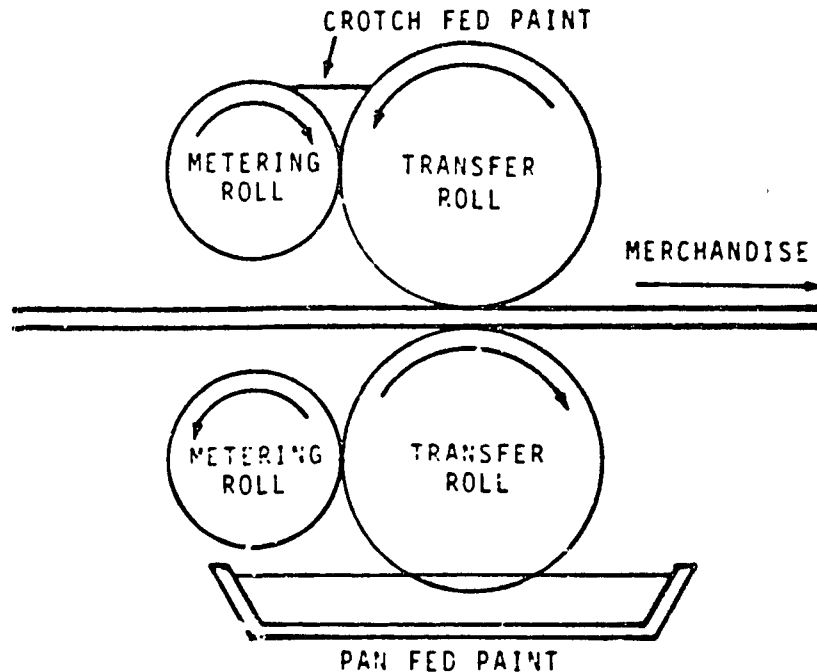


Figure 33. Roll coating [45].

#### 5.3.1.5 Electrodeposition [45]--

In this method, the merchandise is submerged into a dilute (low viscosity) dispersion of specially formulated nonvolatile paint solids mixed with water. A low-voltage (50 to 500 volts), direct current electrostatic field is applied, which attracts the non-volatile paint particles to the surface of the merchandise, where they form a highly viscous deposit. The merchandise is then lifted out of the electrocoating bath and subjected to several ultrafiltrate rinse stages. Any droplets of paint lifted out of the bath on the newly painted surface are rinsed back into the dip tank (Figure 34).

#### 5.3.1.6 Powder Coating [45]--

The principle of the powder coating method is to apply a layer of fusible powdered plastics (powder paint) to the surface of the merchandise where it is melted and heat cured into a nonvolatile solid film coating. There are three principal techniques for applying the powder paint composition to the manufactured product.

Fluidized-Bed Technique--A "fluidized bed" is achieved by installing a false bottom made from a porous material inside the paint tank. A thin layer of powder paint is placed on the top of the porous material. A controlled flow of air or an inert gas such as nitrogen is pumped into the tank chamber below the porous material. The turbulence caused as the air or gas passes through the porous material and out the top of the tank causes the particles of paint

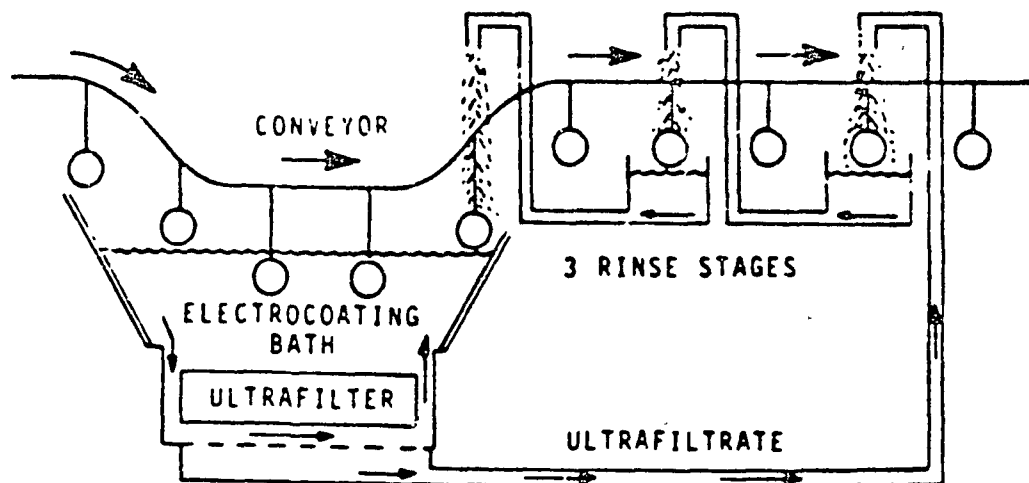


Figure 34. Electrocoating [45].

powder to rise and remain suspended like dust particles in the air. The flow rate is controlled at a point where none of the particles is raised as high as the top of the tank. The merchandise is preheated to a temperature about the melting point of the paint powder and then is dipped into the fluidized bed. The paint powder particles that contact the hot surface melt and form a film coating.

Fluidized Bed Plus Electrostatic Field Technique--A shallow "fluidized bed" is formed as described above, then the paint powder particles are charged by a high voltage electrostatic field (Figure 35)

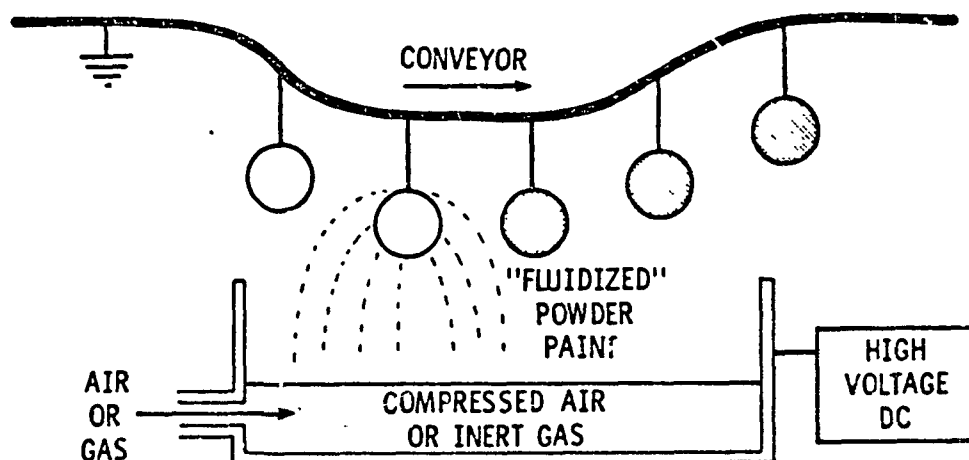


Figure 35. Electrostatic fluidized bed [45].



In this technique, the merchandise is not preheated but is electrically grounded to the power source that supplies the electrostatic field. The merchandise does not actually enter the fluidized bed, but when it passes above the surface the charged paint powder particles are attracted to it and form a coating of powder. The particles are retained on the surface of the merchandise by the residual electrostatic charge. The merchandise is then processed into a heating chamber where the paint powder particles melt and form a film coating.

Fluidized Spray Technique--The powder paint is fluidized by mixture with air or an inert gas such as nitrogen and sprayed from a paint gun under a very small pressure. The paint particles are charged by an electrostatic field at or near the point at which they leave the spray gun and the merchandise is grounded electrically to the power source that provides the field. The paint powder particles are attracted to the surface of the merchandise where they form a powder coating (Figure 36).

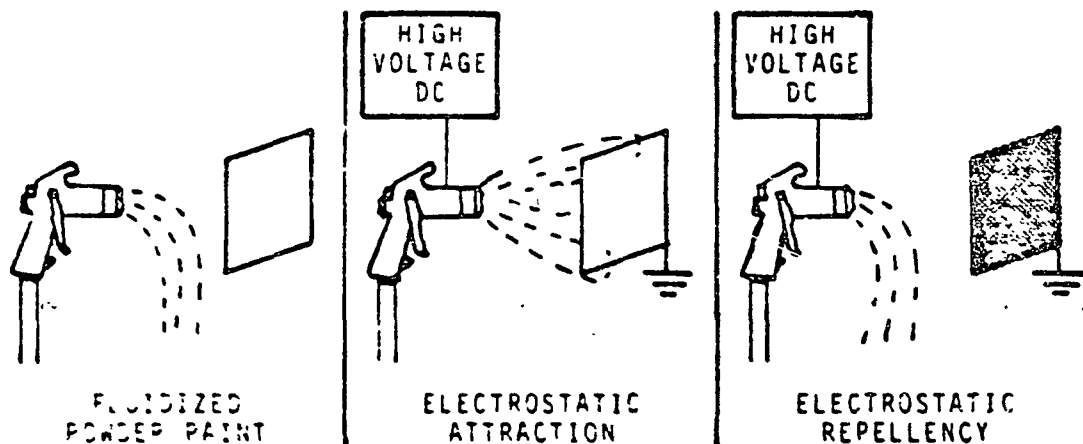


Figure 36. Fluidized electrostatic powder spraying [45].

The thickness of the powder coating on the merchandise can be predetermined and controlled by the strength of the electrostatic field. Due to the weight of the paint particles and the low pressure of the operation, without the electrostatic charge they would settle as they emerged from the paint gun. Even if they contacted the surface of the merchandise they would not be retained. When the powder coating has reached the desired thickness, the attraction is counteracted by the residual charge in the particles already attached and no more particles will be retained. This residual charge in the particles attached to the merchandise will also cause them to be retained on the surface while the merchandise is processed to a heat chamber where they melt and form a film coating.

Unlike liquid paint spraying, all the "overspray" in powder spraying operations is collected in a filter chamber and reused.

#### 5.3.1.7 Paint Curing Methods [45]--

The process by which the fresh paint composition is transformed into a solid, wear-resistant nonvolatile film coating on the merchandise is known as curing. Most paint compositions are formulated to function best when a specific curing method is used. However, some compositions may be used under several curing methods, or even with a combination of methods. Curing methods fall into the three general types described below.

Ambient Temperature Curing--The simplest method of curing is provided by those paint compositions that "dry" in an atmosphere at or near the ambient temperature of the work area. There are three general classes of paint compositions that are normally cured at ambient temperature: (1) solvent and/or water-borne paints that cure through evaporation of the liquid components; (2) paints which cure through the absorption of moisture from the atmosphere; and (3) two component paint compositions which, when mixed, form a polymerized film and solidify within a few minutes. Since only a limited time is available to apply the paint after the two components are mixed, they are usually used in spray operations where they are mixed in the spray gun chamber.

Bake Curing--The application of heat to accelerate the evaporation process is the curing method most widely used by industry. There are a number of ways to achieve bake curing, but they all function on the principle of subjecting the painted merchandise to temperature in the range of 120°C to 175°C (250°F to 350°F) for a period usually about 8 to 30 minutes. Continuous air circulation through the baking chamber is essential to remove the organic volatile waste and to dilute the vapors to below the explosive level.

Radiation Curing--There are several classes of liquid paint compositions that will solidify quite rapidly when exposed to radiant energy. Electronic beam radiation-curable paint compositions may be applied by a variety of methods such as spray, roll, flow, dip, etc. After the paint is applied, the merchandise is placed in a chamber containing a relatively oxygen-free atmosphere (usually less than 500 ppm) and exposed to high energy electron beams ( $\beta$ -rays). When the  $\beta$ -rays impinge on the liquid paint components, a chemical reaction is initiated which causes them to solidify into a solid film coating. Paints in this class are used where a comparatively thick film coating is required on a flat surface.

Ultraviolet ray-curable paint compositions are used where a comparatively thin film coating is required on virtually flat surfaces, therefore, they are generally applied to the merchandise by the roll coating method. The freshly-coated merchandise is then passed within a few inches of one or more ultraviolet lamps (usually mercury vapor tubes) which emit 315 to 400 nanometer waves.

### 5.3.2 Raw Materials

#### 5.3.2.1 Composition--

Surface coatings consume more than 600 chemicals and chemical intermediates, a greater number and variety than in any other segment of the chemical industry. Figure 37 presents typical lists of the various chemical raw materials used in surface coatings [8]. In 1980, surface coatings consumed an estimated 4.3 billion kilograms of raw materials, excluding water [9]. Over 2.3 billion kilograms were resins and pigments, the part of the coating that ends up on the coated product [9].

Paint is a dispersion of pigment in a liquid "vehicle." The vehicle consists of a volatile solvent and a nonvolatile portion called the binder. Organic solvents or water may be used as the former and resins or oils function as a binder.

Surface coatings consist of four basic components: film formers, pigments, solvents, and additives. These components are discussed below.

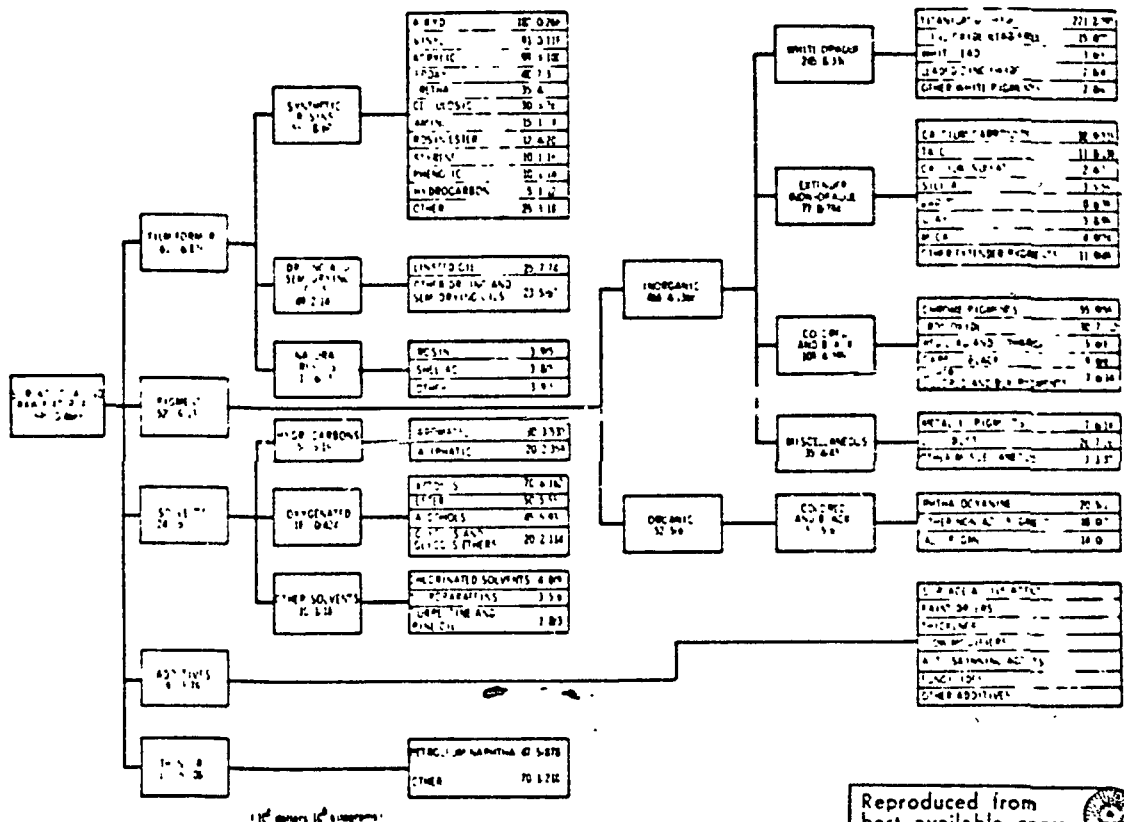


Figure 37. Raw materials flow diagram for the paint and allied products industry [8].

Film Formers--Film formers consist of synthetic resins (alkyd, vinyl, acrylic, epoxy, urethane, cellulosic, etc.), drying oils (linseed oil, tall oil, tung oil, castor oil, etc.), and natural resins (resin, shellac, etc.). These materials form the protective film of the surface coating and, hence, they are the backbone of the protective coating.

The surface coating industry classifies the surface coatings by the chemical type of the film former (alkyd paint, acrylic lacquer, etc.) [8].

- Resins are the usual binders which contribute to the durability, adhesion, flexibility, and gloss of coatings. They may be purchased either as solutions or as solids and fall into three general classes: (1) those used in lacquers which dry purely by the evaporation of solvent (cellulose derivatives, acrylic, vinyl, and bituminous resins); (2) those which dry by a chemical reaction with air (alkyds) or moisture (urethanes); and (3) those which dry (or set) at high temperature (phenolics and others) [46]. Many coatings involve blends of more than one type of resin, and the division between classes is not always sharp. Table 28 shows resins used by the United States paint industry [46].
- Plasticizers - Many of the resins used by the coating industry, such as cellulose nitrate, many phenolics, vinyls, and others, are, by themselves, too brittle to have adequate adhesion or exterior durability. For that reason, they are usually mixed with plasticizers, a procedure which will yield flexible films. The plasticizers are relatively soft materials which resist oxidation on exposure and provide continuing compatibility with the resin so it will remain plasticized. One must be selected which will not come off the film at high temperatures. Some of the common plasticizers are esters, such as castor oil, or polymerized oils. Alkyds made with nondrying oils are often used to plasticize urea resins [46].
- Oils - Traditionally, before the present resins were developed, drying oils--primarily linseed with lesser amounts of soybean, tung, oiticica, perilla, and dehydrated castor--

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[46] Scofield, F.; Levin, J.; Beeland, G.; and Larid, T. Assessment of industrial hazardous waste practices, paint and allied products industry, contract solvent reclaiming operations and factory application of coatings. Washington, DC; U.S. Environmental Protection Agency; 1975 September. 304 p. EPA 1530/SW-119c. PB 251 669.

TABLE 28. RESINS USED BY PAINT INDUSTRY [46]

<u>Resins for solvent-thinned vehicles</u>	<u>Water emulsions</u>
Acrylic, lacquer type	Acrylic emulsions
Acrylic, thermo-setting type	Casein
Alkyds	Polyvinyl acetate emulsions
Cellulose acetate	Polyvinyl chloride emulsions
Cellulose butyrate	Styrene-butadiene emulsions
Cellulose nitrate	Other emulsions
Epoxy resins	
Epoxy ester resins	<u>Water-soluble resins</u>
Ethyl cellulose	Water-soluble oil and alkyd types
Hydrocarbon resins	Other water-soluble types
Maleic resins	
Phenolic resins, pure	<u>Miscellaneous</u>
Polyurethane resins	Asphalt and coal-tar pitch
Silicone resins	Chlorinated paraffins
Urea and melamine formaldehyde resins	Natural resins (Manila, Dammar, Copal, etc.)
Vinyl (formal and butyral) acetal resins	Shellac
Vinyl acetate solution-type copolymers	Waxes
	Other miscellaneous resins and polymers

were used as paint vehicles, either by themselves or cooked with natural resins as varnishes. The newer resins, some of which (particularly alkyds) incorporate some of these oils, have largely replaced the straight oils due to cost advantages. A few nondrying oils, such as coconut and cottonseed, are used in small amounts, usually in alkyds. Various oils used in paints are given in Table 29 [46].

Pigments--Pigments are, in general, finely divided, insoluble, organic (phthalocyanine, azo, and nonazo pigments, etc.) and inorganic (titanium dioxide, zinc oxide, carbon black, etc.) powders which contribute color, opacity, consistency, and durability to paint [48]. They may be described as white, transparent, colored, and metallic. However, they are also used for fillers, reinforcers, corrosion inhibitors, and mildew control. The pigment section of the NPCA Raw Materials Index lists several thousand different materials, but many of these differ only slightly in color, particle size, or surface treatment. There are probably five hundred different pigments available to the paint industry, many of which are used in only very small amounts for specialty products. The amount

TABLE 29. OILS USED BY PAINT  
INDUSTRY [46]

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Oils

Castor oil, raw  
Castor oil, dehydrated  
Tung oil  
Coconut oil  
Linseed oil  
Safflower oil  
Soybean  
Fish oil  
Cottonseed oil

Fatty acids

Coconut  
Linseed  
Soybean  
Tall oil  
Other fatty acids

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of pure pigments required can be reduced by the use of cheaper materials which are classified as extenders. These include calcium carbonate and talc. Table 30 lists the major pigments used in paints and coatings [46].

Solvents--Solvents are used to reduce the viscosity of the surface coating for easier handling and application. They influence setting rate, drying time, flow properties, and flammability. The solvents used are either petroleum derivatives (hydrocarbons, oxygenated hydrocarbons, chlorinated hydrocarbons, etc.) or water [8].

The primary function of solvents used in coatings is to adjust the viscosity for easy application. Since the solvent does not form a part of the final film and contributes little to the properties of that film, the cheapest material which will dissolve the resin and will evaporate at the desired rate is usually chosen. A major consideration in the choice of solvents is air pollution control regulations. If a mixture of solvents is used, they should be chosen so that any change of solvency due to the lower boiling solvent coming off first will not have an adverse effect on the performance of the coating. Other things being equal, a petroleum fraction of suitable boiling range--mineral spirits, VM&P naphtha, textile spirits, etc.--is used. When these will not dissolve the resin, aromatic solvents, such as toluene or xylene, esters (ethyl acetate, etc.) or ketones (methyl ethyl ketone, etc.) are employed. A few alcohol-soluble resins, such as shellac, are dissolved in ethanol or isopropanol.

TABLE 30. PIGMENTS USED BY THE PAINT INDUSTRY [46]

<u>Greens</u>	<u>Whites</u>
Chrome green <sup>a</sup>	Antimony oxide
Chromium oxide and hydrated chromium oxide	Lithopone
Phthalocyanine green	Titanium dioxide, pure (usually 50% TiO <sub>2</sub> )
Pigment green B	Zinc oxide, leaded
	Zinc oxide (pure)
	Other white pigments
<u>Reds and Maroons-inorganic<sup>b</sup></u>	
<u>Reds and Maroons-organic</u>	<u>Blacks</u>
B. O. N. maroon	Carbon black
Chlorinated para reds	Lamp black
Lithol red and rubine	Other black pigments (except black iron oxide)
Other organic reds and maroons	
<u>Flushed Colors</u>	<u>Yellows &amp; Oranges-inorganic</u>
<u>Aqueous Dispersions</u>	C.P. cadmium oranges and reds <sup>a</sup>
Hansa yellow	Cadmium lithopone <sup>a</sup>
Iron oxides	Chrome yellow <sup>a</sup>
Phthalocyanine blue <sup>a</sup>	Molybdate orange <sup>a</sup>
Phthalocyanine green <sup>a</sup>	Strontium chromate <sup>a</sup>
Toluidine red	Zinc chromate <sup>a</sup>
Other aqueous dispersions	Other inorganic yellow and orange pigments
Other pigment dispersions	Organic yellows and oranges
<u>Metallic</u>	<u>Blues and Violets</u>
Aluminum pastes	Iron blue (Milor-Chinese-Prussian)
Aluminum powder	Ultramarine blue
Bronze powders	Other inorganic blues and violets
Copper powders <sup>a</sup>	Phthalocyanine blue <sup>a</sup>
Other metallic flakes	Other organic blues and violets
<u>Iron oxides</u>	<u>Miscellaneous</u>
Synthetic iron oxides (reds)	Cuprous oxide <sup>a</sup>
Synthetic iron oxides (yellows)	Fluorescent pigments
Synthetic iron oxides (other)	Zinc dust
Natural iron oxides	Other miscellaneous pigments
Ochres, siennas, and umbers	
<u>Extenders</u>	<u>Lead</u>
Calcium carbonate - precipitated	Basic lead carbonate <sup>a</sup>
Calcium carbonate - natural	Basic white lead silicate <sup>a</sup>
Magnesium silicate (talcs)	Red lead <sup>a</sup>
Barytes - natural	Other lead pigments <sup>a</sup>
Diatomaceous earths	
Kaolin (calcined and other clays)	
Mica, dry and water-ground	
Silicas, ground	
Other extender pigments	

<sup>a</sup> Indicates hazardous materials.

<sup>b</sup> Except iron oxide.

Water is increasingly used for water-soluble resins and to thin emulsions. Small amounts of other solvents are used in paint and varnish removers, spirit stains, and other miscellaneous materials. Solvent usage in the paint industry is summarized in Table 31 [46].

TABLE 31. SOLVENTS USED BY PAINT INDUSTRY [46]

<u>Aliphatic hydrocarbons<sup>a</sup></u>	<u>Terpenic hydrocarbons</u>
Mineral spirits, regular and low odor	(Pine oil and turpentine)
Mineral spirits, odorless	<u>Ketones<sup>a</sup></u>
Kerosene	Acetone
Mineral spirits, heavy	Methyl ethyl ketone (MEK)
Other aliphatic hydrocarbons	Methyl isobutyl ketone (MIBK)
	Other ketones
<u>Aromatic and naphthenic hydrocarbons<sup>a</sup></u>	<u>Esters<sup>a</sup></u>
Benzene	Ethyl acetate
Toluene	Isopropyl acetate
Xylene	Normal butyl acetate
Naphtha, high flash	Other ester
Other aromatic hydrocarbons	

<sup>a</sup>Indicates hazardous material.

Additives--Additives are used to facilitate production and to improve the application and performance properties of the coating system. Additives consist of surface agents, driers, thickeners, flow modifiers, anti-skinning agents, fungicides, flame retardants, etc. [8].

A wide variety of materials is added to many paint formulations in small amounts for specific purposes. Driers are used to accelerate the oxidation (or drying) of drying oils and alkyd resins. They are organic soaps of cobalt, lead, manganese, or other metals. The organic portion confers solubility in the organic solvents used but otherwise does not appear to affect the catalyst properties, which are determined by the metal. A few nonmetallic materials are also used as driers [46].

Anti-skinning agents are the reverse of driers in that they delay the drying of oils or alkyds in the can with the formation of a "skin." They are usually volatile, so that they evaporate rapidly after the coating is applied [46].

Various mercury compounds have historically been used as preservatives and fungicides. Water-thinned paints are, for various reasons, excellent food for many bacteria. Without a preservative,



many of those paints will decay in the can. Both water- and solvent-thinned paints are susceptible, after application, to an assortment of fungi, which are often called mildew although there is some doubt about this nomenclature. Mercury is effective both as a bactericide and a fungicide. For that reason it is preferred by paint manufacturers. Although a wide variety of nonmercurial bactericides and fungicides are available, they rarely perform both functions, and their durability on exposure has been found to be poor compared to that of mercury compounds [46].

A wide variety of materials, generally classified as surface-active agents, are used to adjust the mixing and dispersing of pigments, consistency of the paint, settling properties, ease of application, and flow and leveling of the applied coatings. These are often proprietary compounds whose composition is not disclosed. The proper use of these materials is more an art than a science, and often small amounts of several may be used in the same formulation [46].

Miscellaneous materials used as additives in paints and surface coatings are listed in Table 32

TABLE 32. MISCELLANEOUS MATERIALS ADDED TO SURFACE COATINGS [46]

<u>Anti-skinning agents</u>
<u>Metallic soaps</u>
Aluminum stearate
Zinc stearate <sup>a</sup>
Calcium stearate
Other metallic soaps
<u>Bodifying agents, solvent systems</u>
(other than above)
<u>Bodifying agents, water systems</u>
Carboxymethyl cellulose (C.M.C.)
Hydroxethyl cellulose
Methyl cellulose
Others
<u>Dispersing and mixing aids</u>

(continued)

<sup>a</sup>Indicates potentially hazardous materials.

TABLE 32 (continued)

Driers

Calcium soaps  
 Cobalt soaps<sup>a</sup>  
 Lead soaps<sup>a</sup>  
 Manganese soaps<sup>a</sup>  
 Zirconium soaps<sup>a</sup>  
 Other driers

Fungicides, Germicides, and Mildewcides

Phenols, halogenated phenols, and  
 their salts<sup>a</sup>  
 Phenyl mercuric acetate<sup>a</sup>  
 Phenyl mercuric oleate<sup>a</sup>  
 Others

<sup>a</sup>Indicates potentially hazardous materials.

5.3.2.2 Classification--

Product coatings are classified as one of three basic types:  
 (1) solvent-borne, (2) water-borne, or (3) powder coatings.

Solvent-Borne--Solvent-borne coatings may be subdivided into conventional solvent-based coatings (composition <70 percent solids) and high solids coatings (>70 percent solids) [9]. The three types of solvent-based coatings used in industry are paints, enamels, and lacquers. Paints are highly pigmented drying oils diluted with a low-solvency-power solvent known as thinner. Applied paints dry and cure in the oven by evaporation of the thinner and by oxidation during which the drying oil polymerizes to form a resinous film. Enamels are similar to paints in that they cure by polymerization. Many coatings contain no drying oils but cure by chemical reaction when exposed to heat. Applied lacquers are dried by evaporation of the solvent to form the coating film.

The amounts and types of solvents and thinners used in surface coating composition varies. The solvents used in enamels, lacquers, and varnishes are aromatic hydrocarbons, alcohols, ketones, ethers, and esters. The thinners used in paints, enamels, and varnishes are aliphatic hydrocarbons, mineral spirits, naphtha, and turpentine [10].

High solids coatings contain a solid composition up to 70-80 percent by volume. The remaining organic solvent portion is necessary for proper application and curing.

Use of conventional solvent-based coatings for metal product coatings is declining because high solids coating formulations can more readily comply with current air pollution regulations limiting solvent emissions [9].

Water-Borne [47]--The term water-borne refers to any coating which uses water as the primary carrier combined with organic solvent and is differentiated from pure organic solvent-borne paints. There are basically three types of water-borne coatings: latex or emulsion paints, partially solubilized dispersions, and water-soluble coatings. Table 33 lists the properties of these three types of paints. Most current interest is centered around the partially solubilized dispersions and emulsions. Emulsions are of particular interest because they can build relatively thick films without blistering and they contain no noxious amine solubilizers.

TABLE 33. PROPERTIES OF WATER-BORNE COATINGS [47]

Properties	Latex or emulsion paints	Partially solubilized dispersions	Water-soluble coatings
Molecular weight	Up to 1 million	50,000 to 200,000	20,000 to 50,000
Viscosity	Low - not dependent on molecular weight	Somewhat dependent on molecular weight	Very dependent on molecular weight
Viscosity control	Require thickness	Thickened by addition of co-solvent	Governed by molecular weight and solvent control
Solids content	High	Medium	Low
Gloss	Low	Medium	High
Chemical resistance	Excellent	Good to excellent	Fair to good
Exterior durability	Excellent	Excellent	Very good
Impact resistance	Excellent	Excellent	Good to excellent
Strain resistance	Excellent	Good	Fair to good
Color retention on oven bake	Excellent	Good to excellent	Fair to good
Reducer	Water	Water	Water or solvent/water mix
Wash-up	Difficult	Moderately difficult	Easy

[47] Surface coating of metal furniture - background information for proposed standards. Research Triangle Park, NC; U.S. Environmental Protection Agency; 1980 September. 406 p. EPA-450/3-80-007a. PB 82-113938.

Most of the solubilized water-born paints are based on alkyd or polyester resins. Table 34 shows the solids and water content of several types of water-borne paints.

TABLE 34. SOLIDS AND SOLVENT CONTENT OF WATER-BORNE PAINTS [47]

Waterborne paint system	Solids content volume percent	Water to solvent ratio
High solids polyester	80	80/20
Coil-coating polyester	51	51/49
High solids alkyd	80	80/20
Short oil alkyd	34	34/66
Water reducible polyester	48	82/18
Water reducible alkyd	29	67/33
High solids water reducible conversion varnish	80	90/10

A common method of solubilizing is to incorporate carboxyl-containing materials such as maleic anhydride and acrylic acid into the polymer. The acids are then "solubilized" with low molecular weight amines such as triethylamine. After application, the coatings are baked and the water, solvent, and amine evaporate leaving a pigment film on the object.

The use of water-borne coatings can reduce the explosion problem associated with organic solvent-based paints. Some organic solvents are used, but the amount used is greatly reduced. Water-borne coatings have the additional value of reducing the amount of air flow needed from the application areas and curing ovens and can reduce energy consumption.

In organic solvent-based paints, relatively few monomers can be used because of solubility and viscosity. Molecular weights are especially restricted. In water-borne coatings, the selection of usable monomers is much wider. In addition, water-borne paints can contain a higher solids content than organic solvent-based coatings without an increase in viscosity. An additional advantage of water-borne paint systems can usually be cleaned with water whereas organic solvent-based systems require solvents for cleaning. Organic solvent may be needed for cleanup of water-borne systems if the paint has dried.

Summaries of the advantages and disadvantages of water-borne paints are present in Tables 35 and 36. The use of these coatings in the metal finishing industries is limited at present; however, it is expected to increase.

TABLE 35. ADVANTAGES OF WATER-BORNE COATINGS [47]

- 
- 
1. Reduction of fire or explosion potential and toxicity in both the storage and application areas.
  2. Greater variety of available monomers.
  3. Higher solids content possible at same viscosity.
  4. Lower raw material cost (e.g., water vs. solvent).
  5. Ease of clean-up.
  6. Good selection of colors.
  7. Good quality finish.
  8. Can be formulated for metallics.
  9. Rapid color changes possible.
- 
- 

TABLE 36. DISADVANTAGES OF WATER-BORNE COATINGS [47]

- 
- 
1. Protection of equipment against rust needed.
  2. More pretreatment may be required than for organic solvent-based paint.
  3. Longer flash-off may be required.
  4. Humidity control equipment may be necessary.
  5. Possible emission of amines to the atmosphere.
  6. "Faraday effect" is a problem for certain shapes.
  7. Metallic finishes from organic solvent-based coatings have not been matched with other waterborne coatings.
- 
- 

Powder Coatings--Powder paint compositions have characteristic differences from liquid paint compositions. A bulk volume of liquid paint composition contains a specific volume percentage of nonvolatile solids, with the balance being volatile liquids. A bulk volume of powder paint composition contains only about 50 volume percent of nonvolatile solids, with the balance being air. Powder paint compositions "as bought" have a bulk volume density weight in the range of 0.6 to 0.84 kg/L (5 to 7 lb/gal); however, when the powder is melted into a nonvolatile solid, the solid density is in the range of 1.2 to 1.8 kg/L (10 to 15 lb/gal) [45].

Before powder can be applied as a coating, part size, part mass, part shape, paint thickness, color changing and matching, and "Faraday Effect" are the most important evaluations to be made.

Chemical compositions of powder coatings used in surface coating industries consist of synthetic resins, pigments, solid additives, and from 0 to 10 percent entrapped volatiles. The film formers are the synthetic resins (alkyd, vinyl, acrylic, epoxy, urethane, etc.). The surface coating industry classifies surface coatings by the resin type (e.g., alkyd paint, vinyl paint, etc.). Pigments consist of both inorganic and organic compounds which are used for color and opacity. Additives are used to aid in production and improve application and performance properties of the film former [47].

There are two general synthetic resin types of powder coatings: thermoset and thermoplastic types. Thermosetting powders harden during heating inside a bake oven as a result of cross-linking or polymerizing of the resin. Thermoplastic powders soften with the application of heat and resolidify during cooling. Table 37 lists the powder coatings groups by synthetic resins. Thermosetting and thermoplastic coatings are usually applied by electrostatic spray and fluidized bed, respectively. Most thermoplastic coatings require a solvent or powder primer before the coating can be applied. The most widely applied thermosets in the metal finishing industry are epoxies and polyesters. These materials provide a tough, chemical and abrasive resistant coating which achieves excellent adhesion to almost any metallic substrate. Several of the thermoplastics listed in Table 37 are being applied successfully to metal products. Most of the thermoplastics are applied to thick films for wear resistance [47].

TABLE 37. POWDER COATING RESIN GROUPS [47]

Thermosetting	Thermoplastics
Epoxy	Polyvinyl chloride or "vinyl"
Polyester	Polyethylene
Acrylic	Cellulose acetate butyrate (CAB)
	Nylon
	Polyester
	Acrylic
	Cellulose acetate propionate (CAP)
	Fluoroplastics

Both powder coating types offer several advantages and disadvantages (Table 38) when compared to solvent-based coatings.

### 5.3.3 Waste Coating Description

Factory application of coating will normally generate waste because of coating over spray, spillage, dripping, spoiled batches, and equipment cleanup. This waste is commonly known as paint

TABLE 38. COMPARISON OF POWDER COATINGS TO SOLVENT-BASED COATINGS [47]

Advantages	Disadvantages
1. Provides tougher, more abrasive resistant finish	1. Color changes require that application area and powder recovery system be thoroughly cleaned.
2. Fewer rejects and sags	2. Tapped holes in parts require masking.
3. Lower energy consumption.	3. Almost all thermoplastics presently require an organic or powder primer.
4. Production rates can sometimes be increased.	4. Certain shapes cannot be electrostatically coated because of the "Faraday Effect."
5. Less metal products are damaged during packing and shipping because coating is more abrasive resistant.	5. Difficult to coat small numbers of parts.
6. Eliminates OSHA requirements for solvents.	6. Powders are explosive, but minimum ignition temperature of powders is higher than for organic solvents.
7. Usually no final refinishing required.	7. High capital costs for manufacturing and application equipment for powder coatings.
8. Less metallic preparation for parts to be coated.	8. Electrostatic gun hoses may plug frequently.
9. Preferred for wire-type parts.	9. Difficult to touch-up complex surfaces
10. Superior for tubular parts.	10. Metallic and some other types of finishes available from organic solvent-based coatings have not been duplicated commercially in available powder coatings.
11. No additional solvents for controlling viscosity or cleaning equipment required to be purchased or stored at facility.	
12. Less powder required to cover same surface area at same coating thickness.	
13. Good coatings for electrical insulation and ambient temperature variations.	
14. Significant reduction of VOC emissions	
15. No primer required for thermosets and some thermoplastics.	
16. Problems associated with water usage are reduced or eliminated.	
17. In many applications powder can be reclaimed and reused, providing a higher powder utilization efficiency than transfer efficiencies achieved with conventional solvent-based coatings	

sludge. Factors affecting quantity and composition of wastes are described in the following subsections along with an estimation of the quantity of waste generated by the industry and its geographic distribution.

#### 5.3.3.1 Waste As a Function of Application Method--

Generally some paint loss is expected during transfer of a paint composition from its container to the surface of the merchandise [48]. Losses will generally occur regardless of the degree of sophistication of the methods of application and equipment used. These are so-called "unavoidable losses" since they are inherent to the method of application and equipment used for the painting operation. The method of application may be dictated by the size and shape of the article being coated, the type of coating and the curing conditions required [46].

The total amount of "unavoidable losses" represents the difference of the volume of nonvolatile solids in the paint used in the operation and the volume of nonvolatile solids in the film coating on the finished merchandise. For planning and calculation purposes, this is usually expressed as "percent expected transfer efficiency" (% exp.t.e.).

However, a single distinct % exp.t.e. cannot be established for each painting method. "Unavoidable losses" for each method will vary with the peculiarities of the specific operation. For example, there are more overspray losses when painting small irregular pieces of merchandise than when painting large flat surfaces; there are more clean-up losses if the operation requires frequent changeover or shutdown; etc. The range of % exp.t.e. is presented in Table 39, followed by brief description of waste volume generated by various application methods.

The loss from spray application will run from 10 to 70 percent of the total coating applied, depending on shape and size of the article being coated and equipment used, with the majority of such wastes falling in the range of 40 to 60 percent [46].

Other application methods generate considerably smaller amounts of wastes since nearly no paint is wasted, and all excess paint is captured and suitable for reuse. Most wastes result from equipment cleanup following a change of color or coatings. Thus, the losses from these applications are a function of the frequency with which such changes are made and are not related to the amount of coating used. In general, each cleanup of roll and powder equipment results in very little waste, but changes may be made fairly frequently [46]. The amount of total wastes from roll

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[48] Calculations of painting wasteloads associated with metal finishing. Cincinnati, OH; U.S. Environmental Protection Agency; 1980. EPA-600/2-80-144.



TABLE 39. EXPECTED TRANSFER EFFICIENCY [48]

Painting Method	Percent expected transfer efficiency
Air atomized, conventional	43, <sup>a</sup> 50, <sup>b</sup> 30-60 <sup>c</sup>
Air atomized, electrostatic	87, <sup>a</sup> 68-87 <sup>d</sup>
Pressure atomized, conventional	65-70 <sup>e</sup>
Pressure atomized, electrostatic	85-90 <sup>f</sup>
Centrifugally atomized, electrostatic	93, <sup>a</sup> 85-95 <sup>d</sup>
Dip, flow, and curtain coating	75-90, <sup>f</sup>
Roll coating	90-98, <sup>f</sup> 96-98 <sup>g</sup>
Electrocoating	90-96, <sup>f</sup> 99, <sup>b</sup>
Powder coatings	50-80, <sup>h</sup> 98, <sup>b</sup> 90-99 <sup>i</sup>

<sup>a</sup>E. P. Miller, Ransburg Co., SME Paper, FC73-553.

<sup>b</sup>J. A. Antonelli, du Pont Co., SME Paper, FC74-654.

<sup>c</sup>J. A. Antonelli, du Pont Co., "depending upon requirement and shape of merchandise" (direct communication).

<sup>d</sup>E. P. Miller, Ransburg Co., "depending upon object being coated" (direct communication).

<sup>e</sup>W. H. Cobbs, Jr., Nordson Corp., (direct communication).

<sup>f</sup>F. Scofield, Wapora, Inc., EPA Contract 68-01-2656.

<sup>g</sup>M. Wismer, PPC Industries, (direct communication).

<sup>h</sup>S. B. Levinson, D. Litter Lab., Journal of Painting Technology, pp. 35-56, July 1972.

<sup>i</sup>T. W. Seitz, Sherwin-Williams Co., "newer reuse methods" (direct communication).

coating varies from two percent to 10 percent of the weight of purchased coating material [46]. However, this waste includes cleaning solvents and other contaminants in addition to paint wastes.

In dip coating, any paint which drains from articles which have been coated flows back to the dip tank for reuse. However, this process and electrocoating will generate much larger amounts of cleaning wastes at the end of a run than roll and powder equipment, but the runs are usually much longer [46].

In many plants, the coating material in the dye tanks is drummed at the end of a production run and stored for reuse when that type and color of coating is required again. This means wastes are generated only from the cleaning of tanks and hangers [46].

#### 5.3.3.2 Waste as Function of Materials Coated [46]--

Waste quantities are principally a function of application method and the physical shape of the object being coated. A range of application methods are used for most substrates, the nature of which is only one of a number of factors considered when the application method and coating are chosen. No correlation is evident between the quantity of waste generated and materials coated.

#### 5.3.3.3 Waste Composition--

Waste composition is largely a function of the type of coating used. As discussed in Section 5.3.2, surface coatings consist of four basic components: film formers (resins or oils), pigments, solvents (organic or water), and additives. Wastes consist primarily of these four basic components since there are no chemical changes occurring in surface coating operations.

Raw waste coatings composition data obtained from the state environmental regulatory agencies are presented in Appendix C. Also waste source is identified wherever it is known. Each composition listed is that of a specific waste stream generated by a specific firm, and is provided to serve as an example of wastes generated by the surface coating industry. Waste composition will vary from company to company. Examination of data indicates a waste paint sludge may have high concentrations of organic solvents, resins, and heavy metals. Waste paint sludge may or may not be a hazardous waste depending on its composition. Disposal practice will depend on whether waste is hazardous or nonhazardous. Resource Conservation and Recovery Act (RCRA) testing will be required to classify a waste paint sludge as hazardous or nonhazardous. Also it might be economical to recover organic solvents from solvent based waste paint depending on solvent concentrations. Various paint reclamation techniques and recycle/reuse/disposal alternatives along with economic aspects are discussed in Section 6.

#### 5.3.3.4 Geographic Distribution--

Insufficient information was found in the literature, state environmental regulatory agencies offices, and industry to provide accurate data on the quantities of waste generated by the application of coatings in the metal finishing industry. Approximately 60 percent of the coatings are spray applied. The waste from this process constitutes approximately 90 percent of the total industry waste. Other methods of application account for the remaining 10 percent of waste generated [48].

On the average, an estimated 20 percent of the total coating applied become waste due to overspray, drip-off, and spillage [45]. As reported in Section 5.3.2, in 1980 an estimated 101 million dry gallons of coatings were used by the metal finishing industry. Based on this, in 1980 total coating wastes from all factory-applied coating operations in the metal finishing industry are estimated to be 20 million dry gallons annually.

Since insufficient data are available to accurately determine waste volume produced by each state, the total estimated industry waste volume is proportionately distributed between states according to the total number of metal finishing plants (with more than twenty employees) in each state. The geographic distribution of wastes is presented in Table 40, and Figure 38. Seven industrial states (California, Illinois, Texas, Michigan, New York, Ohio, and Pennsylvania) generate approximately 53 percent of the total industry waste.

TABLE 40. GEOGRAPHIC DISTRIBUTION OF COATING WASTES  
GENERATED BY METAL FINISHING INDUSTRY

State	Million dry liters/ year
1. Alabama	0.973
2. Alaska	0
3. Arizona	0.477
4. Arkansas	0.534
5. California	9.576
6. Colorado	0.636
7. Connecticut	2.127
8. Delaware	0.079
9. District of Columbia	0.019
10. Florida	1.673
11. Georgia	1.048
12. Hawaii	0.049
13. Idaho	0.106
14. Illinois	5.730
15. Indiana	2.672
16. Iowa	0.814
17. Kansas	0.712
18. Kentucky	0.795
19. Louisiana	0.568
20. Maine	0.201
21. Maryland	0.681
22. Massachusetts	2.812
23. Michigan	5.261
24. Minnesota	1.495
25. Mississippi	0.549
26. Missouri	1.416
27. Montana	0.057
28. Nebraska	0.333
29. Nevada	0.087
30. New Hampshire	0.382
31. New Jersey	3.384
32. New Mexico	0.117

(continued)

TABLE 40 (continued)

State	Million dry liters/ year.
33. New York	5.640
34. North Carolina	1.646
35. North Dakota	0.061
36. Ohio	5.564
37. Oklahoma	0.825
38. Oregon	0.704
39. Pennsylvania	4.603
40. Rhode Island	0.874
41. South Carolina	0.556
42. South Dakota	0.080
43. Tennessee	1.340
44. Texas	3.728
45. Utah	0.310
46. Vermont	0.144
47. Virginia	0.825
48. Washington	0.825
49. West Virginia	0.307
50. Wisconsin	2.271
51. Wyoming	0.019

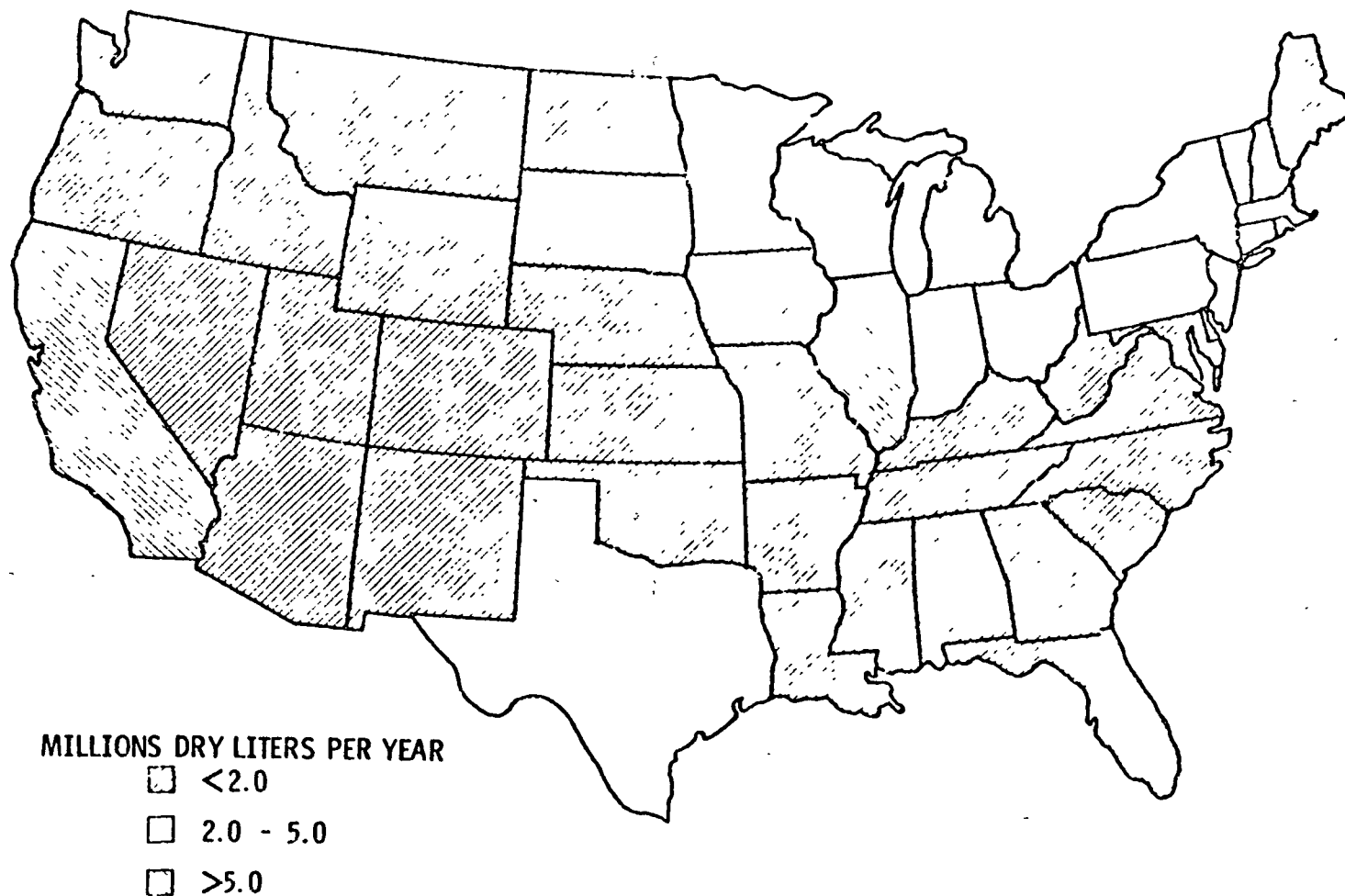


Figure 38. Geographical distribution of coating wastes generated by metal finishing plants in the United States.

## SECTION 6

### IDENTIFICATION OF BYPRODUCT UTILIZATION SCHEMES

#### 6.1 DISPOSAL AND RECLAMATION OF EMULSIFIED OILS

The disposal, recycling, or reclamation of emulsified oils used in metalworking operations are heavily influenced by environmental regulations and economic considerations. Oil and other contaminants are usually separated from water to meet regulations governing the discharge of water into the environment. Wastewater discharge regulations limit the concentration of oil discharged to a surface stream to 5-15 mg/L, provided the oil is not floating or visible.

Since most emulsified oils used in metalworking typically contain less than 10 percent of oil, separation of oil for reuse is not economical, and many machining operations tend to extend the life of the metalworking fluids for as long as possible.

The most common technologies employed in recycling include gravity separation and skimming, centrifuging, filtration, and water coalescing [49]. Recycling equipment can be associated either with individual machines or through central systems. Since water and solids are the two most common contaminants, these physical recycling technologies offer low cost methods for recycling large quantities of low or medium quality oils.

Handling spent metalworking fluids is an expense for the owners of machining operations. When the fluid becomes spent and is no longer usable, owners must pay a contractor to have the spent fluid hauled away. In some cases, where the volume of spent fluids generated is small, the cost to have a contractor haul away metalworking fluid as it becomes spent is exorbitant. In these cases, typical of small machining operations, the spent fluids are temporarily stored in tanks or lagoons. The spent fluids are then hauled away on an intermittent basis, with storage costs adding to disposal costs. Less scrupulous firms may simply dump the spent fluids down the drain.

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[49] Making recycling work for you through proper process selection. Fluid and Lubricant Ideas. 10-13, 1979 Summer.

In many operations, the spent emulsified oil becomes incorporated into oily wastewater, either intentionally or unintentionally. When the volume of oily wastewater generated exceeds about 200 gallons per day, it becomes economical for the machining operation to maintain its own wastewater treatment plant rather than pay a contractor to haul away the oily wastewater.

Figure 39 is a diagram of the steps involved in fluid reclaiming. Reclaimers and refiners charge on a sliding scale for oil waste pick-up. The scale depends upon: (1) percent oil, (2) percent bottom sediment and waste, (3) the distance the waste must be hauled, (4) the size of the generator, (5) how the generator has been doing business with a reclaimer or rerefiner, (6) how well the personalities involved get along, (7) how much the generator wants to get rid of the waste (most reclaimers will not handle over the legal limit for PCBs), and (8) how much the reclaimer or rerefiner wants that particular batch of oil. Many large cases are handled on a bid basis only [50].

#### Fluid Reclaiming

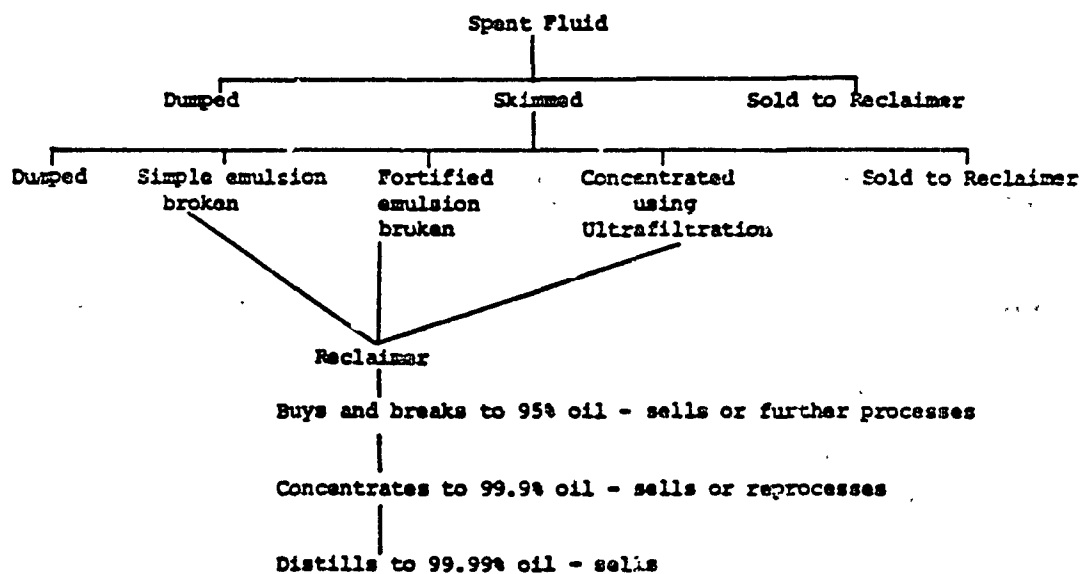


Figure 39. Fluid reclaiming [50].

Reclaimers' feedstocks are generally fairly constant from source to source over time; however, the everyday input of feedstock waste oils varies from 2 percent to 98 percent oil. Reclaimers

[50] Gabris, T. Emulsified industrial oils recycling. Bartlesville, OK; U.S. Department of Energy; 1982 April. 155 p. DOE/BC/10183-1.

find most of their feedstocks falling between 25 percent and 70 percent oil. It is preferred that the waste oils be pretreated and concentrated first by the generator. This is to the generator's benefit also as they can then get paid for their waste and profit rather than pay to have it hauled away. This pretreatment varies from use of a simple gravity settling tank to sophisticated in-plant waste treatment facilities installed for water clean-up. Getting money for the oil or reprocessing it themselves is a by-product of complying with Federal and State clean water standards in the latter case.

A categorical description of the sources of the emulsified waste oil has been adopted by some reclaimers as follows:

Small users - produce 50,000 gallons/year  
Medium users - produce between 50,000 and 2 million gallons/year  
Large users - produce over 2 million gallons/year

In a wastewater treatment plant the following technologies may be employed [50]:

- Skimming
- Coalescing
- Emulsion breaking
- Flotation
- Centrifugation
- Ultrafiltration
- Reverse osmosis
- Carbon adsorption
- Aerobic decomposition

In-plant recycling can be either batch or continuous. In a typical batch system spent fluid is transferred into the dirty oil tank and pre-filtered. The pre-filter removes large dirt particles before the fluid is centrifuged and heated. The final clean up is accomplished by ultrafiltration and the fluid is recycled back to the clean oil tank. A continuous system accomplishes the same degree of clean up in an operation which continuously processes small amounts of spent fluid. No containment of spent fluid is needed; however, maintaining an acceptable level of contaminant removal is required at all times. The use of one or the other system normally depends upon factory logistics.

#### 6.1.1 Description of Technologies and Equipment Used for In-Plant Processing

This section discusses nine generic types of technologies commonly used by the metal finishing industry to clean up and recover metal working fluids.

To assess relative applicability, comparison of advantages and disadvantages for the nine oil removal technologies is presented



in Table 41 [2, 51] with a more detailed discussion of each technology to follow.

#### 6.1.1.1 Gravity Separation and Skimming--

Gravity separation and oil skimming are used in the metal finishing industry to remove oily wastes from many different process wastewater streams. They are applicable to any waste stream containing pollutants which float to the surface. They are used in conjunction with emulsion breaking, dissolved air flotation, clarifiers, and other sedimentation devices.

Gravity separation used in metalworking operations are simply large circular or rectangular vessels which allow the oil to float to the top and solids and water to settle to the bottom. Time required for separation may be in days or weeks, so the tank is normally large enough to handle thousands of gallons at a time. Gravity separation often includes provisions for heating (to lower the viscosity) and extended baffle surfaces (to decrease the effective height that must be traversed by a rising oil globule). Still, reasonable capital and manpower costs make this a relatively low cost-per-gallon process. More elaborate units contain baffles to facilitate oil/water separation and drag conveyors for swarf removal.

Gravity separators equipped with skimmers are the most widely used [52]. The most common skimming designs include the blade, which skims the floating oil from the surface and directs it into a trough, and the rotor, which continuously removes oil from the surface as it turns. More elaborate units contain belts or drums which attract the oil and are scraped of the oil in a skimming chamber. Some units incorporate pipes that contain slotted suction openings for oil removal. Another version includes a telescoping pipe that lowers and allows oil to enter by gravity flow [53]. In addition, chain and flight, rotating pipe and helical model skimmers are available [54].

A decanter is used if the skimmed oil is frothy. This allows the oil to separate from the water because of the difference in specific gravity. An oil skimmer is employed to remove leaking lubricant and hydraulic oils from rolling mills to prevent damage to

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[51] Ford, D.; and Elton, R. Removal of oil and grease from industrial wastewater. Chemical Engineering. 49-56, 1977 October 17.

[52] Evans, R. A. Solving the oil pollution problem. Lubrication Engineering. 521-524, 1968 November.

[53] Paulson, E. Keeping pollutants out of troubled water. Lubrication Engineering. 508-513, 1968 November.

[54] FMC Corporation, Product Literature.

TABLE 41. OIL-REMOVAL PROCESS SUMMARY [2,51]

Process	Advantages	Disadvantages
Gravity separation (API, CPI, PPI separators)	<ul style="list-style-type: none"> <li>• Economical</li> <li>• Simple operation</li> </ul>	<ul style="list-style-type: none"> <li>• Limited efficiency</li> <li>• Susceptible to weather conditions</li> <li>• Removes little or no soluble oils</li> <li>• Limited removal of emulsified oil</li> </ul>
Centrifuging	<ul style="list-style-type: none"> <li>• Economical</li> <li>• Simple operation</li> <li>• Requires less space</li> </ul>	<ul style="list-style-type: none"> <li>• Higher power cost</li> <li>• Noise</li> <li>• Disposal of concentrate</li> </ul>
Filtration	<ul style="list-style-type: none"> <li>• Handle high solids</li> </ul>	<ul style="list-style-type: none"> <li>• Requires backwashing</li> <li>• Backwashing stream a subsequent problem</li> <li>• Disposal of sludge and filter media</li> </ul>
Coalescing filter	<ul style="list-style-type: none"> <li>• High potential efficiency</li> <li>• High reliability</li> <li>• Low capital and operating costs</li> </ul>	<ul style="list-style-type: none"> <li>• Cannot handle high solids due to fouling, but vertical type can handle higher loadings</li> <li>• Potential biological fouling</li> <li>• Not generally effective in removing soluble or chemical stabilized emulsified</li> </ul>
Emulsion breaking	<ul style="list-style-type: none"> <li>• High percentage of oil removal</li> </ul>	<ul style="list-style-type: none"> <li>• High chemical and energy costs</li> </ul>
Air flotation (DAF and IAF)	<ul style="list-style-type: none"> <li>• Handles high solids</li> <li>• Reliable process (handles shock load)</li> </ul>	<ul style="list-style-type: none"> <li>• Chemical sludge disposal when coagulants are used (DAF only)</li> <li>• Requires chemicals</li> </ul>
Membrane processes	<ul style="list-style-type: none"> <li>• Soluble oil removal indicated in laboratory tests</li> </ul>	<ul style="list-style-type: none"> <li>• Low flux rates</li> <li>• Membrane fouling and questionable membrane life</li> </ul>

(continued)

TABLE 41 (continued)

Process	Advantages	Disadvantages
Membrane processes (continued)		<ul style="list-style-type: none"> <li>• Narrow temperature range</li> <li>• Not demonstrated as a practical process for oil and grease removal</li> <li>• Pretreatment required</li> </ul>
Carbon adsorption	<ul style="list-style-type: none"> <li>• Removes soluble oil</li> <li>• High potential efficiency</li> </ul>	<ul style="list-style-type: none"> <li>• Expensive</li> <li>• Regeneration required</li> <li>• Requires extensive pretreatment</li> <li>• Full-scale operation not proven in refinery</li> </ul>
Biological	<ul style="list-style-type: none"> <li>• Removes soluble oil</li> <li>• Relatively high tolerance for oil and grease</li> </ul>	<ul style="list-style-type: none"> <li>• Solid carryover</li> <li>• Prone to upset</li> <li>• Pretreatment pre-requisite</li> </ul>

pumps and pipes. Skim oil is usually hauled away for disposal or re-refining.

Common gravity separator designs include API (American Petroleum Institute), CPI (corrugated plate interceptor) and PPI (parallel plate interceptor) separators [55]. The API gravity separator is most frequently used. It contains a basin from which free oil droplets rise due to buoyance forces (see Figure 40).

The corrugated plate interceptor is composed of groups of plates parallel to one another. Oil floats into the corrugations and coalesces on the plates. The advantage of CPI and PPI systems is that 20 percent less installation area is needed. Disadvantages of the API include construction cost, fire hazard, evaporation losses, and high steam consumption [56].

[55] Tabakin, R. B.; Trattner, R.; and Cheremisinoff, P. N. Oil/water separation technology: The options available, Part 1. Waste and Sewage Works. 74-77, 1978 July.

[56] Stone, R.; and Smallwood, H. Aerospace industrial waste pretreatment. 29th Industrial Waste Conference 1976 May 7-9. West Lafayette, IL; Purdue University, 1976. pp. 51-59.

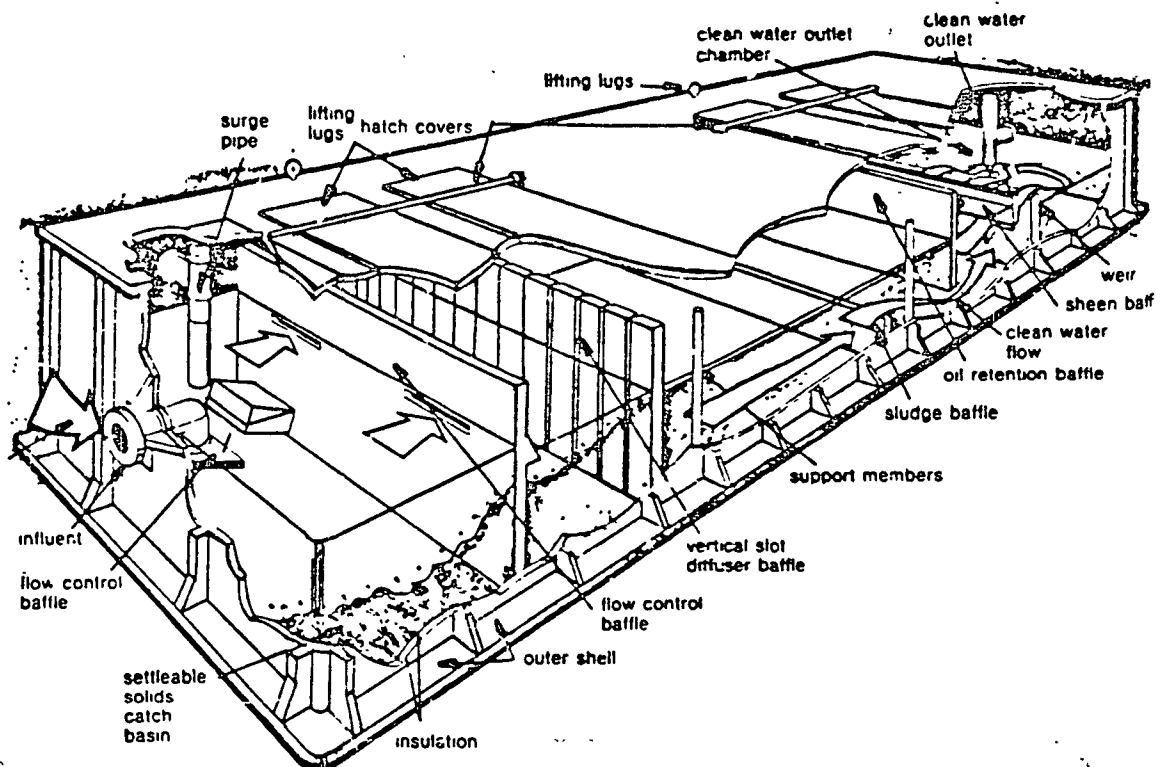


Figure 40. API separator [55].

The PPI reduces the path that the oil must travel, as oil coagulates on the undersurface of the plates and moves upward. Solid particles, on the other hand, collect on top of the plate and slide down to the bottom.

To determine utilization of gravity separators in the machining operation, the following points are considered: (1) type of swarf; (2) type of coolant/oil; (3) type of installation; (4) type of operation; (5) availability and cost of floor space; (6) finish and accuracy requirements; (7) initial and continuing cost of cleaning equipment; and (8) production downtime [57].

Table 42 illustrates examples of the performance of a skimmer system [2].

[57] Patterson, M. M. Why separation filtration for abrasive machining. *Lubrication Engineer*, 458-461, 1979 December.

TABLE 42. SKIMMER SYSTEM PERFORMANCE FOR OIL AND GREASE REMOVAL [2]

Sample number	Influent mg/L	Effluent mg/L	Removal, %
1	149,779	17.9	>99.9
2	19.4	8.3	57.2
3	232	63.7	72.5
4	61	14	77.0

#### 6.1.1.2 Centrifuging--

Centrifuging is primarily used in metal finishing operations to remove metallic particles and/or to separate water from the oil that has been gravity separated or skimmed from the waste emulsified oil. It will not break emulsions and therefore cannot be used for removing oil from emulsified oil.

Centrifuging uses the same principle as gravity separation, but the higher gravitational force in centrifuging permits separation to take place more quickly and efficiently and within a smaller space. Forces several thousand times higher than the force of gravity may be developed in centrifuges to achieve separation of solids and suspended water from mineral-based fluids and lubricants or to separate tramp oils from water-based coolants [49]. In the metalworking industry, by removing metal fines and tramp oils, the coolant and cutting tool life can be greatly extended [58-61].

Centrifuging may be accomplished either with a batch or a continuous process. Batch centrifuging is normally employed when there is a low rate of impurities accumulation or when a considerable amount of accumulation may be tolerated. Otherwise, continuous centrifuging is used. Typically, the centrifuged fluid is emptied from the machine sump into the transfer tank and the sump is cleaned. The cleaned oil is returned to the sump after the addition of additives [50].

- [58] Sluhan, C. A. Grinding with water miscible grinding fluids. Lubrication Engineering. 352-354, 1970 October.
- [59] Improving coolant life. Fluid and Lubricant Ideas. p. 28, 1979 Winter.
- [60] Centrifugal oil purification at an aluminum can plant. Fluid and Lubricant Ideas. 19-20, 1980 May/June.
- [61] Recycling metalworking coolants through central systems. Fluid and Lubricant Ideas. 24-25, 1981 January/February.

There are three common types of centrifuges: the disc, basket, and conveyor types. The fundamental difference between the three types is the method by which solids are collected and discharged [50].

In the disc centrifuge (see Figure 41), suspended particles are collected and discharged continuously through small orifices in the bowl wall. The oil-water mixture spreads out across a series of conical discs which allow the light oil fraction to separate and flow across the topside of the disc to a discharge pipe. The heavier water flows across the bottom of the discs to a separate discharge pipe.

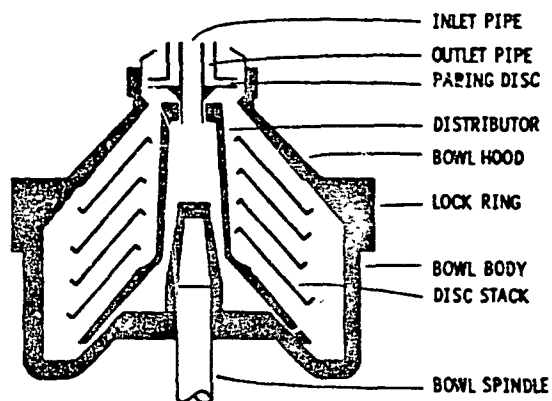


Figure 41. Disc-type centrifuge.

In the basket centrifuge, dirty oil is introduced at the bottom of the basket, and solids collect at the bowl wall while clarified effluent overflows the lip ring at the top. Since the basket centrifuge does not have provision for continuous discharge of collected cake, operation requires interruption of the feed for cake discharge for a minute or two in a 10- to 30-minute overall cycle.

In the conveyor type or decanter centrifuge (see Figure 42), an electric motor drives the decanter bowl via a V-belt drive. The bowl drives the conveyor through a gearbox. Waste oil enters the revolving bowl through an inlet pipe in the center of the screw conveyor. Aided by strong centrifugal force, the solids "settle" out of the liquid and are transported by the screw conveyor to the narrow end of the bowl, where they are discharged by centrifugal force. Both solids and purified oil collect in compartments in the center cover of the machine before falling by gravity into receivers.

Decanter centrifuges can reduce the amount of solids reaching a disc-type centrifuge. Thus, for many oils, a two-stage operation consisting of a decanter followed by a disc-type unit is used.

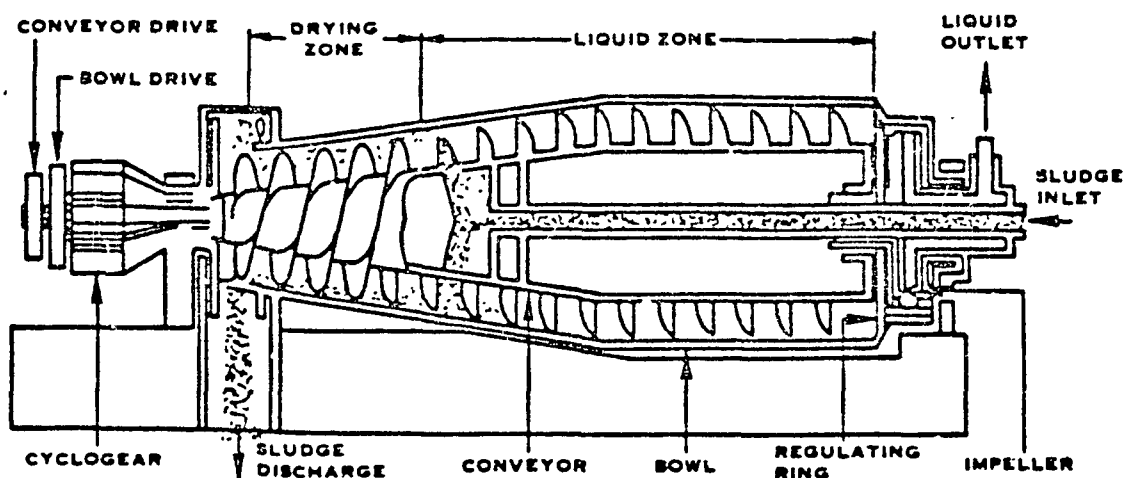


Figure 42. Decanter centrifuge [2].

In one test, a decanter reduced solids in the disc-type units feed by 50 percent [62].

Centrifuges have minimal space requirements and achieve a high degree of effluent clarification. The operation is simple, clean, and relatively inexpensive. The area required for a centrifuge system installation is less than that required for a filter system of equal capacity, and the initial cost is lower.

The major difficulty encountered in the operation of centrifuges has been the disposal of the concentrate, which is relatively high in suspended, nonsettling solids.

Table 43 illustrates centrifuge performance in removing oil and grease from oily wastewater [2].

TABLE 43. OIL AND GREASE REMOVAL PERFORMANCE  
DATA FOR CENTRIFUGE [2]

Sample number	Influent mg/L	Effluent mg/L	Removal, %
1	373,280	3,402	98.9
2	14,639	1,102	92.5

[62] Centrifuges for re-refining and reprocessing waste oils.  
ALFA-LAVAL Inc., Product Literature.

#### 6.1.1.3 Filtration--

Filtration is widely used in metal finishing plants to remove metallic particles from the metalworking fluids during daily operations, and the filtered fluids are recycled. Filtration increases the life expectancy of the fluids. At the same time, with use of filtered fluids, better products are attained along with increased metalworking tool life. Also, filtration is used as a treatment step in a total waste emulsified oil treatment scheme.

Although centrifugation and gravity separation have been discussed as suitable methods of solid particle removal, filtration appears to be the most common means of removing solid particles. The selection of filtration methods depends on cost, the type of contaminants present, and personal preference.

Several different types of filtering devices are used to reclaim oil coolants. Some of these have permanent media such as screens which permit their regeneration within the system, others utilize a moving filter media; and some utilize a diatomaceous earth as a precoat to assist in the filtration [63].

Smaller size chips, which arise from grinding or surface finishing operations are usually handled by filters. The driving force of filtration can be either vacuum or pressure [2]. Vacuum filters operate by employing a vacuum under the media which draws the particles to the media. The pressure filters require a pump, which feeds fluid to the media. The diagrams of these two filters are shown in Figures 43 and 44, respectively. The advantages and disadvantages of these two filters are summarized in Table 44. Generally, pressure and vacuum equipment can remove particles as small as 3 micrometers, though 25 micrometers is the most common filter size [49].

Cartridge type filters are available for smaller loads of particles. Cartridge is a broad term for a self-containing device, which has a filtering medium that may be replaced or regenerated.

These filters may contain paper, cloth, or nonwoven media [64]. When filtering waste oils it is best to use several different

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[63] Fochtman, E. G.; and Tripathi, K. C. Research needs in coolant filtration. Proceedings in Lubrication Challenges in Metalworking and Processing; 1978 June 7-9; Chicago. ITT Research Institute, First International Conference, 117-121.

[64] Brooks, K. A., Jr. A review of disposable nonwoven filtration media for cutting coolant and process fluids. Lubrication Engineering. 542-548, 1974 November.



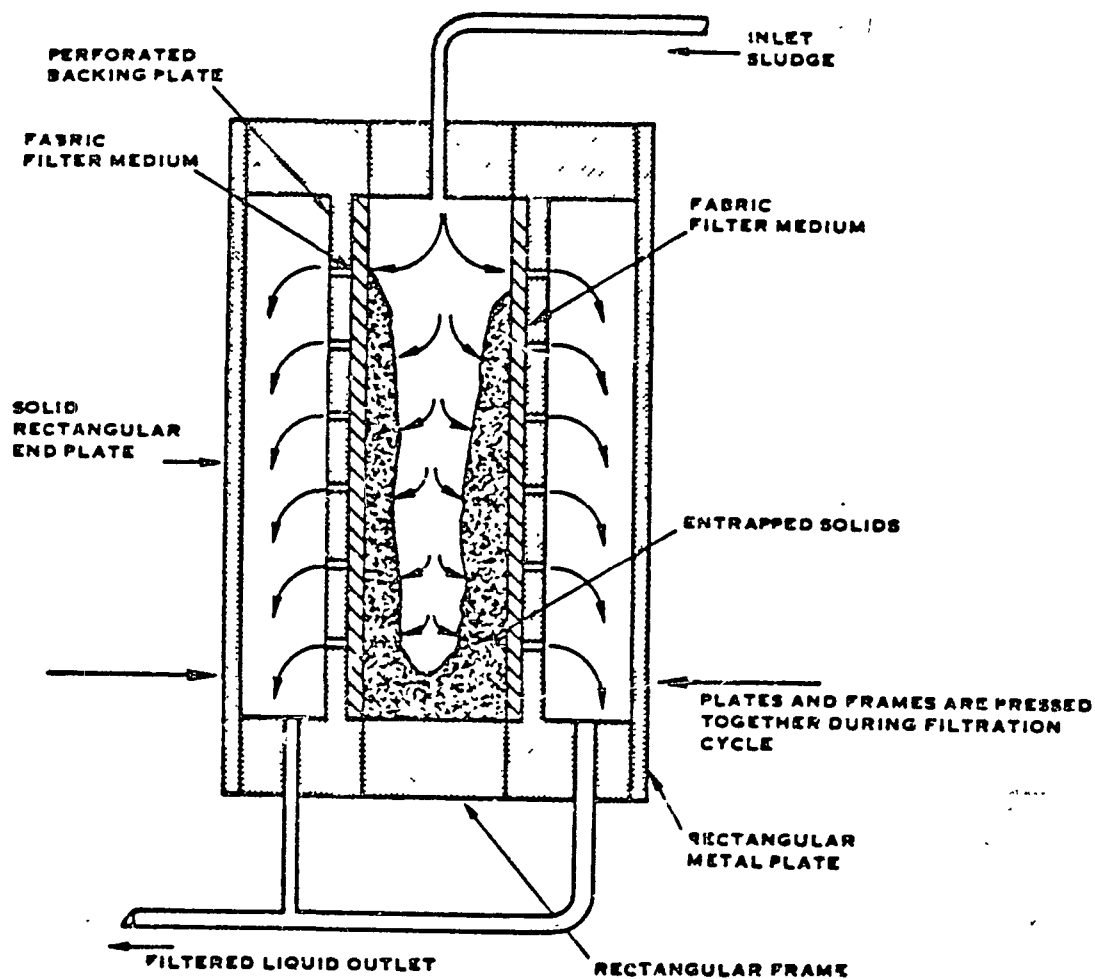


Figure 43. Pressure filtration [2].

size cartridges in series, rather than one fine filter. A 25-micrometer filter can be used to remove most of the large particles, followed by a 10-micrometer filter to remove most of the remaining contamination. Stepwise filtration will require the least number of filter changes, particularly the finer filters, which are often more expensive.

Another type of filter, wedge wire, allows the metal chips to perform the actual filtering. The wedge wire filter is a screen of wires with triangular cross sections which support the collected chips.

Paper filters are used for soluble oils and are considered acceptable for filtering steel, aluminum, and brass fines from soluble oils. However, paper is viewed by some as being too expensive.

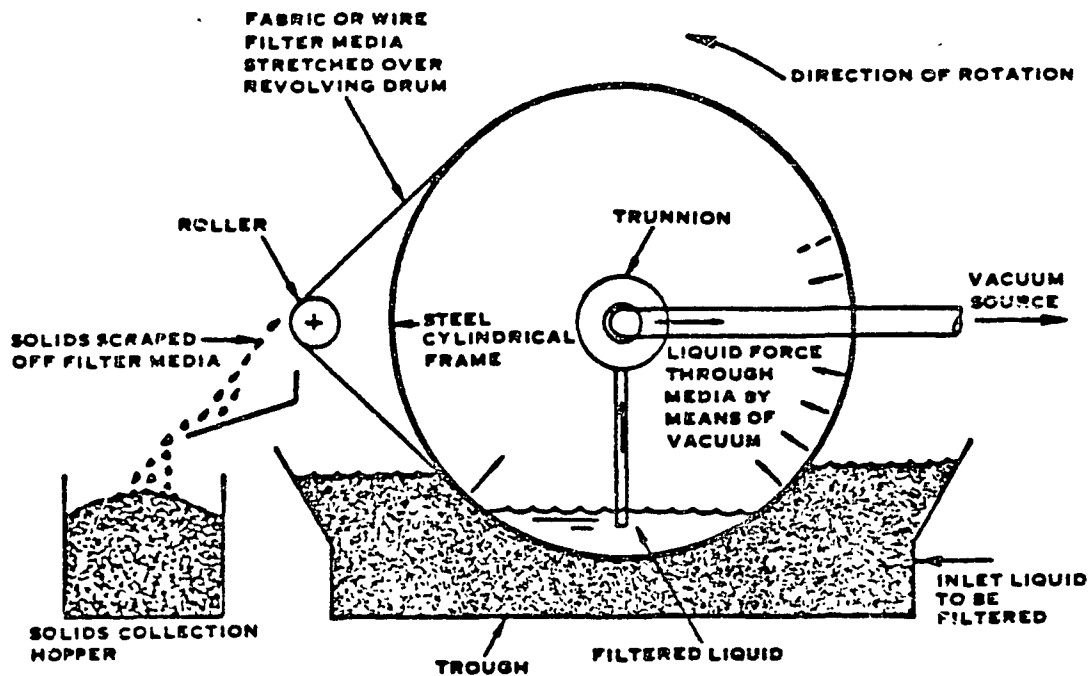


Figure 44. Vacuum filtration [2].

TABLE 44. COMPARISONS OF VACUUM AND PRESSURE FILTERS

Filters	Advantages	Disadvantages
Pressure	<ol style="list-style-type: none"> <li>1. Simple</li> <li>2. Indexes automatically</li> <li>3. Cleanable medium</li> <li>4. Moderate investment</li> <li>5. Dry sludge cake</li> </ol>	<ol style="list-style-type: none"> <li>1. Initial pressure forces particles into filter medium. Impending permeability.</li> <li>2. Possible high cost for filter paper</li> <li>3. Disposal of filter media</li> </ol>
Vacuum	<ol style="list-style-type: none"> <li>1. Removes fine particles</li> <li>2. Efficient with low viscosity fluids</li> <li>3. Indexes automatically</li> </ol>	<ol style="list-style-type: none"> <li>1. May require additional filtration</li> <li>2. Disposal of sludge and filter media</li> <li>3. Blinds off because of tramp oils</li> </ol>

Very fine material arises from honing or superfinishing operations. Filtering very fine material requires the use of a pre-coat filter, which is a pressure filter using diatomaceous earth. A pre-coat filter or a centrifuge is necessary for removing sub-micron particles. Pre-coating is the application of material such as diatomaceous earth, fuller's earth, etc., on the media prior to filtration. The pre-coat application will prevent media from being clogged and provides greater filtrate clarity.

Other types of filtration/separation equipment include hydrocyclones and magnetic separators. The hydrocyclone is for smaller chips. It has been estimated that hydrocyclones are capable of reclaiming particles larger than 20 microns in size with a flow rate ranging from 100-600 gpm. Hydrocyclones and cartridges are often used together, with the hydrocyclone used for larger particles and the cartridge for separation of fines.

Magnetic separation uses a magnetic drum rotating in a pool of oil coolant. The magnetic systems attract the particles of swarf which are in turn scraped from the drum [57]. In metalworking, large ferrous particles may be removed with the use of a magnetic separator which captures the particles by means of dense magnetic field. These particles, in turn, form a filter medium for removing other solid particles. The magnetic filter may be employed as a primary device for grinding, rolling, polishing and honing operations and as a secondary apparatus in drilling, hobbing, milling and broaching operations. The advantages and disadvantages of hydrocyclone and magnetic separators are summarized in Table 45.

TABLE 45. COMPARISONS OF HYDROCYCLONE AND MAGNETIC SEPARATOR

Filters	Advantages	Disadvantages
Hydrocyclone	<ol style="list-style-type: none"> <li>1. Automatic discharge of solids minimizes service requirements</li> <li>2. Inexpensive</li> <li>3. Small size</li> <li>4. Nonmechanical</li> </ol>	<ol style="list-style-type: none"> <li>1. Will not clean oil based coolants</li> <li>2. May become clogged with large particles</li> <li>3. Will not remove tramp oil</li> </ol>
Magnetic separator	<ol style="list-style-type: none"> <li>1. Does not remove coolant additives</li> <li>2. Very compact</li> <li>3. Removes ferrous particles</li> </ol>	<ol style="list-style-type: none"> <li>1. Does not remove tramp oil</li> <li>2. Does not remove particles smaller than 35 micrometers</li> <li>3. Does not remove non-ferrous particles</li> </ol>

In many cases it is more economical to install a central filtration equipment and return the recovered oil coolant to each machining operation. Filtering is difficult to perform on individual machines but the removal of swarf and chips in order to prevent their recirculation with the cutting fluid is necessary [65].

Several hundred percent increases in tool life and in oil life due to good coolant filtration have been reported [63]. Great improvements in the quality of metal surface finish are also reported.

#### 6.1.1.4 Coalescing--

Coalesers are primarily used to remove tramp oil (free floating oil) from waste emulsified oil from metal finishing plants in the cases where oil may become suspended in the waste emulsified oil and cannot be removed by gravity separation. This suspended oil can be efficiently removed with a coalescing filter. The basic principle of coalescing involves the preferential wetting of a coalescing medium by oil droplets which accumulate on the medium and then rise to the surface of the effluent. The same principle is applied to removal of water from oil effluent [2,49]. The most important requirements for coalescing media are wettability for oil and large surface area.

Coalescing stages may be integrated with a wide variety of gravity oil separation devices (see Figure 45). In this design, coalescing plates generate a flowpath of modified sinusoidal shape in order to create velocity changes in the flow stream. This produces a high incidence of particle collision which results in the coalescing of small particles of oils into particles of 20 micrometers or larger in size. These then move upwards, due to their lower specific gravity, and are collected above the plates. The design of the coalescing plate section makes use of laminar flow, oleophilic plate material, and reduced plate spacing. All these factors, together with the pulsation of flow achieved by changes of cross-section, enable removal of oil droplets down to 7 micrometers. The collected oil will generally contain less than 5 percent water [66].

The separator can be supplied with plates arranged horizontally, vertically or in a combination of both horizontal and vertical.

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[65] Coursey, W. M. The application, control, and disposal of cutting fluids. Lubrication Engineering. 200-204, 1969 May.

[66] Fram Industrial Filtration and Separation. Product Publications.

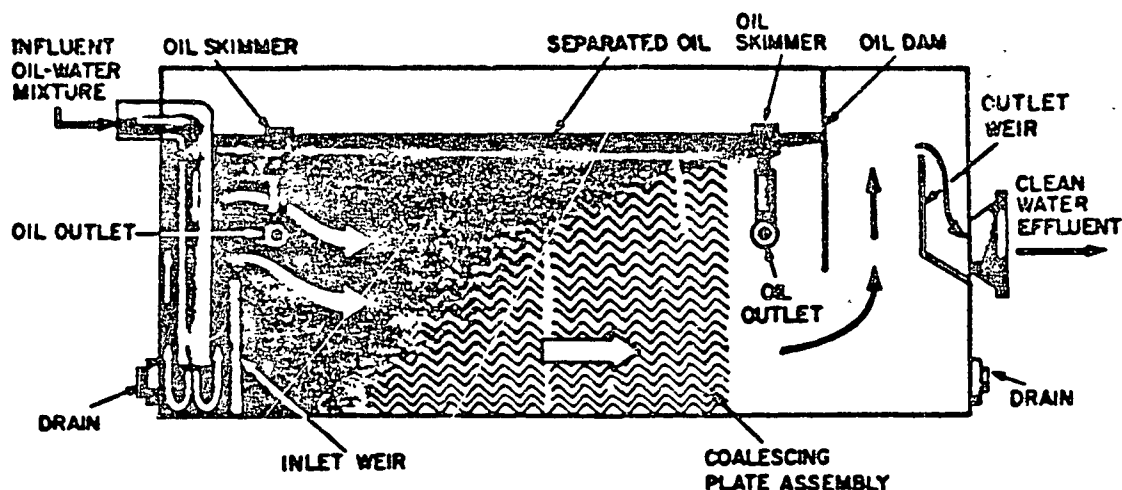


Figure 45. Coalescing gravity separator [2].

For influent oil concentrations less than 10 percent by volume and solids concentrations less than 500 ppm, the horizontal configuration of plates is usually suitable. This configuration is also particularly efficient in reducing the oil content of the effluent to the lowest possible amount.

The vertical plate configuration is especially suitable for high oil and/or solids loadings. The solids separate out under gravity and are collected below the plates. The oil, meanwhile, rises along the plates to the surface. Maintenance is exceptionally easy since the plates can be hosed down in place.

For many applications a combination of both types of plates will achieve the most effective separation. In this case, vertical plates are used for the first stage and horizontal plates for the second.

Some systems may be incorporated with several coalescing stages. In general, the provision of preliminary oil skimming treatment is desirable to avoid overloading the coalescer.

Coalescing allows removal of oil droplets too finely dispersed for conventional gravity separation/skimming technology. It can also significantly reduce the residence times (and therefore separator volumes) required to achieve separation of oil from some wastes. Because of its simplicity, coalescing oil separators provide generally high reliability and low capital and operating costs.

The units have no moving parts, require no filters or electricity, and can operate with influent temperatures to 212°F (100°C) and a pH range of 2-12. They require no chemicals or absorbents and are virtually maintenance free. They can handle flow rates up to 10,000 gallons per minute (360,000 barrels/day) and surges

of up to 100 percent oil with effluent quantities down to 5 ppm of oil. They can capture solids and oil drops as small as 5 micrometers.

Coalescing is not generally effective in removing soluble or chemical-stabilized emulsified oils. To avoid plugging, coalescers must be protected by pretreatment from very high concentrations of free oil, grease, and suspended solids. Frequent replacement of prefilters may be necessary when raw waste oil concentrations are high.

Coalescer oil and grease removal efficiency is illustrated in Table 46 [2].

TABLE 46. COALESCER OIL AND GREASE REMOVAL EFFICIENCY [2]

Sample	Raw waste mg/L	Effluent mg/L	Removal, %
1	8,320	490	94
2	4,240	619	85

#### 6.1.1.5 Emulsion Breaking--

Emulsion breaking technology can be applied to the treatment of emulsified oil from the metal finishing operations wherever it is necessary to separate oils, fats, etc., from wastewater.

Breaking of oil-in-water emulsions is a major waste-handling problem for automotive and other manufacturing plants involved with the cutting, machining, and grinding of metals because the maximum allowable concentration of oil that can be discarded in wastewater is no more than 50 ppm.

The individual plant wastes--including "soluble oil" emulsions, cutting fluids, and cleaners--are typically combined and treated with chemicals to separate oil and water. Other available methods of emulsion breaking include thermal processes and combinations of the chemical and thermal processes [2].

Chemical emulsion breaking can be accomplished either as a batch process or as a continuous process. A typical system (with skimming incorporated) is illustrated in Figure 46. The mixture of emulsified oils and water is initially treated by the addition of chemicals to the wastewater. A means of agitation, either mechanical agitation or by increasing the turbulence of the wastewater stream, is provided to ensure that the chemical added and the emulsified oils are adequately mixed to break the oil/water emulsion bond. Finally, the oily residue (commonly called scum) that results rises to the surface and is separated from the remaining

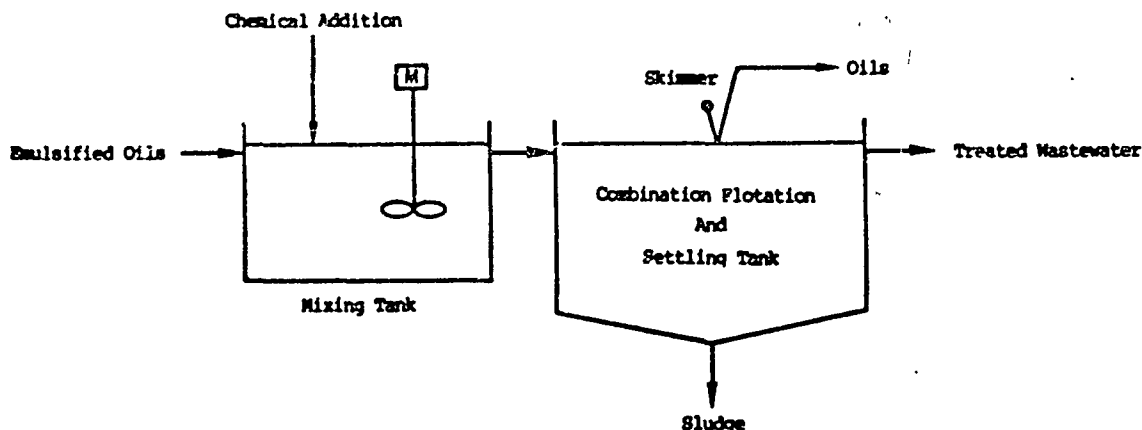


Figure 46. Typical emulsion breaking/skimming system [2].

wastewater by a skimming or decanting process. The skimming process can be accomplished by any of the many types of mechanical surface skimmers that are presently in use. Decanting methods include removal of the oily surface residue via a technique such as controlled tank overflow or by removal of the demulgated wastewater from the bottom of the tank. Decanting can be accomplished with a series of tap-off lines at various levels which allow the separated oils to be drawn off the top or the wastewater to be drawn off the bottom until oil appears in the wastewater line. With any of these arrangements, the oil is usually diverted to storage tanks for further processing or hauling by a licensed contractor.

Chemical emulsion breaking can be accomplished by a large variety of chemicals which include acids, salts, or polymers. These chemicals are sometimes used separately, but often are required in combination to break the various emulsions that are common in the wastewater. Acids are used to lower the pH to 3 or 4 and can cleave the ion bond between the oil and water, but they can be very expensive. Acids are more commonly employed in oil recovery systems than in oily waste removal systems. Iron or aluminum sulfate are more commonly used because they are less expensive. These salts combine with the wastewater to form acids, which in turn, lower the pH and break the oil/water bond (and have the additional benefit that these salts aid in agglomeration of the oil droplets), but the use of these salts produces more sludge because of the addition of iron or aluminum. Polymers, such as polyamines or polyacrylates and their copolymers, have been demonstrated to be effective emulsion breakers and generate less sludge than do metal salts [2, 67].

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[67] Montens, I. A. Treatment of wastes originating from metal industries. West Lafayette, IN; Purdue University, 782-791.

A less frequently employed method involves the addition of a cation such as  $\text{Fe}^{+2}$ ,  $\text{Fe}^{+3}$ ,  $\text{Al}^{+3}$ ,  $\text{Cu}^{+1}$ , or  $\text{Cu}^{+2}$ , in a volume of at least 1 ppm to the oil in water emulsion. The pH is adjusted to the range of 6 to 10. The emulsion is then treated with a dissolvable iron electrode. An electric current is transmitted to dissolve the electrode, resulting in a ferrous ion/oil weight ratio of at least 0.02. The optimum efficiency of the process is obtained when 3 to 5 ppm of the cation is added to the emulsion at a pH range of 6 to 8. The addition of the cation reduces the time required to break the emulsion from 24 hours to forty minutes or less [68].

After chemical addition, the mixture is agitated to ensure complete contact of the emulsified oils with the demulsifying agent. With the addition of the proper amount of chemical and thorough agitation, emulsions containing 5 percent to 10 percent oil can be reduced to approximately 0.01 percent remaining emulsified oil. The third step in the emulsion-breaking process is to allow sufficient time for the oil/water mixture to separate. Differences in specific gravity will permit the oil to rise to the surface in approximately 2 hours. Heat can be added to decrease the separation time. After separation, the normal procedure involves skimming or decanting the oil from the tank.

The main advantage of the chemical emulsion breaking process is the high percentage of oil removal possible with this system. For proper and economical application of this process, the oily wastes (oil/water mixture) should be segregated from other wastewater either by storage in a holding tank prior to treatment or by feeding directly into the oily waste removal system from major collection points. Further, if a significant quantity of free oils are present, it is economically advantageous to precede the emulsion breaking with a gravity separator. Chemical and energy costs can be high, especially if heat is used to accelerate the process [2].

In addition to the chemical treatment of emulsion breaking, a continuous electrolytic treatment is being developed to remove emulsified oil from dilute oily wastewater streams, such as is generated in metalworking operations. In this work, electrophoretic transport of charged oil droplets was exploited as a concentrating mechanism, using the cell shown schematically in Figure 47. A porous diaphragm is placed between the two electrodes which inhibits convective mixing of the treated and concentrate streams, while permitting the emulsified oil droplets to pass through unhindered. Separate emulsion streams containing the negatively charged oil droplets are passed through both the cathode and anode compartments. The oil droplets migrate through the diaphragm under the influence of

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[68] Golovoy, A. Method of breaking an oil-in-water emulsion. U.S. patent 4,087,338.



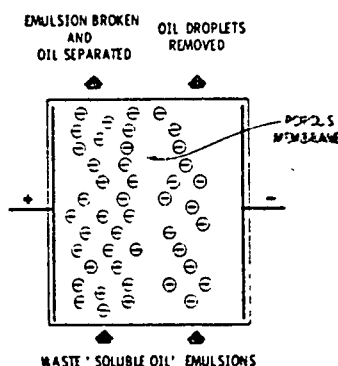


Figure 47. Electrochemical oil removal/recovery cell: negatively charged oil droplets [69].

an electrical field to the analyte, where the emulsion is broken by electrochemical action to yield a separate oil layer [69-71]. In a pilot plant test run, wastewater with initial oil concentrations in the range of 300 to 7,000 ppm of solvent extractables has been reduced to less than 50 ppm in 90 percent of the test runs and to less than 25 ppm in 83 percent [71].

The recovered oil from emulsion breaking can be burned, reused for another purpose, sold, or disposed of by any acceptable method.

The water constituent obtained from the split emulsion must then receive further treatment before the water may be discharged into the plant wastewater system. The degree of treatment required on the water phase of emulsion will be governed by local pollution regulations.

The performance attainable by a chemical emulsion breaking process is dependent on addition of the proper amount of de-emulsifying agent, good agitation and sufficient retention time for complete emulsion breaking. Since there are several types of emulsified oils, a detailed study should be conducted to determine the most

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- [69] Snyder, D. D.; and Willihinganz, P. A. A new electrochemical process for treating spent emulsion. 31st Industrial Waste Conference; 1976 May 4-6. West Lafayette, IN; Purdue University. 782-791.
  - [70] Kramer, G.; Buyers, A.; and Brownlee, B. Electrolytic treatment of oily wastewater. 34th Industrial Waste Conference; 1979. West Lafayette, IN; Purdue University. 673-680.
  - [71] Gealer, R. L.; Golovoy, A.; and Weintraub, M. H. Electrolytic treatment of oily wastewater from manufacturing and machining plants. Cincinnati, OH; U.S. Environmental Protection Agency; 1980 June. 48 p. EPA-600/2-80-143. PB 80-225113.

effective treatment techniques and chemicals for a particular application. Table 47 illustrates emulsion breaking process performance data [2].

TABLE 47. EMULSION BREAKING PROCESS OIL AND GREASE REMOVAL DATA [2].

Sample	Influent mg/L	Effluent mg/L	Removal, %
1	3,320	42	98.7
2	210	24	38.6
3	12,500	27	>99.9
4	2,300	52	97.7
5	13,800	18	>99.9
6	192.8	10.6	94.5
7	6,260	98	98.4

#### 6.1.1.6 Flotation--

Flotation units are commonly used in metal finishing operations to remove free and emulsified oils and grease. Flotation is the process of causing particles such as oil or metal hydroxides to float to the surface of a tank where they can be concentrated and removed. This is brought about by releasing gas bubbles which attach themselves to the particles, increasing their buoyancy, and causing them to rise to the surface and float [2].

Dissolved air flotation (DAF) utilizes the emulsion-breaking techniques that were previously discussed and in addition uses bubbles of dissolved air to assist in the agglomeration of the oily droplets and to provide increased buoyancy for raising the oily droplets to the surface. Coagulants, i.e., lime, alum ferric salts or polyelectrolytes are added to enhance floc formation. In addition, air will oxidize sulfides, which will release adsorbed oil [50,2]. Equipment required for the process includes the flotation tank, recycle pumps, dissolved tank, and the air supply and controls (see Figure 48) [72].

A dissolved air flotation unit may be incorporated in a treatment system utilizing an oil-water separator. Wastewater passes through an API oil-water separator and following the skimming off of free oil is passed to a dissolved air flotation unit. Oil is again skimmed off and the water is processed through the clarifiers in a biological oxidation system. This system may not

[72] Hoover, W.; Sitman, W.; and Stack, V. Treatment of wastes containing emulsified oils and greases. Lubrication Engineering. 1964 May.

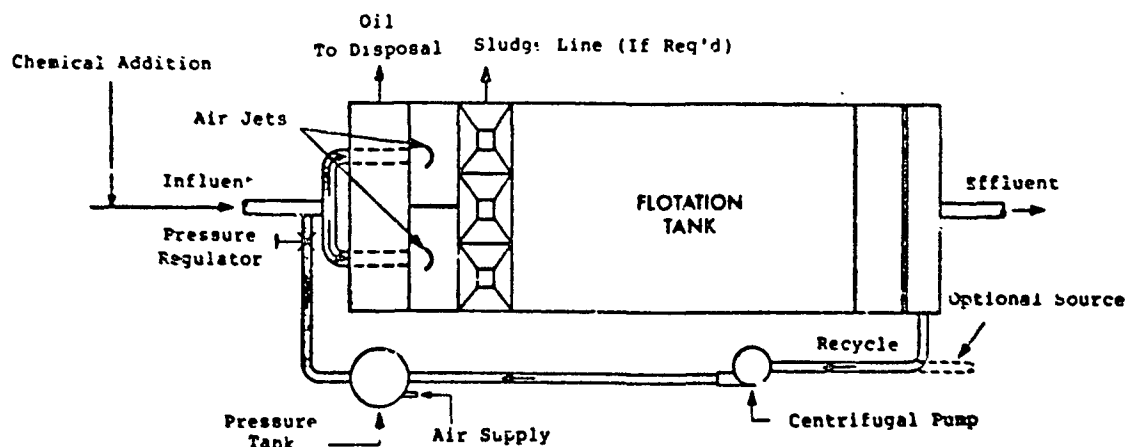


Figure 48. Typical dissolved air flotation system [2].

effectively separate the oil and water if the volume of oil is too great. The concentration of oil in the effluent from the dissolved air flotation unit may be 100-150 ppm, which exceeds the capability of the bio-oxidation process [2]. When low molecular weight organic polymers are added to the inlet of the dissolved air flotation unit, the concentration of oil in the effluent was reduced to 15-30 ppm [73]. Generally, with dissolved air flotation, the effluent will contain less than 50 ppm of oil. It will contain less than 100 ppm if the influent does not contain more than 1 000 ppm of oil.

Results of emulsion breaker application in the API-DAF system is presented in Table 48 [2].

TABLE 48. RESULTS OF EMULSION BREAKER APPLICATION IN THE API-DAF SYSTEM - OIL AND GREASE [2]

	API influent	API effluent	Removal, %	DAF effluent	Removal, %
No treatment	1,500	200-300	83	100-150	50
Emulsion breaker treatment	1,500	100-125	93	15-30	79

Determination by Freon extraction; values expressed in parts per million (volume basis).

[73] Gruette, J. Primary wastewater treatment and oil recovery in the refining industry. National Petroleum Refiners Association Meeting; 1978 March 19-21.

The use of dissolved air for oily waste flotation subsequent to emulsion breaking can provide better performance in shorter retention times (and therefore smaller flotation tanks) than with emulsion breaking without flotation. A small reduction in the quantity of chemical needed for emulsion breaking is also possible. Dissolved air flotation units have been used successfully, in conjunction with subsequent processes, to reclaim oils for direct reuse and/or use as power plant fuels.

However, flotation requires higher operating costs and yields a thicker sludge.

Induced air flotation (IAF) is an available means of removing oil and suspended solids from waste waters. Induced air flotation would not be selected in instances where turbulence would be undesirable since it would disturb flocculation. It is considered by some to be a simpler and less expensive method than dissolved air flotation, although its present usage is about 1/5 that of DAF. Dispersed air flotation requires less floor space (100 square feet or greater, depending on the machine), and a shorter retention time (4 minutes) [74]. The method of producing air and introducing it into the liquid differs from the dissolved air flotation system.

The apparatus has been identified as the dispersed air flotation machine because it contains air dispersing mechanisms that produce dispersed air in the form of finely divided bubbles. The bubbles rise to the top carrying oil droplets and are removed by a revolving froth skimmer. The individual dispersed air flotation mechanism is composed of a vertical shaft with an attached impeller surrounded by a diffuser and circulation hood attached to a vertical pipe. The impeller displaces liquid which results in the flow of air down the standpipe. Liquid mixes with the air flowing from the standpipe resulting in the formation of air bubbles. The amount of aeration is produced by adjusting the speed of the impeller and the rate of fluid circulation through the impeller [74].

An electrolyte flotation method requires electrocoagulation cells, flotation basins, and a chemical treatment and sludge system. The advantages of the system lie mainly in the need for less chemicals and the creation of less turbulence in removing of suspended and emulsified materials. The electrocoagulation cell functions by destabilizing suspensions and promoting flocculation. This unit operates by passing electrical current through water between a series of electrodes. The electroflotation basin concentrates the floc and separates it from other floatables. Material is floated to the top by means of bubbles created by an electrical current [2].

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[74] Tylor, R. W. Dispersed air flotation. Pollution Engineering. 1973 January.

The performance of a flotation system depends upon having sufficient air bubbles present to float essentially all of the suspended solids. An insufficient quantity of air will result in only partial flotation of the solids, and excessive air will yield no improvement. The performance of a flotation unit in terms of effluent quality and solids concentration in the float can be related to an air/solids ratio. The shape of the curve obtained will vary with the nature of the solids in the feed. Table 49 illustrates dissolved air flotation system performance data [2].

TABLE 49. DISSOLVED AIR FLOTATION SYSTEM OIL AND GREASE REMOVAL DATA [2]

Sample	Influent mg/L	Effluent mg/L	Removal, %
1	412	108	73.8
2	65.8	28.9	56.1

#### 6.1.1.7 Ultrafiltration (UF)--

Ultrafiltration is employed in metalworking plants for the separation of oils, toxic organics, and residual solids from waste emulsified oils. In an ultrafiltration system, a wastewater feed is introduced into a membrane module (see Figure 49). Water and low-molecular weight solutes (for example, salts and some surfactants) pass through the membrane at a pressure of 0.767 kg/cm<sup>2</sup> and are removed as permeate (filtered effluent), which may contain less than 100 mg/L of oil and 10 mg/L suspended solids. If this effluent discharge level does not attain effluent limitation guidelines, the permeate may be treated by a filtration process such as biological degradation, carbon adsorption or reverse osmosis. Emulsified oil and suspended solids are retained by the membrane, concentrated to about 60 percent oil and solids content, and removed as concentrate [75,76]. At present, an ultrafilter is capable of removing materials with molecular weights in the

- [75] Wahl, J. R.; Hayes, T. C.; Kleper, M. H.; and Pinto, S. D. Ultrafiltration for today's oily wastewaters: A survey of current ultrafiltration systems. 34th Industrial Waste Conference; 1979 May 8-10; West Lafayette. Ann Arbor, MI, Ann Arbor Science Publications, Inc., 1980, 719-733.
- [76] Pinto, S. D. Ultrafiltration for dewatering of waste emulsified oils. First international conference on lubrication challenges in metalworking and processing; 1978 June 7-9; Chicago. IIT Research Institute, 1978, 129-134.

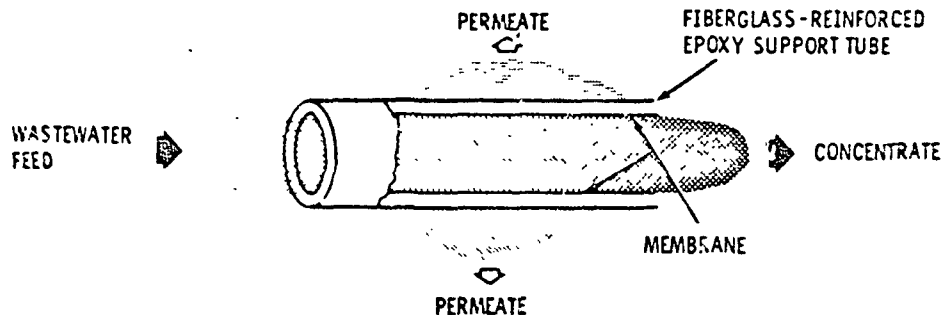


Figure 49. Simplified ultrafiltration membrane module.

range of 1,000 to 100,000. A survey of plants utilizing ultrafiltration revealed the mean removal efficiency for oil and grease removal to be 92 percent and for total toxic organics to be 88 percent [50]. The liquid oil concentrate can be disposed of by hauling or incineration. Solid waste is practically nonexistent because there is no addition of the chemicals required for demulsification.

The semipermeable membrane is a thin film of a proprietary non-cellulosic polymer that will withstand high operating temperatures and extremes in pH and solvent exposure. The thin "skin" ( $<0.5 \mu\text{m}$ ) of the membrane covers a highly porous substance. Since the pores of the ultrafiltration membranes are much smaller than the particles rejected, the particles cannot enter the membrane structure and plug the pores. The pore structure and small size (less than 0.005 micrometers) of the membrane are quite different from those of ordinary filters. With an ordinary filter, pore plugging results in drastically reduced filtration rates and requires frequent backflushing, which may produce extra solid or liquid wastes.

The performance of ultrafiltration systems is typically characterized by two parameters: membrane flux and membrane rejections (for a specific species). The flux is defined as the rate of permeate production per unit membrane area and is usually expressed as gallons per square foot per day ( $\text{gal}/\text{ft}^2/\text{day}$ ). The design flux for oily waste treatment is typically  $30 \text{ gal}/\text{ft}^2/\text{day}$  [75].

The rejection measures the degree to which the membrane prevents permeation of a given constituent from the feed into the permeate. Rejection for oil and grease is normally greater than 99 percent [75].

A typical ultrafiltration system for treating oily water is shown in Figure 50. The process begins with oily wastewater collection in an equalization tank, with 1-2 days retention time, from which free-floating oil and settleable solids are removed. The remaining oily wastewater is transferred to a process tank.

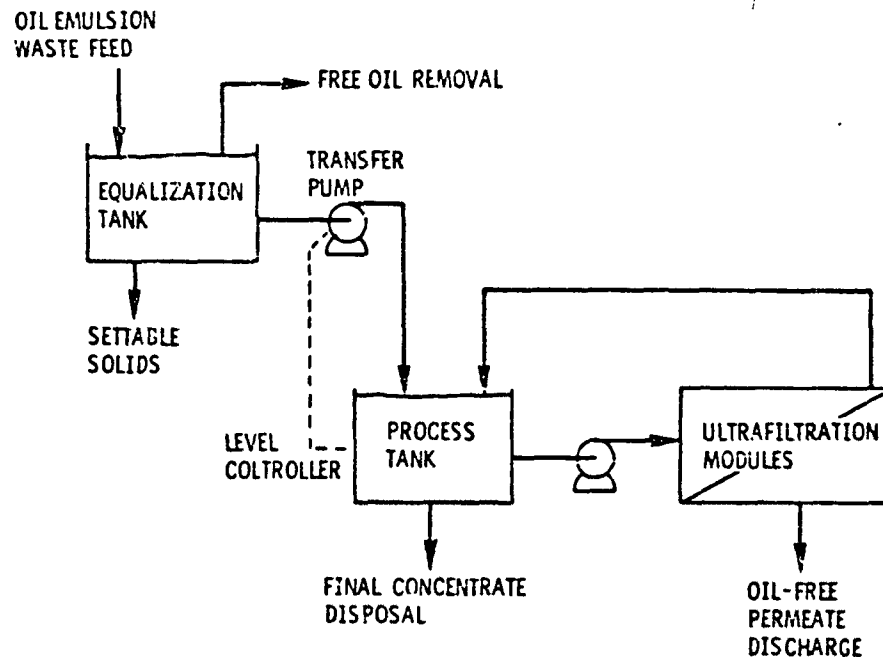


Figure 50. Semi-batch ultrafiltration system [75].

The process tank is sized for 0.5-1 day capacity depending upon feed concentration. Wastewater is pumped through the membrane modules from the process tank at about 50 psig.

Usually, a semi-batch concentration cycle is employed. In this cycle, the permeate is discharged continuously, while the oily wastewater is retained in the system and gradually concentrated with time. Oily makeup water is added to the process tank to maintain a constant process level.

On the final day of the semi-batch concentration cycle, flow to the process tank is stopped and a batch concentration on the process tank contents is performed. This final step reduces the concentrated wastewater to the minimum residual volume. The final concentrate is removed from the system for further processing or disposal. The system is then cleaned in preparation for the next concentration cycle.

In large oil-water systems, cleaning of the membranes normally will be required once a week to remove foulants that build up on the membrane surface. These cleaning methods are [75]:

- (1) Mechanical cleaning,
- (2) Dispersing, and
- (3) Solubilizing.

Mechanical cleaning is only applicable in practice to large diameter ultrafiltration membranes and is very effective in removing chemically precipitated species that adhere tenaciously to the membranes and are difficult to remove by any other method. This method works best when the adhesion between the fouling layer and the membrane is weak.

Dispersing methods of cleaning function by breaking up deposits in the membrane and dispersing them into colloidal sized particles. The most commonly used dispersants are detergents.

Cleaning by solubilizing consists of dissolving, by physical or chemical means, fouling deposit. This is the most effective of the three cleaning methods. It is most often used to clean the membranes of metal hydroxide or other chemical deposits. Solutions of acids and chelating agents are usually used for this purpose. The filtering membrane used for emulsified industrial oils should therefore be resistant to acidic, alkaline, and caustic cleaners.

Ultrafiltration is recommended by metalworking fluid manufacturers as a disposal method for oily wastewater for the following reasons:

- (1) Reduces sludge disposal problem
- (2) Less expensive than incineration
- (3) Less expensive than contract hauling
- (4) Costs less per gallon for treatment
- (5) Requires less skill for operation

A limitation of ultrafiltration for treatment of process effluents is its narrow temperature range (18°C to 30°C) for satisfactory operation. Therefore, surface area requirements are a function of temperature and become a trade-off between initial costs and replacement costs for the membrane [2]. Table 50 illustrates ultrafiltration performance data for oil and grease removal [2].

#### 6.1.1.8 Reverse Osmosis (RO)--

Reverse osmosis is the process of applying a pressure to a concentrated solution and forcing a permeate through a semi-permeable membrane into a dilute solution. With respect to oily wastewater, reverse osmosis is used primarily as a polishing mechanism to remove oils and metals that still remain after treatments such as emulsion breaking or ultrafiltration [2].

Feed water is pumped under pressure of either 400 or 600 psi through the reverse osmosis permeators, where 50 or 75 percent of the water permeates through the minute pore spaces of the membrane and is delivered as purified product water. Impurities in



TABLE 50. ULTRAFILTRATION PERFORMANCE DATA  
FOR OIL AND GREASE REMOVAL [2]

Sample	Influent mg/L	Effluent mg/L	Removal, %
1	95.0	22.0	76.8
2	1,540	52.0	96.6
3	38,180	267	99.3
4	31,000	21.4	99.9
5	1,380	39.0	97.2
6	3,702	167	95.2
7	1,102	195	82.3
8	7,500	640	91.5
9	360	18.0	95.0
10	70.0	10.0	85.7
Mean removal efficiency			92.0

the water are concentrated in the reject stream [77]. Small drying bed lagoons are proposed for disposal of the small amount of RO concentrate. However, if appreciable amount of oil is to be collected from the gravity oil skimmer, the small amount of the RO concentrate can probably be incinerated [78]. Reverse osmosis is capable of removing 90-98 percent of total dissolved solids and 99 percent of organics, and it is an effective shield against pyrogens, bacteria, and other microorganisms.

While a new technology, membrane systems appear more attractive than a chemical treatment process with its attendant sludge disposal problems. The improved effluent could be more easily incorporated into existing water reclamation systems, thereby eliminating direct discharge of treated water. Although the UF/RO system requires a higher capital investment than would a UF system, utilizing RO permeate as a substitute for deionized water in the reversing mills might eliminate the need for an additional deionizer at the plant. Table 51 lists the estimated capital and operating costs for chemical, membrane, and evaporation processes on pilot-scale equipment. All costs were based on treating 100,000 gal/day and indexed to 1978. Credits were given to all processes for potential oil recovery and, in the case of

[7'] Product literature. Continental Water Systems Corporation, El Paso, Texas.

[78] Chian, E. S. K.; and Gupta, A. Recycle of wastewater from vehicle washracks. 29th industrial waste conference; 1974 May 7-9. West Lafayette, IN, Purdue University, 9-20.

TABLE 51. ESTIMATED COST ANALYSIS [79]

System	Capital cost	Total unit operating cost (\$/1000 gal)	Net unit operating cost (\$/1000 gal)
Chemical	\$1,730,000	\$11.33	\$5.36
Evaporation	2,650,000	8.75	2.90
UF	1,450,000	7.73	1.77
UF/RO	1,550,000	8.81	1.12

UF/RO, for production of a high purity water that could be used as a substitute for mill water and/or deionized water. Recovery and utilization of waste heat to generate steam is planned for the evaporation process.

Examples of reverse osmosis performance are presented in Table 52 [2].

TABLE 52. REVERSE OSMOSIS OIL AND GREASE REMOVAL PERFORMANCE DATA [2]

Sample	Influent mg/L	Effluent mg/L	Removal, %
1	117	8.5	92.7
2	10.6	4.1	61.3
3	129	41	68.2

#### 6.1.1.9 Carbon Adsorption--

Alternatively, a carbon adsorption process may be employed to remove oils and toxic organics [80] that have not been removed by emulsion braking and ultrafiltration. Activated carbon is an efficient means of removing organics with an adsorption capacity of 500-1,500 square meters/gram. It is limited to treatment of less than 5,000 gal/day, due to column saturation [76]. Pretreatment is desirable to maintain an influent of less than 50 ppm suspended solids and less than 10 ppm for oil and grease [2].

[79] Sonksen, M. K.; Sittig, F. M.; and Maziarz, E. F. Treatment of oily wastes by ultrafiltration/reverse osmosis; a case history. 33rd industrial waste conference; 1978 May. West Lafayette, IN, Purdue University, p. 696.

[80] Skovronek, H. S.; Dick, M.; and Des Rosiers, P. E. Selected uses of activated carbon for industrial wastewater pollution control. Second annual conference on new advances in separation technology; 1976 September 23-24; Cherry Hill, NJ.

In addition to a filtration unit, a granular activated carbon adsorption treatment system requires two or three activated-carbon-containing adsorption columns, a holding tank, liquid transfer pumps, and equipment for reactivation; i.e., a furnace, quench tank, spent carbon tank, and reactivated carbon tank [2].

The necessary equipment for a two-stage powdered carbon unit is as follows: four flash mixers, two sedimentation units, two surge tanks, one polyelectrolyte feed tank, one dual media filter, one filter for dewatering spent carbon, one carbon wetting tank, and a furnace for regeneration of spent carbon.

Powdered carbon is less expensive per unit weight than granular carbon and may have slightly higher adsorption capacity, but it does have some drawbacks. For example, it is more difficult to regenerate; it is more difficult to handle (settling characteristics may be poor); and larger amounts may be required than for granular systems in order to obtain good contact.

Thermal regeneration, which destroys adsorbates, is economical if carbon usage is above roughly 454 kg/day (1,000 lb/day). Reactivation is carried out in a multiple hearth furnace or a rotary kiln at temperatures from 870°C to 988°C. Required residence times are of the order of 30 minutes. With proper control, the carbon may be returned to its original activity; carbon losses will be in the range of 4-9 percent and must be made up with fresh carbon. Chemical regeneration may be used if only one solute is present which can be dissolved off the carbon. This allows material recovery. Disposal of the carbon may be required if use is less than approximately 454 kg/day (1,000 lb/day) and/or a hazardous component makes regeneration dangerous. Wet oxidation for regeneration has been introduced for powdered carbon systems [2]. The resins, generally microporous styrene-divinylbenzenes, acrylic esters, or phenol-formaldehydes, can be used to substitute carbon in the adsorption system [2].

Table 53 illustrates performance data for oil and grease removal by carbon adsorption [2].

TABLE 53. CARBON ADSORPTION PERFORMANCE DATA  
FOR OIL AND GREASE REMOVAL [2]

Sample	Influent mg/L	Effluent mg/L	Removal, %
1	4.1	3.3	19.5
2	41.0	2.0	95.1

#### 6.1.1.10 Aerobic Decomposition--

Aerobic decomposition is the biochemically actuated decomposition or digestion of organic materials in the presence of oxygen. The chemical agents effecting the decomposition are microorganism secretions termed enzymes. The principal products in a properly controlled aerobic decomposition are carbon dioxide and water. Aerobic decomposition is used mainly in the treatment of organic chemicals and lubricants used in the industries that use organic lubricants [2].

As a waste treatment aid, aerobic decomposition plays an important role in the following organic waste treatment processes:

1. Activated sludge process
2. Trickling filter process
3. Aerated lagoon

Advantages of aerobic decomposition include: (1) low BOD concentrations in supernatant liquor, (2) production of an odorless, humus-like, biologically stable end product with excellent dewatering characteristics that can be easily disposed of, (3) recovery of more of the basic fertilizer values in the sludge, and (4) few operational problems and low initial cost. The major disadvantages of the aerobic decomposition process are (1) high operational cost associated with supplying the required oxygen, and (2) sensitivity of the bacterial population to small changes in the characteristics of their environment

#### 6.1.1.11 Evaporation [50]--

Evaporation is used in West Germany to dewater emulsified oils. The emulsified oil is heated in an unit as shown in Figure 51. The oil concentrate is taken off by a pump and further dewatered in an evaporator. A typical example of this process is the Faudi process. The Faudi process involves the evaporation of water by an evaporator with several (different level) platforms. This provides best utilization of the energy since the oil phase furnishes the calories needed by the process. A preliminary filtration is applied to catch the oils which escaped. An active carbon bed is connected to the equipment, which eliminates the odor of the water phase.

In the process a water phase of less than 20 mg of oil per liter is produced. Completely automatic and continuous type installations exist with capacities of 250 to 3,000 liters per hour.

#### 6.1.2 Economic Evaluations

The literature indicates that metal finishers perform emulsion treatment only to fulfill environmental regulations and local sanitary sewer ordinances. Also, reclaimers are willing to handle only emulsions of high oil concentrations. Such circumstances may suggest that no or weak economic incentives exist for

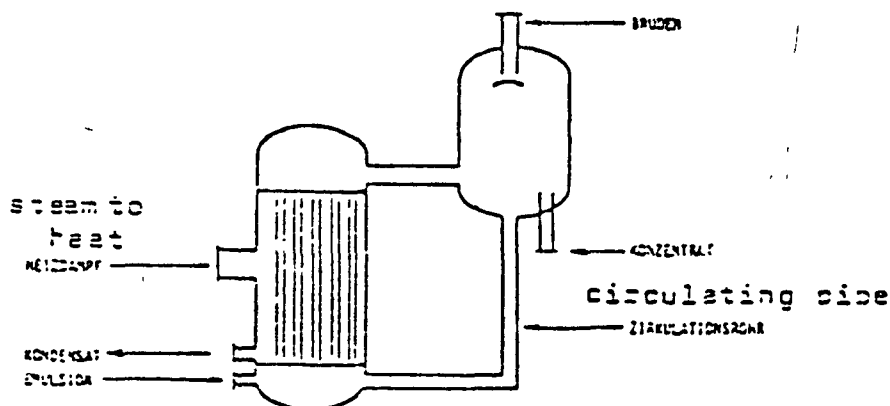


Figure 51. Evaporation unit for emulsified oil [50].

handling emulsions for the purposes of oil recovery. However, this generally speaking, is not the case.

For those end users/reclaimers/re-refiners who are highly cost conscious and technically capable, there are economic benefits to be gained from emulsion treatment. Technically capable end-users can save significant amount of money from treating emulsions and knowledgeable reclaimers/re-refiners have lucrative businesses treating these materials. The following sections present a compilation of information available in the open literature concerning costs of emulsion treatment.

#### 6.1.2.1 In-plant Processes and Costs--

No two companies process the same fluid compositions, or have the same equipment and the same overhead; hence, there are no "typical" cost examples. Equipment costs vary considerably depending upon type, size, and supplier. Table 54 gives approximate equipment costs at different processing volumes for continuous gravity settling tanks, oil separators and skimmers, pressure and vacuum filters, dissolved air flotation, and centrifuges. Table 55 gives approximate equipment costs at 1,000 gal/day for ultrafiltration systems and coalescing filters.

Table 56 shows the estimates of capital and operating costs for electrolytic treatment for a plant size of about 76 m<sup>3</sup>/day (20,000 gallon/day). Economic projections are presented for a process with air bubble--without automation, with dissolved air flotation--without automation, and with dissolved air flotation--with automation.

Purchase costs can vary considerably by the volume to be processed.

Costs of operating a waste oil recycling plant include variable costs (chemicals, utilities), fixed costs (labor, overhead), and if processed and sold by the company, corporation expenses and tax

TABLE 54. SOME EQUIPMENT CHOICES AND ESTIMATED COSTS  
AT DIFFERENT PROCESSING LEVELS FOR 1981 [50]

	Continuous flow gravity settling tanks	Oil separator and skimmer	Pressure filter	Vacuum filter	DAF	Centrifuge
<u>Purchase cost</u>						
50,000 gallons	\$ 7,000	\$ 3,000	\$ 1,500	\$40,000	\$8,000	\$27,000
500,000 gallons	8,000	10,000	2,000	40,000	8,000	27,000
1,000,000 gallons	14,000	13,000	3,000	40,000	8,000	35,000
5,000,000 gallons	18,000	15,000	15,000	50,000	8,000	55,000
<u>Installation cost</u>						
50,000 gallons	\$4,000	\$3,000	\$1,500	\$5,000	\$16,000	\$ 54,000
500,000 gallons	6,000	3,000	2,000	5,000	16,000	54,000
1,000,000 gallons	9,000	3,000	3,000	5,000	16,000	70,000
5,000,000 gallons	9,000	3,000	5,000	5,000	16,000	110,000
<u>Yearly maintenance cost</u>						
50,000 gallons	\$500	\$1,500	\$ 1,000	\$1,000	\$ 600	\$1,000
500,000 gallons	500	1,500	2,000	2,000	600	1,100
1,000,000 gallons	500	1,500	5,000	4,000	600	1,300
5,000,000 gallons	700	2,000	20,000	8,000	3,000	1,500

(continued)

TABLE 54 (continued)

	Continuous flow gravity settling tanks	Oil separator and skimmer	Pressure filter	Vacuum filter	DAF	Centrifuge
<u>Depreciation cost</u> (Average total costs over 10 year equipment life)						
50,000 gallons	\$1,600	\$2,100	\$ 1,300	\$ 5,500	\$2,000	\$ 9,100
500,000 gallons	1,900	2,800	24,000	6,600	2,700	9,200
1,000,000 gallons	2,800	3,100	4,600	8,500	2,700	11,800
5,000,000 gallons	3,400	3,800	13,000	13,500	5,400	18,000
-----						
	<u>Gallons</u>	<u>Gallons/hour</u>	<u>Gallons/minute</u>			
	50,000	125	2	(operates one shift, 20% at time)		
	500,000	250	4	(one shift)		
	1,000,000	500	8	(one shift)		
	5,000,000	800	13	(three daily shifts)		

TABLE 55. ESTIMATED COSTS FOR ULTRAFILTRATION  
SYSTEM AND COALESCING FILTER, 1981

	Ultrafiltration <sup>a</sup>	Coalescing <sup>b</sup> (vertical)
Purchase cost, \$	56,490	26,500 (with separator 29,500)
Operating cost, \$ (250 days per year, 2 shift per day)	28,938	Low
Depreciation (over 8 years, 50% after tax), \$	3,630/year	10%
Maintenance, \$		Low
Membrane replacement, \$	2,550/2 years	No

<sup>a</sup>Derived from Table 18 of Reference [35].

<sup>b</sup>Manufacturer contact.

TABLE 56. CAPITAL AND OPERATING COSTS OF  
ELECTROLYTIC TREATMENT [71]

Process	Capital cost, \$	Operating cost, \$/m <sup>3</sup>
With air bubblers - without automation	50,000	0.09
With dissolved air flotation - with automation	80,000	0.08
With dissolved air flotation - without automation <sup>a</sup>	85,000	0.08

<sup>a</sup>Manpower would be decreased.

expenses. These are broken down in Table 57 for a company annually recovering 200,000 gallons of oil from one million gallons of waste fluid. According to figures in Table 57, the cost of reclaimed oil is \$0.88/gallon. Virgin oil costs range from \$0.80-1.90/gallon depending upon the oil grade and additive content. So oil reclamation is economical.

The potential for reuse depends on the original application and on how clean the recycled oil is. If not suitable for the original



TABLE 57. WASTE OIL RECYCLING PLANT OPERATION COSTS [50]

Cost item	Cents/gallon of recovered oil	\$/Million gallons of waste fluid
Chemicals	25.000	50,000
Electricity	6.000	12,000
Total variable costs	31.000	62,000
Direct labor	16.000	32,000
Supervision and indirect labor	16.000	32,000
Building maintenance	0.187	375
Equipment maintenance	1.460	2,920
Insurance and property taxes	1.470	2,940
Depreciation	9.9550	19,900
Capital interest	11.595	23,191
Total fixed costs	56.662	113,386
Total process costs	87.662	\$175,386

application, a new application with less stringent quality specifications must be found. Typically, because of price variations, the soluble oils are more likely to be recycled than the cutting oils (Table 58).

TABLE 58. METALWORKING FLUID TYPES AND PRICES, 1981 [50]

Fluid	\$/gallon
Cutting oil	0.55
Lube start	1.30
Hydraulic oil	1.60
Soluble oil	1.85 (may cost \$7-10/gallon with additives)

The water phase from emulsion breaking can be discharged in the local sewer system after appropriate clarification or recycled back into the plant for nonpotable uses.

The sludges produced in the process can be either hauled away or further processed to a 95 percent oil concentrate at a cost of about 5-35¢/gallon. Selling the oil concentrate may bring 20-70¢/gallon in revenues while substantially reducing disposal costs.

The solids which are separated during concentration steps are mostly metal fines suitable for landfill or can be sold as scrap.

#### 6.1.2.2 Reclaimer Costs [50]--

Reclaimers work with oil emulsions varying in concentrations from 5 to 95 percent oil and available from the metal finishing industry at a cost of 10-20¢/gallon plus up to 20¢/gallon freight charges. Heat, acid, and polymer may be added to break the emulsion and form a 95 percent oil concentrate.

The concentrate from in-house processing and the 95 percent oil concentrate purchased from outside sources are treated with earth and clay followed by solids filtration (refer to Section 6.2.2). This costs about 54¢/gallon and produces a 99.9 percent oil concentrate. This concentrate is worth \$0.70-\$1.50/gallon (average \$1.10/gallon) and it may be sold as fuel or gear cutting fluid, or be further processed.

The oil concentrate can be vacuum stripped (medium temperature re-refining at 550°F) producing a 99.99 percent oil at a cost of about, 30¢/gallon. The value of the oil ranges from \$1.50 to \$2.20/gallon (average \$1.80/gallon) and may be sold as base stock for new lubricants or fluids or as fuel.

Some reclaimers/re-refiners may replace lost additives before the oil is sold back to the user. This may cost 10-65¢/gallon for hydraulic oils and even more for the expensive additives for rolling fluids. Rejuvenated fluids are generally sold back to the user at anywhere between \$0.70-1.00/gallon for hydraulic fluids and from \$1.00-3.00/gallon for rolling oils.

#### 6.1.3 Alternative Disposal Technologies

Waste oils can be disposed of by incineration, landfilling, land application, or road oiling. The following discussion addresses these disposal technologies.

##### 6.1.3.1 Incineration--

Waste oil from metalworking operations may be thermally decomposed by incineration. Usually the incinerators are privately owned and centrally located. A few plants may have sufficient waste to economically justify installation of an incinerator on site. It is possible to recover the heat generated via incineration and use it to heat the plant, produce hot water, etc. This results in a reduction in the quantity of fuel needed for these heating and process requirements.

The types of incinerators available for combustion of waste oils include: liquid waste incinerators, rotary kilns, multiple hearth furnaces, and fluidized beds [81-83]. Waste oils are

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[81] Wachter, R. A.; Blackwood, T. R.; and Chalekode, P. K. Study to determine need for standards of performance for new sources

(continued)

also sometimes combined with refuse and disposed of by incinerators designed primarily for solid waste. Table 59 shows waste oils and other liquid wastes from metalworking operations which can be burned by incineration.

TABLE 59. LIQUID WASTES BURNED BY INCINERATION

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Separator sludges
Skimmer refuse
Oily waste
Cutting oils
Coolants
Phenols
Vegetable oils
Still and reactor bottoms
Animal oils and rendering fats
Lube oils
Soluble oils
Polyester paint
PVC paint
Latex paint
Thinners
Solvents
Resins

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Liquid injection incinerators can be used to dispose of most combustible liquid waste with a viscosity less than 10,000 SSU. Fluidized bed and rotary kiln incinerators can be used to dispose of solid, liquid, and gaseous combustible wastes. The multiple hearth incinerator has been utilized to dispose of sewage, sludges, tars, solids, gases, and liquid combustible wastes.

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(continued)

- of waste solvents and solvent reclaiming. Washington, DC; U.S. Environmental Protection Agency; 1977 February. 106 p. Contract 68-02-1411.
- [82] Sittig, M. Incineration of industrial hazardous wastes and sludges. Pollution Technology Review No. 63. Noyes Data Corporation, 1979.
- [83] Ottinger, R. S.; Blumenthal, J. L.; Dal Proto, D. G.; Gruber, G. I.; Santy, M. J.; and Shih, C. C. Recommended methods of reduction, neutralization, recovery, or disposal of hazardous waste; Volume III, disposal process descriptions - ultimate disposal, incineration, and pyrolysis processes. Cincinnati, OH; U.S. Environmental Protection Agency; 1973 August. 251 p. EPA-670/2-73-053C. PB 224 582.

In order to determine the proper type of incinerator system for use in a particular waste disposal situation, certain basic factors must be considered. These include waste toxicity, disposal rate, corrosiveness, operating temperature and material selection, secondary abatement requirements (air, water or solid pollution control), steam plume generation, waste heat recovery and costs.

The exhaust gases resulting from incineration may contain materials such as trace metals from waste oils that should be removed from the gas before expulsion. Not all the metals leave the incinerator in the flue gases. Some form of organic-metallic compounds are left in the ash, so consideration should be given to the environmental impact of disposing of ash with a high metallic content.

Although incineration can be extremely effective in destroying certain types of wastes, it is important to recognize that the cost of incineration for wastes can vary widely. The cost depends especially on the type of facility required to handle the waste, which determines the capital investment, the costs of energy (e.g., as auxiliary fuel), and the cost for air and water emission control equipment required [82-84].

The cost of incineration of high-Btu-value waste with no acute hazard is in the range of \$50-300/metric ton (\$0.19-1.14/gallon). For highly toxic heavy metals liquid wastes, the cost of incineration can be as high as \$300-1,000/metric ton (\$1.14-3.78/gallon) [85].

Generally speaking, incineration is technically viable and environmentally desirable, although the high unit costs will cause industry to prefer to utilize other less costly alternatives if they are acceptable to regulatory agencies.

#### 6.1.3.2 Landfill Disposal--

Landfill disposal of waste oils in an environmentally safe method when properly regulated. This method of disposal is also economically attractive since it is relatively cheap.

The RCRA does not list waste metalworking oils as hazardous waste, so it is necessary to conduct RCRA testing to determine whether waste oil is hazardous or nonhazardous. Disposal practice and

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[84] Ackerman, D.; Clausen, J.; Grant, A.; Johnson, R.; Shih, C.; Tobias, R.; Zee, C.; Adams, J.; Cunningham, N.; Dohnert, E.; and Harris, J. Destroying chemical wastes in commercial scale incinerators; Final Report - Phase II. Washington, DC; U.S. Environmental Protection Agency; 1978. 130 p. EPA-630/SW/55C. PB 278 816.

[85] Industry Week, p. 56, 1971 June 15.

costs will depend on whether waste oil is hazardous or nonhazardous. If waste oil is hazardous, its disposal must meet RCRA requirements, and must be disposed of in a hazardous waste landfill. Nonhazardous waste oil can be disposed of cheaply in a sanitary landfill. Waste oil is often mixed with refuse or soil or other oil absorbent materials to solidify it prior to landfill disposal. This practice will minimize leachate problems. Potential contamination of the groundwater through leachate is a major concern in disposing of waste oil by landfilling; nevertheless, landfilling is safe if properly managed and regulated.

#### 6.1.3.3 Land Application--

Waste oil can be disposed of by breaking it down into harmless products. This is accomplished by soil microorganisms. The used oil is spread atop the land where it can be biodegraded. The soil microorganisms oxidize the oils or convert oily waste into cell protoplasm, producing byproducts of gases and humus (partially reacted organics) along with organic acids (an intermediate product). The bacteria and fungi which grow the fastest are those using hydrocarbons for food. Some mineral nutrients important for microbial growth are carbon, hydrogen, oxygen, potassium, sodium, calcium, and especially nitrogen and phosphorus. Microbial growth, and therefore oil decomposition, is increased by the use of fertilizers. Soil microorganisms favor neutral soil; therefore, soil which is acidic may require the addition of agricultural-grade limestone as a neutralizing agent.

Temperature also plays a role in the oil decomposition rate. Oil decomposes much faster in warm than in cold climates. The optimum temperature for the incubation of most hydrocarbon-oxidizing organisms is reported to be 86°F. To provide oxygen for soil microorganisms, the soil is aerated by disking. This disking or stirring of the soil also disperses the hydrocarbon molecules, making them more readily available to microbial attack. Soil saturated with oil or water has its air spaces filled, reducing the oxygen available to soil microorganisms. Without sufficient oxygen the number of microorganisms are few, resulting in a very slow oil decomposition rate. Some hydrocarbons, such as waxes and heavy oils, are more resistant to decomposition, because less surface area is exposed to microbial attacks.

Oil, when discharged without adequate treatment or proper disposal, is a serious pollutant of water and land. In 1969, the Marathon Oil Company in Robinson, Illinois, used land spreading to dispose of oily sludge stored in two lagoons over a period of five years. The sludge, consisting of 35 percent oil, was spread on the ground to a depth of about 4 inches. When the sludge was dry it was mixed with the soil by disking to a depth of about 18 inches. A rainstorm occurred before cultivation of the sludge

and resulted in erosion of the oily sludge and its deposition in a small lake, killing some fish [86].

Plants may also be affected by such oil. Large applications of oil to land are often toxic to plants due to the narcotic effect that volatile fractions have on plants and the reduction of manganese to the toxic manganous form. Plants growing on the land-spread area may acquire high levels of metal ions. Trace metals may be found in many used oils. If oils containing trace metals are deposited on the ground, vegetation may be contaminated and eventually animals may eat this vegetation.

The British attempted to use municipal sewage sludge as a soil conditioner until they discovered that the metal content of the sludge constituted a hazard to agriculture. Twelve years after the project was discontinued, vegetables grown on the soil still contained abnormally high levels of chromates, copper, nickel, lead, and zinc. Land saturated with oil eventually returns to a productive state, however, Humble Oil Company near Houston, Texas, land-spread oily sludge 4 to 5 inches thick; 3 to 4 months later grass was growing. More oil may be added to the soil of a land-spreading site when the soil returns to a brown friable condition [85].

Other used oil components, such as aromatic hydrocarbons, may present problems because of their lengthy degradation process. In addition, many of the additives that are combined with industrial oils may cause adverse environmental effects if not properly treated before disposal. Additive compounds containing phosphates or phenols can adversely affect water quality. Minute quantities of phenols cause objectionable taste and odor in drinking water and induce cancer in lower animals [86].

Favorable locations for land-spreading sites are those with deep, fine-textured soils which readily absorb oil, thereby reducing the chances of a contaminated water table. Clay subsoils also help prevent contaminated water tables. To reduce surface water contamination, the site should be flat with poor drainage. Indiscriminate dumping on porous, coarse, or shallow soils is likely to cause runoff water pollution.

Soil farming can be a viable disposal method for oily waste under diverse and sometimes adverse conditions of topography, soil type and climate. One aluminum manufacturer has successfully disposed of over 55 million gallons of waste oil emulsion coolant from their rolling mills by means of soil farming. The waste oil emulsion,

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[86] Yates, J. J.; Groke, K. G.; Klazura, A. G.; Spaite, A. R.; Chiu, H. H.; Mousa, Z.; and Budach, K. Used oil recycling in Illinois: data book. ETA Engineering, Inc., 1978 October. 135 p.

containing approximately 0.5 to 1.0 percent mixed hydrocarbons, is being applied at a rate of 0.5 inch per week in a 14.6-acre field situated on the flood plain of the Ohio River with minimal cost. Continuous monitoring of the disposal area has indicated no obvious deterioration of the physical, chemical, or biological conditions of the soil, other than the accumulation of approximately 40 mg of hexane-extractable residue per 100 grams of soil in the surface horizon [87,88].

#### 6.1.3.4 Road Oiling/Dust Control [86]--

Road oiling and dust control are indirect methods for the disposal of used oil. Although virgin petroleum products are used for road oiling, a large fraction is used oil, which is generally cheaper than a specially compounded oil and thus more economically attractive in the short run. In 1974, it was estimated that 200 million gallons of used crankcase oils plus unknown amounts of other used oils were used annually in the United States for road oiling and dust control.

The oil is usually applied to rural dirt roads through drilled pipe spray headers mounted on tank trucks. The application rate is left to the discretion of the applicator and ranges from 0.025 to 0.05 gallon per square foot of road, depending on road composition and dust conditions. Very little of the oil applied to the road actually remains there, necessitating periodic reapplications. A road may be oiled from one to four times a year. In a study dealing with used oil applied to rural roads, it was observed that one percent of the total oil applied to the roads remained in the top inch. The rest was lost in a number of ways, including being washed from the road by rain, leached through the road, carried away by the wind on dust particles, picked up by passing vehicles and carried elsewhere, biodegraded, and volatilized. The extent and rate of oil loss depends on road composition, weather conditions, the time of the first rain after oiling, the type and quantity of oil applied, road traffic conditions, and the ability of the road surface to biodegrade the oil. Around 25 to 30 percent of the oil applied to the road is lost by biodegradation, adherence to vehicles, and volatilization. The remaining 70 to 75 percent leaves the road with water runoff and dust transport, contaminating surface waters.

Oil which makes its way into a water system becomes a nuisance and, in sufficient quantities, a health and ecological hazard. Used oil enters water systems in many ways: direct discharge

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[87] Kincannon, C. B. Oily waste disposal by soil cultivation process. Washington, DC; U.S. Environmental Protection Agency; 1973. EPA R2-72-110.

[88] Liu, D. L.; and Townsley, P. M. Lignosulfonates in petroleum fermentation. Journal of the Water Pollution Control Federation. 531-537, 1970 April.

into waterways, dumping into storm sewers, washing off roadways into water ways (rainwater may scavenge oil from road surfaces and then percolate into the groundwater), or direct deposition on or in the ground.

Along with the oil that leaves the road surface and is deposited into the surrounding ecosystem are heavy metals and other additives which are taken up by plants and consumed by animals, either by drinking contaminated water or by eating plants that have taken up metals. In Alberta, Canada, in 1971, cattle were poisoned by drinking water containing lubricating oil from a road treated with an oil that contained triaryl phosphate as an additive.

Because of the negative environmental effects resulting from the runoff of used oils from roads, most states prohibit the use of any used oil for road oiling or dust control. Because this regulation is difficult to enforce, used oil may still be widely used for road oiling and dust control.

#### 6.1.4 Sludges Generated by Oily Waste Treatment

Sludges are produced from in-plant processing equipment such as oil/water separators, centrifuges, filters, coalescers, ultrafiltration and/or reverse osmosis systems, dissolved air flotation, and still bottoms from vacuum distillation. Composition data for these sludges are difficult to find in published literature except for sludges from oil/water separators. Table 60 gives characterization data for sludges obtained from various sources (as indicated at the footnote of the table). Table 61 shows the organic components in sludges designated in Column 3 of Table 60. The concentrations and even presence of various hazardous materials varies due to differences in the characteristics and origins of the various sludges collected during any given time period. Sludges from in-plant processing usually contain a large amount of heavy metals and are considered to be potentially hazardous.

Sludges can be disposed of by using compatible techniques mentioned in Section 6.1.3. However, incineration is the most popular method for disposal. The disposal methods are used both on-site and off-site, using either plant facilities or contractor plant.

### 6.2 DISPOSAL AND RECLAMATION OF STRAIGHT MINERAL OILS

#### 6.2.1 In-Plant Reclamation Technologies

In-plant reclamation technologies are usually employed to remove the two most common contaminants, solids and water, in used mineral oils and offer a low-cost method for recycling large quantities of used oils. These include gravity separation of solids and water, centrifuging, filtration, and water removal by coalescing. Descriptions of processes and equipment have been discussed in Sections 6.1.1.1 through 6.1.1.4.



TABLE 60. ANALYTICAL CHARACTERIZATION OF SLUDGES  
COLLECTED FROM IN-PLANT PROCESSING  
EQUIPMENT FOR EMULSIFIED OILS

Sample designation <sup>a</sup>	1	2	3
Sample collected at	oil separator	oil separator	API separator
Inorganic metals, mg/kg			
Ag		0.6	
Be	ND <sup>b</sup>		0.84
Cd	ND	7.4	13
Co		2.6	
Cr	48	15.0	370
Cu	Trace	436	970
Fe		317	
Hg	ND	0.2	0.6
Li		0.5	
Ni	ND	13.6	200
Pb	ND	402	1,700
Zn	510	4,905	8,400
Inorganic nonmetals, mg/kg			
Br	ND		5.7
Cl	ND		1,300
P	650	1,550	730
S	ND		6,300
As	ND		4.6
Noncombustible ash, %	ND	8.02	
Solids, %	24	9.1	85
Compounds contained, mg/kg	Phosphates, 1988		Cyanides, 0.94 organic com- pounds, see Table 61
Major components	Oil, 40% Water, 60%	Oil, 41.1% Water, 49.8% Dirt, 8.1%	
Flash point, °F		Over 200	206
pH		8.5	6.2

<sup>a</sup> Designation No. 1 to 3 are from generator waste analysis form to landfill ob-  
tained from State EPA offices.

<sup>b</sup> Not detected, detection limit = 0.2 mg/kg.

TABLE 61. ORGANIC COMPONENTS IN SLUDGES DESIGNATED  
IN COLUMN 3 OF TABLE 60.

Parameter	Results, ppm
<u>Base/neutral fraction</u>	
Combined anthracene and phenanthrene	24.0
Bis(2-ethylhexyl)phthalate	8
Chrysene	2.3
1,3-Dichlorobenzene	8.9
Fluoranthene	1.8
Fluorene	8.6
Naphthalene	58
<u>Acid fraction</u>	
Phenol	2.6
Pentachlorophenol	0.11
<u>Volatile fraction</u>	
Benzene	0.23
1,1-Dichloroethane	5.2
1,1-Dichloroethene	0.91
Ethylbenzene	10
Methylene chloride	1.6
Tetrachloroethene	0.52
1,1,1-Trichloroethane	6.0
Trichlorofluoromethane	0.034
Toluene	21
Xylene	17.2

(continued)

TABLE 61 (continued)

Parameter	Results, ppm
3,5-Dimethylheptane	4.4
Octane	4.8
Propanol	0.7
2,3-Dimethylcyclobutanone	1.6
Benzene (1-1 methylethyl)	0.33
<u>Miscellaneous base/neutral</u>	
Various saturated hydrocarbons C <sub>11</sub> -C <sub>25</sub>	4,000
<u>Miscellaneous acid fraction</u>	
Thallic acid	2.5
Hexadecanoic acid	22.0
Octadecanoic acid	16.0
<u>Miscellaneous volatile</u>	
2-Methyl-1-pentene	0.46
2,2-Dimethyl propanol	2.26
1,1-Dimethylcyclopentane	0.23
4-Methyl-1-hexene	0.82
Methylcyclohexane	5.9
Ethylcyclopentane	0.1
4-Methyl-2-pentanone	1.46
3,4-Dimethylheptane	2.96
2,3,3-Trimethylhexane	0.94
1,2,3-Trimethylcyclopentane	0.46
Ethylcyclohexane	4.6
1,3-Dimethylcyclohexane	3.65

For highly refined mineral oils, which are generally formulated without polar additives and usually are removed from service after only slight contamination, more sophisticated equipment is used to return the used oil to a like-new condition. The two most common processes are flash distillation and chemical adsorption [49].

The flash distillation step is usually carried out around 200°F and with a partial vacuum. This temperature ensures rapid and complete removal of water and low-boiling-point materials such as solvents, yet is not high enough to thermally degrade the oil itself. Chemical adsorption uses polar absorbent materials to remove the usually polar acid degradation products. Chemical adsorption is most effective with waste oils that have an acid number of 2.0 mg KOH/g or less and that have been treated to remove particles and water. High acidity oils require larger volumes of adsorbent, which makes the adsorption uneconomical. The most common filter material is fullers earth, though other clays are available.

Reclamation systems are available for either fixed or portable, batch or continuous operation. Reclamation services are also available from independent companies.

Used straight mineral oils can also be used on site as fuel. However, special furnace design considerations are necessary. Low flash point, introducing the risk of explosions, and presence of sulfur and chlorine compounds used as additives, may cause damage to furnace linings and other equipment and also form gaseous pollutants which require control.

#### 6.2.2 Re-refining Technology

Most straight mineral oils can be re-refined by independent re-refiners. The waste oil is pre-filtered to remove most of the solids, solvents, and water, leaving essentially the base oil and additive package. The additives and degradation products are then removed so that a high quality basestock is produced. This basestock is reformulated with a conventional additive package to produce a product which can be used in the same applications as an oil using a virgin basestock. The prevalent re-refining technologies are discussed in the following section.

##### 6.2.2.1 Re-Refining Technologies--

6.2.2.1.1 Acid/Clay Treatment [89-92]--This is the most commonly used re-refining process for waste mineral oils, (see Figure 52).

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[89] Hess, L. Y. Reprocessing and disposal of waste petroleum oils. Park Ridge, NJ, Noyes Data Company, 1979.

(continued)

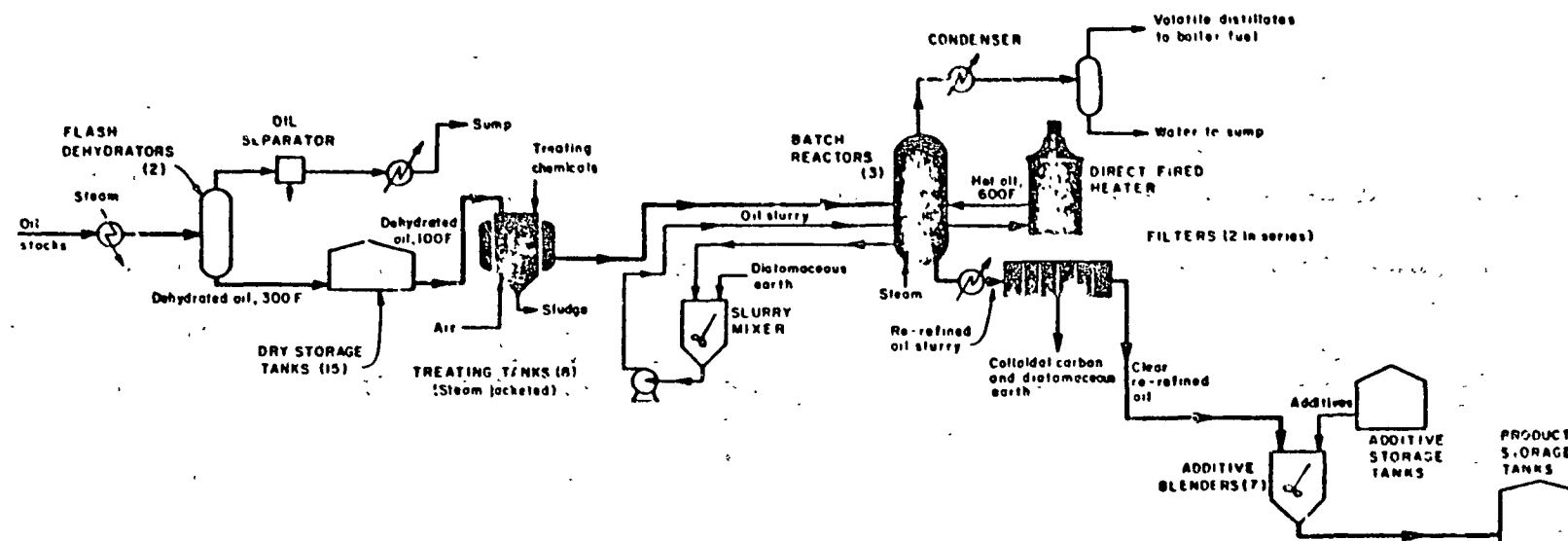


Figure 52. Acid/clay treatment [92].

Waste oil is dehydrated by flash distillation at 300°F and atmospheric pressure. Light oils are also removed in this step. When the product oil has cooled to 100°F, it is transferred to an acid treating unit where 4-6 volume-percent of 93 percent sulfuric acid are added. The mixture is then agitated for 24-48 hours. The oxidized products and ash thus produced separate from the oil and are removed as acid sludge from the reactor bottom.

The acid-treated oil is transferred to a stripping tower and heated to 550-600°F by steam to remove the remaining light oils and odorous compounds. The heating is discontinued after 12-15 hours and the oil is transferred to a clay slurry tank where it is allowed to cool to 100°F. About 0.4 lb of clay, consisting of materials such as fullers earth, bentonite, attapulgite and diatomaceous earth, per gallon of oil is then added while the mixture is actively stirred. The cleaned oil is separated by filtration, and the necessary additives are replaced before the oil is reused.

The acid/clay process is quite effective in removing the additives and degradation products, but unfortunately it generates considerable amounts of acid sludge and contaminated clay. Some of this clay and sludge is used as fuel, but most has to be disposed of at waste disposal sites, (see Section 6.2.2.3). The increased cost of waste disposal and limited availability of disposal sites has prompted a number of companies to develop alternative clay and sludge disposal approaches. Some of the processes have reduced the amount of acid and clay necessary to treat a gallon of re-refined oil, while others have completely eliminated the use of acid and/or clay.

6.2.2.1.2 The IFP (Institut Francais du Pétrole) Process [89, 93-96]--Originally, the IFP process was based on propane extraction of the dehydrated waste oil followed by conventional acid/clay treatment. It has since incorporated distillation to replace the acid treatment and hydrofinishing as a final treatment, (see Figure 53).

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- [90] Whisman, M. L.; Goetzinger, J. W.; and Cotton, F. O. Waste lubricating oil research. An investigation of several re-refining methods. U.S. Department of the Interior, Bureau of Mines; 1974. 25 p. RI-7884.
- [91] Blatz, F. J.; and Pedall, R. F. Re-refined locomotive engine oils and resource conservation. Lubrication Engineering. 618-624, 1979 November.
- [92] Waste oil recycling. U.S. Department of the Interior, Bureau of Mines; 1975. Issue Report Paper.
- [93] Quang, D. V.; et al. Spent oil reclaimed without acid. Hydrocarbon Processing. 130-131, 1976 December.

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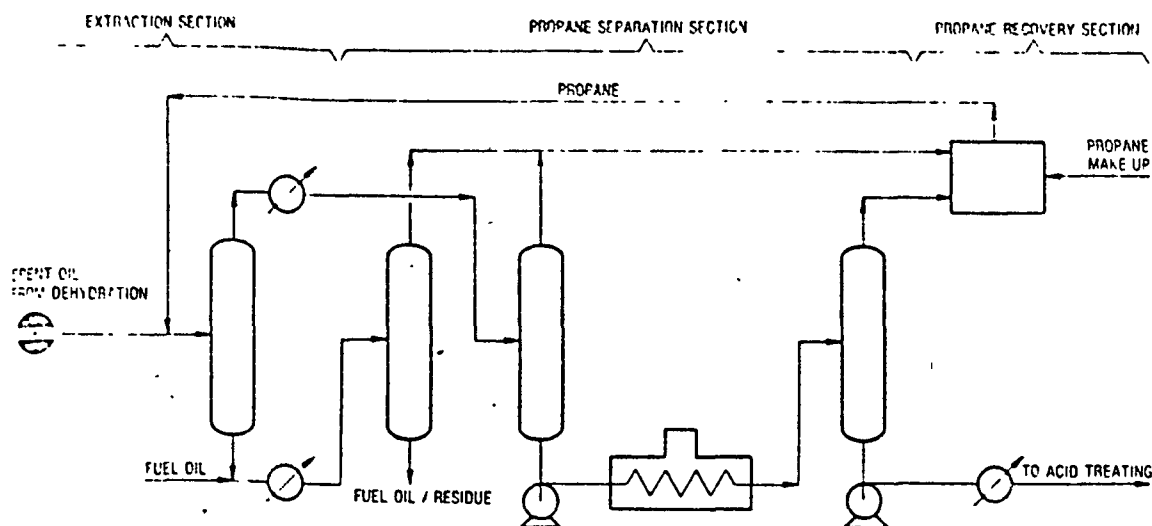


Figure 53. IFP Process [95].

Dehydrated and preheated spent oil is mixed with liquid propane in a reactor. Propane addition is from 6 to 13 times the volume of used-oil feed [96]. Propane containing the dissolved oil is removed from the reactor top while insoluble residues are drawn off at the reactor bottom. Bottoms are mixed with a small amount of fuel oil and are flashed to recover the propane. The remaining residues with fuel oil are burned in a rotary furnace.

Propane is separated from oil in a double-stage flash distillation and is reliquefied and recycled. The product oil is either subjected to acid/clay treatment or distilled, clarified with clay, and hydrofinished.

The IFP process does not totally replace acid/clay treatment, but it uses a smaller quantity of treatment materials which results in less waste. The process also produces a high ash fuel oil which,

(continued)

- [94] Audibert, M. M.; et al. The regeneration of the spent oils. *Chemical Age of India*. 26(12):1015-1019, 1975.
- [95] Quant, D. V.; Carriero, G.; Schieppati, R.; Comte, Al; and Andrews, J. W. Re-refining uses propane treat. *Hydrocarbon Processing*. 129-131, 1974 April.
- [96] Deutsch, D. F. Bright prospects loom for used-oil re-refiners. *Chemical Engineering*. 86(16):28-32, 1979.

if burned in ordinary combustion equipment, causes tube fouling problems.

Although the reported process yield is 82 percent of high quality lube stock, the plant at Lodi, according to a DOE source, shows a much lower yield of about 70 percent.

6.2.2.1.3 The PVH (Propane-Vacuum-Hydrogen) Process [89,97]--The PVH process, developed by Pilot Research & Development Company, consists of filtration and dehydration, followed by treatment with propane at 180-190°F. The propane is then stripped, the oil is vacuum-fractionated at 650°F, and all but 10-15 percent is distilled. The condensed oil is hydrotreated and finished with filtration.

The PVH process has a reported yield of 73 percent of high-quality lube stock. It is known to require considerably less chemicals and energy than many other commercial processes, and hence is more economical.

PVH's dehydration and propane treatment steps are claimed to work without heat-treating the used oil to excessive temperature. Propane requirements are only four times the used oil feed rate, which is two to three times less than other conventional propane-based processes.

6.2.2.1.4 Snamprogetti Process [89,98]--This process, (see Figure 54) was developed by Snamprogetti for Clipper Oil Italiana S.p.A. The process consists of water and light hydrocarbon elimination by flash distillation, followed by selective extraction of metals and polymers with propane. This is followed by fractional distillation and hydrogenation to produce virgin quality base oil. The peculiarity of the process is in the second extraction phase and in the recycle of the residue from this phase to the first extraction stage. It is known that the previous heating of a charge prior to extraction (thermal treatment) allows polymer peptization and makes separation easier.

Construction costs are said to be twice those for a comparable acid/clay plant, but operating costs are lower because of no need for the acid/sludge control system.

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[97] Cutler, E. T. Re-refining: selecting the best process. Third international conference on waste oil recovery and reuse; 1978; Houston. Pilot Research and Development Center, Merlon Station, PA, 163-168.

[98] Antonelli, S. Spent oil re-refining. Third international conference on waste oil recovery and reuse; 1978 October 16-18; Houston. 121-125.



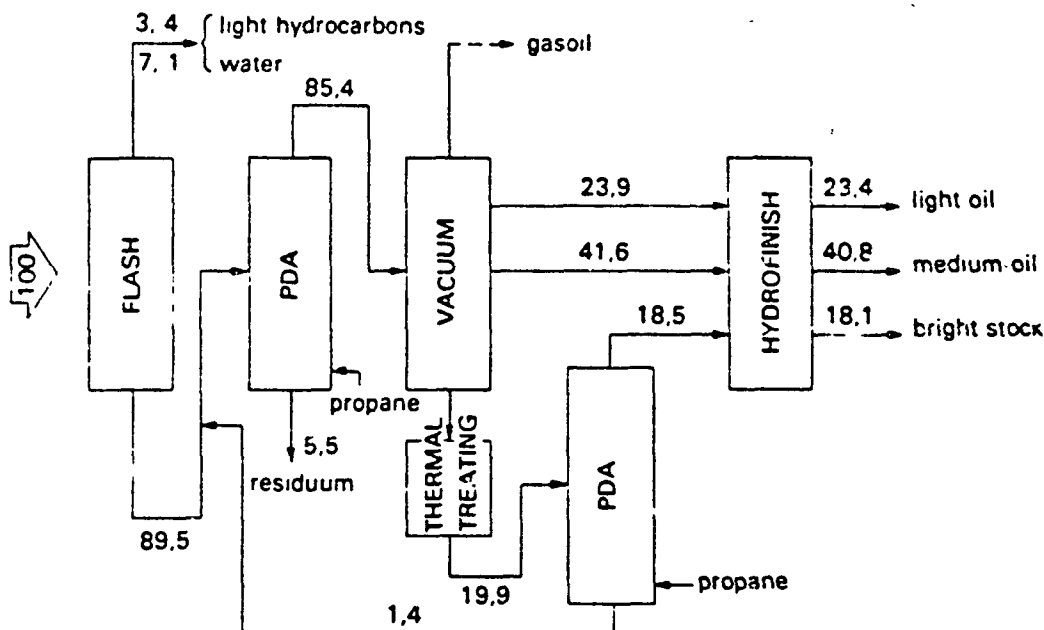


Figure 54. Snamprogetti process [98].

6.2.2.1.5 The Krupp Process [95]--An application of propane at supercritical conditions has been successfully tested at Friedrich Krupp, West Germany. The process uses countercurrent propane extraction to extract usable oil products from a dehydrated waste-oil feed.

Yields are said to be 90 percent (of drier oil, after atmospheric distillation removes water and gas oil) and costs are comparable to those for conventional acid/clay technology. Propane requirements are only one volume of propane per volume of water-oil flow. A patent has been filed but not yet granted for the process,

6.2.2.1.6 The BERC Process [89,91,99-105]--The BERC process, developed at the Bartlesville Energy Technology Center of the U.S. Department of Energy (DOE), (Figure 55) consists of dehydration, solvent precipitation of polymers and additives, vacuum distillation, and clay treating or hydrofinishing.

[99] Whisman, M. L.; et al. U.S. Department of Energy, assignee. U.S. patent 4,073,719. 1978 February 14.

[100] Whisman, M. L.; et al. U.S. Department of Energy, assignee. U.S. patent 4,073,720. 1978 February 14.

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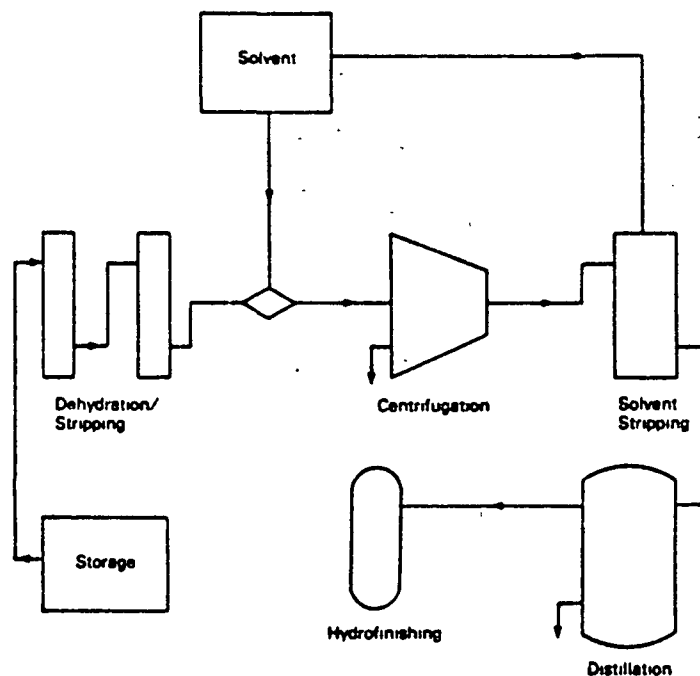


Figure 55. BERT re-refining process outline [105].

(continued) .

- [101] Cotton, F. O.; et al. Pilot-scale used oil re-refining using a solvent treatment/distillation process. U.S. Department of Energy; Bartlesville Energy Technology Center; 1980. BETC/RI-79/14.
- [102] Brinkman, D. W.; et al. Environmental, resource conservation, and economic aspects of used oil recycling. U.S. Department of Energy; Bartlesville Energy Technology Center; 1981 April. DOE/BETC/RI-80/11.
- [103] Brinkman, D. W.; et al. Solvent treatment of used lubricating oil to remove coking and fouling precursors. U.S. Department of Energy; Bartlesville Energy Technology Center; 1978 December. BETC/RI-78/20.
- [104] Engineering design of a solvent treatment/distillation used lubricating oil re-refining. Houston, TX; Stubbs Overbeck and Associates, Inc; 1980 June. Final report to U.S. Department of Energy, Division of Industrial Energy Conservation.
- [105] Brinkman, D. W.; and Whisman, M. L. Waste oil recovery and reuse research at the Bartlesville Energy Technology Center. Third international conference on waste oil recovery and reuse; 1978 October 16-18; Houston. 169-175.

The BERC process uses a solvent mixture of 1-butanol, 2-propanol, and methylethyl ketone in a 1:2:1 ratio by volume. This mixture is used in a 3:1 solvent-to-oil ratio. The solvent is continuously recycled, with sludge the only waste. The sludge can be burned as fuel in the process with proper stack emission control or used as an asphalt extender. Clay-contacting or hydrofinishing are usually incorporated into the BERC process for color and odor improvement.

It appears that operating costs are almost identical for clay treatment and hydrofinishing. Capital costs are higher for the hydrofinishing facility but this initial cost is offset somewhat by higher product yields, better color and odor, and elimination of oily-clay disposal costs.

6.2.2.1.7 Aliphatic Alcohol-Acid Treatment [89,106]--This re-refining process was patented by Brownwell and Renard and assigned to ESSO Research and Engineering Company. It involves treating predistilled oils with 1-butanol. The oil-alcohol solution is then filtered to remove sludge and the alcohol is removed by distillation. Fuming sulfuric acid is then added to strip the oil.

6.2.2.1.8 Gulick Process [89,107]--This method is intended for breaking the films absorbed on colloid-sized contaminants that are held in suspension by detergent additives. The used oil is treated with sodium hydroxide and hydrogen peroxide. After settling, the oil is removed from the sludge and centrifuged. The oil is then either distilled or treated with aluminum chloride, which is effective for colloidal iron and organometallic iron removal.

6.2.2.1.9 Caustic Treatment [89,108]--This process uses caustic instead of acid to treat the oil. Treatment with caustic minimizes the formation of waste products which must be disposed of. The process was patented by Chambers and Hadley to re-refine used lubricating oil. It involves flash dehydration to remove water, mixing with oil with a boiling range of 150-250°F, treatment with 1 weight percent of a 50 percent sodium hydroxide solution, centrifuging, and distillation.

The process eliminates acid sludge, but spent clay disposal remains a problem. In addition, a sludge is produced during

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[106] Brownawell, D. W.; and Renard, R. H. Esso Research and Engineering Company, assignee. U.S. patent 3,639,229. 1972 February 1.

[107] Gulick, G. L. Quove Chemical Industries, Ltd., assignee. U.S. patent 3,620,967. 1971 November 16.

[108] Chambers, J. M.; and Hadley, H. A. Berks Associates, Inc., assignee. U.S. patent 3,625,881. 1971 December 7.

pre-treatment, and a high ash bottoms product results from the distillation step.

6.2.1.1.10 The Philips PROP Process [89,91,96,109-113]--The Philips PROP process, Figure 56, is an oil re-refining technology developed by Philips Petroleum Company. Waste oil is first blended with aqueous diammonium phosphate (DAP), which results in formation of essentially insoluble metallic phosphates. No pre-drying of the feedstock, use of solvents or acids, or settling are required. Following removal of water and other diluents, temperature cycling of the oil agglomerates the solids, which are removed by filtration. The resulting demetalized and dehydrated

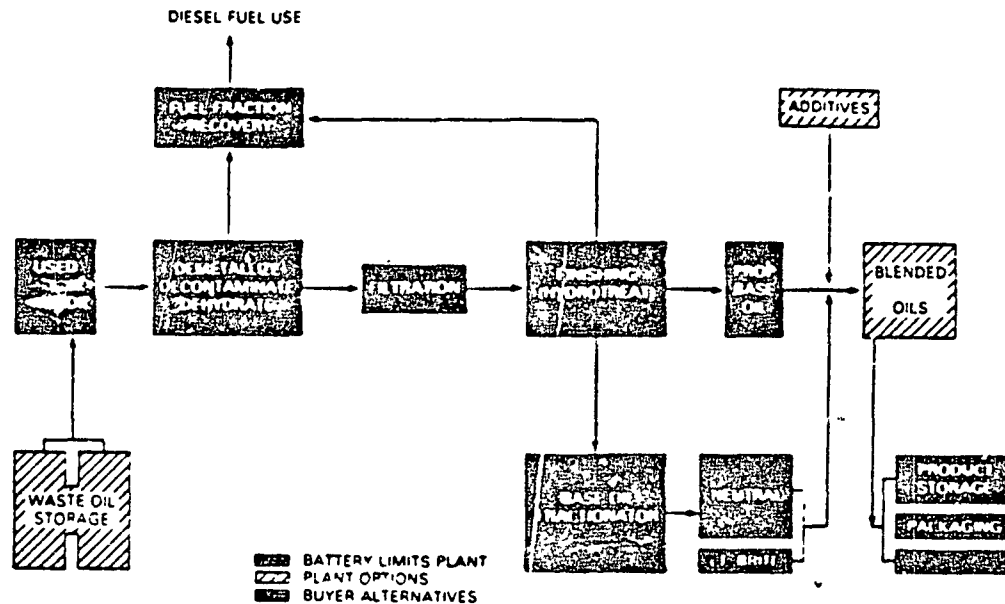


Figure 56. The Philips PROP process [110].

- [109] Berry, R. Re-refining waste oil. Chemical Engineering. 104-106, 1979 April 23.
- [110] Linnard, R. E. Philips re-refining oil program. Third international conference on waste oil recovery and reuse; 1978; Houston. Bartlesville, OK, Philips Petroleum Co., 127-135.
- [111] Re-refining. Fluid and Lubricant Ideas. p. 27, 1980 May/June.
- [112] Packaging re-refining technology: the PROP process. Fluid and Lubricant Ideas. 1979 Fall.
- [113] Linnard, R. E.; and Henton, L. M. Re-refine waste oil with PROP. Hydrocarbon Processing. 1979 September.

oil is hydrotreated to remove unwanted sulfur, nitrogen, oxygen, and chloro compounds and improve color. This is followed by further stripping and fractionation. Pre-fabricated skid-mounted plants are available in 2, 5 and 10 million gallon-per-year capacities, and require only conventional utilities, services, and process materials. The process is claimed to provide 90 percent of recovery from waste oil.

6.2.2.1.11 The Recyclon Process [89,96,114-116]--This method of re-refining spent oil is being marketed world-wide by Leybold-Heraeus of West Germany. The most significant stages of this method, Figure 57, are treatment of waste oil after it has been filtered, dehydrated and freed from low-boiling components with dispersed metallic sodium at elevated temperatures. The sodium serves to polymerize unsaturated olefins into components with high boiling points. When the reaction is completed, the mixture

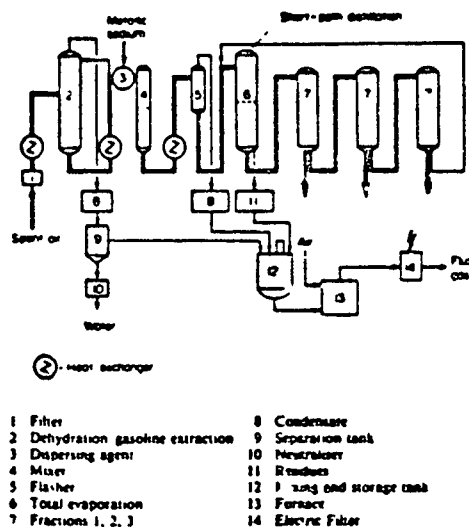


Figure 57. Recyclon process [115].

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- [114] Erdweg, K. J. Recyclon - a new process to revert spent oils into lubricants. Third international conference on waste oil recovery and reuse; 1978 October 16-18; Houston. 93-97.
- [115] Fauser, F. Recyclon - a new method of re-refining spent lubrication oils without detriment to the environment. Conservation and Recycling. 3:135-141, 1979.
- [116] Recyclon - a new process for the re-refining of waste oil. Leybold-Heraeus, Vacuum Process Engineering Division. Trade Literature.

is stripped of its components in a conventional vacuum column. The bottoms of the stripping column are subjected to total evaporation in short-path evaporators, leaving the impurities and reaction products as residue. The distillate is subsequently split into the required fractions. Process yield is over 70 percent re-refined oil; the remaining byproducts are used as fuel.

6.2.2.1.12 The Haberland KTI (Kinetics Technology International) Process [96,109,117]--This process, developed by Kinetics Technology International, B.V. (Zoetermeer, The Netherlands) in close cooperation with Gulf Science and Technology Company, Figure 58, involves a dewatering and gas/oil stripping step, an efficient high vacuum distillation step, and a hydrofinishing step. Fractionation of base oils can be included if desired. A 97 percent effective yield compares favorably with typical acid/clay re-refining yields of about 83 percent. The process also eliminates the problems of disposal of large quantities of contaminated clay and sludge.

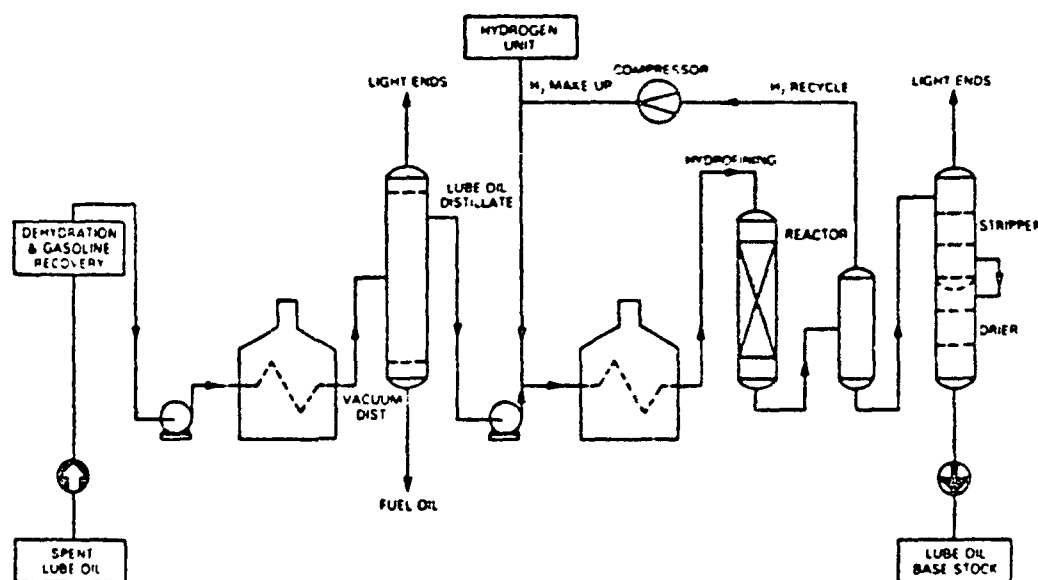


Figure 58. KTI process [117].

[117] Havemann, R. Haberland and company and the KTI waste oil re-refining process. Third international conference on waste oil recovery and reuse; 1978 October 16-18; Houston. 83-92.

6.2.2.1.13 The Matthys/Garap Process [118]--This process includes settling and atmospheric distillation at 180°C to eliminate residual water and solvents. Vacuum distillation is used to obtain the different cuts, and hot centrifuging of the bottoms is used to extract heavy metals and carbonaceous products. Continuous acidification of the cuts and bottoms followed by centrifuging is used to extract the acid tars. Then, neutralization and hot bleaching in a furnace are conducted, followed by continuous cooling and filtration.

6.2.2.1.14 Ultrafiltration Process [119,120]--The ultrafiltration process, Figure 59, involves use of a solvent to provide molecular-scale filtration of used oils. Hexane is used to reduce the viscosity of the oil. The mix is then passed through a semipermeable membrane, usually made of acrylonitrile co-polymers, which allows only the light hydrocarbons to pass through and

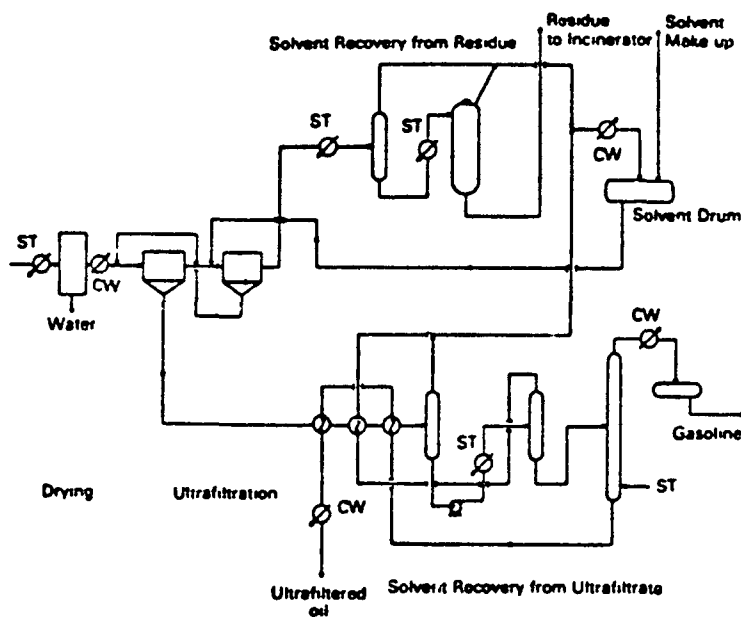


Figure 59. Reclaiming of spent oils by ultrafiltration [119].

- [118] Dumortier, J. Matthys/garap techniques. Third international conference on waste oil recovery and reuse; 1978 October 16-18; Houston. 99-107.
- [119] Audibert, F.; et al. Reclaiming of spent lubricating oils by ultrafiltration. Third international conference on waste oil recovery and reuse; 1978 October 16-18; Houston 109-120.
- [120] Parc, G.; et al. Institut Francais du Petrole, France, assignee. U.S. patent 3,919,075. 1975 November 11.

retains heavier hydrocarbons and metals. Once the bulk of the contaminants have been removed, the filtrate is treated with an acid/clay process to remove the final level of contamination. Hydrofinishing is used to bring the base oil back to virgin quality. The process greatly reduces the amount of acid and clay necessary to achieve high product quality. When an ultrafiltration process is added to an existing conventional plant, the oil yield increases by about 7 percent and the sludge volume is drastically reduced. The ultrafiltration investment is paid off within 3 to 5 years for a plant with 20,000 ton-per-year capacity [120].

6.2.2.1.15 The Pfaudler Test Center Process [121]--The Pfaudler test center process, Figure 60, includes a filtration and dehydration steps that also remove galoline and other low boiling contaminants. A solvent extraction process is then used to remove sludge, with evaporation of the solvent in a wiped film evaporator. The solvent stripped oil is then degassed to remove

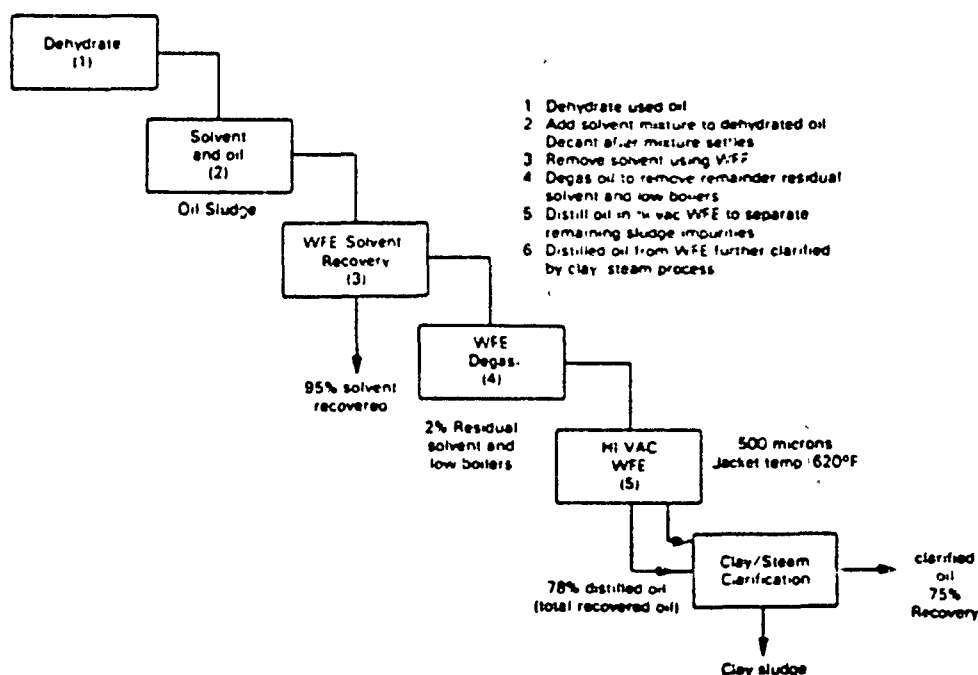


Figure 60. The Pfaudler test center process [121].

[121] Bishop, J.; and Arlidge, D. Recent technology development in evaporative re-refining of waste oil. Third international conference on waste oil recovery and reuse; 1978 October 16-18; Houston. Rochester, The Pfaudler Company, 137-150.



any residual solvent and vacuum distilled. This is followed by clay treatment and filtration to recover 75 percent of the starting material as high quality base oil.

6.2.1.1.16 Luwa Process [122]--The Luwa process uses a thin film evaporator of the "fixed blade clearance" type instead of conventional distillation column. The advantages of Luwa's thin-film evaporator include:

- Short-residence time--allowing heat-sensitive products to be exposed to less severe conditions.
- Minimum fouling of distilling surfaces.
- Lower "real" vacuum because of large evaporation surfaces and the short distance vapor has to travel to escape the liquid (film thickness).
- Internal, self-cleaning mechanical separator.
- External condenser which allows more time for entrained liquid to separate from the vapor.
- High tip speed - consequently, higher heat transferability with lower fouling characteristics.

Figure 61 provides an example of re-refining process using Luwa's thin film evaporator.

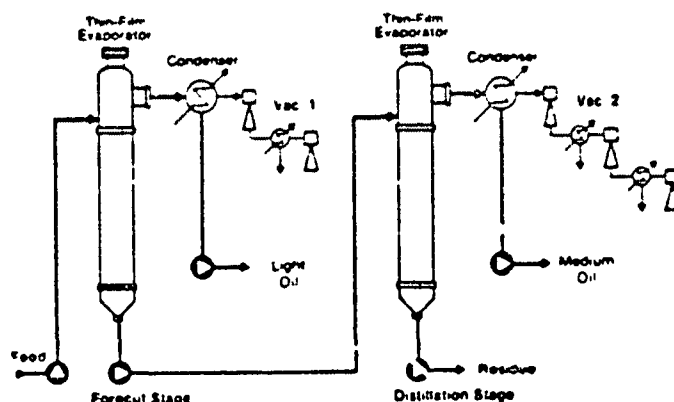


Figure 61. Oil is distilled in two stages using Luwa's thin film evaporator [122].

[122] Pauley, J. F., Jr. Thin-film distillation as a tool in the re-refining of used oil. Third international conference on waste oil recovery and reuse; 1978 October 16-18; Houston. Charlotte, Luwa Corporation, 151-161.

6.2.1.1.17 The MZF Process [123]--This process, developed by M. Z. Fainman Associates, involves diluting the feedstock with selected hydrocarbons (naphtha) and mixing of the combined hydrocarbon stream with a 50/50 solution of isopropyl alcohol and water plus 1 percent sodium carbonate. The overall mixture is then centrifuged. Three fractions result. The alcohol fraction is stripped to recover the isopropyl alcohol. The crude oil fraction is vacuum distilled.

The extraction step removes metals, clearing the way for successful distillation and downstream catalytic hydrogenation for upgrading the crude product.

6.2.2.1.18 Resource Technology Process [124]--Resource Technology, Inc., (Kansas City, Kansas) has developed a new process for re-refining used oils, Figure 62. According to the firm, this method does not require acids, solvents, or additional chemicals and does not produce hazardous wastes as do traditional acid/clay re-refining methods. In contrast, the new technology uses a series of vacuum distillation equipment of unique design that minimizes coking. The method will recover 97 percent of a gallon of dehydrated used oil as marketable products.

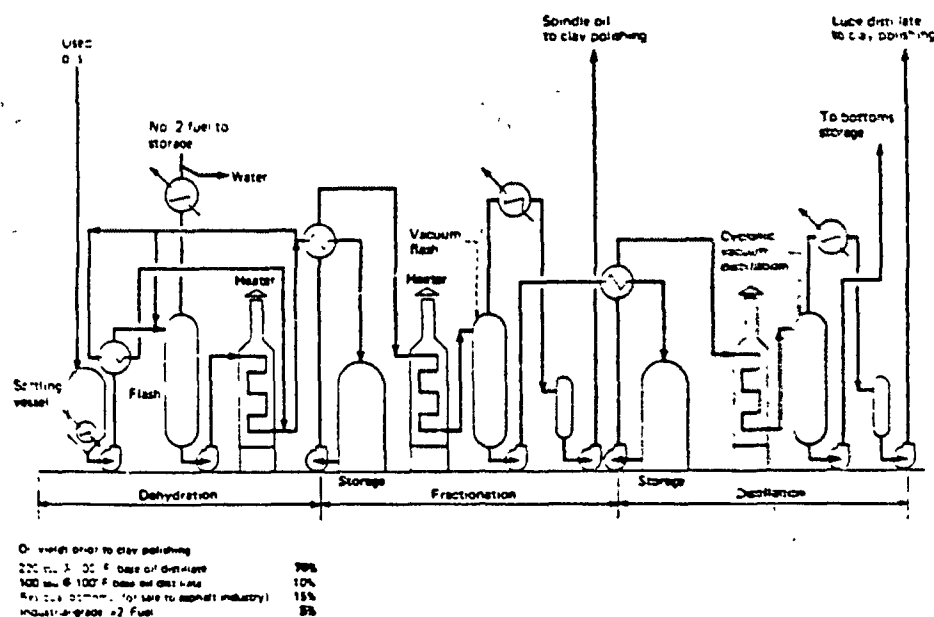


Figure 62. Resource Technology process [124].

[123] Davis, J. C. New technology revitalizes waste-lube-oil re-refining. Chemical Engineering. 63-65, 1974 July 22.

[124] Oil refining route is set for two plants. Chemical Engineering. 92-93, 1981 October 5.

The process costs are less than \$0.30/gallon. Resource Technology projects that, given an oil feedstock cost of \$0.32/gallon, a 5-million-gallon facility will produce a before-tax earning of \$2.5 million/year; a 10-million-gallon plant should produce an estimated \$5.3 million.

It is also possible to retrofit the technology to an existing plant. The retrofitting involves the addition of a cyclonic vacuum distillation tower, which would replace the acid-treatment in an acid/clay process. Cost of skid-mounted equipment with a capacity of 3 million gallons/year is \$525,000. The firm estimates that retrofitting can result in a net process saving of nearly \$0.34/gallon, and at the same time eliminates the problems of hazardous waste generation and disposal.

6.2.2.1.19 Motor Oils Refining Process [96]--Motor Oils Refining Company is already using its own technique at plants in McCook, Illinois, and Flint, Michigan. The process involves an undisclosed pretreatment technique to remove low-boiling materials, followed by vacuum distillation of the lube-base cut, and final treatment using clay filtration. The oily clay waste generated is a fairly dry product disposed of at a controlled landfill. The new technology is claimed to yield higher-quality products, to improve process yields, and to eliminate problems with acid-sludge.

6.2.2.1.20 WORLD (Waste Oil Reclamation through Lube Distillation) Process [96]--This process consists of a two-stage thin-film vacuum distillation column followed by conventional clay contacting. The nonrotary design of the key unit differs from that of other thin-film distillation equipment available. In the first stage, used lube oil is stripped to remove water and light hydrocarbons. The dehydrated oil is then fed to the high-vacuum second stage distillation column. The distillate oil produced is a light neutral lube which is comparable in quality to virgin oil. Residue from the vacuum distillation is asphalt flux which is marketed as an additive for asphalt and roofing tar.

6.2.2.2 Re-Refining Costs--

The cost of re-refining the oil depends on how badly the oil is contaminated. The cost of restoring it with additives depends on how well the spent oil responds to the re-refining treatment. The overall cost depends on collection problems and many other factors, including type and amount of virgin blending stock required for viscosity adjustment due to dilution in use and handling of the used oil before it is received at the re-refinery. Another cost variable is additive addition required to meet quality specifications.

The costs for the various re-refining processes are summarized in Table 62 [28]. Costs for the acid/clay process are about 3¢ to 5¢/gallon of lube product higher than those for the other re-refining processes.

The distillation/hydrotreating alternative has the advantage of producing no waste products, but the process has not yet been demonstrated on a commercial scale.

The economics presented here are for comparison only. An assumption inherent in the economic comparison of the lube producing processes is that product quality is the same for each process. Insufficient data are available to properly examine the validity of this assumption.

Alternative techniques of waste oil disposal, such as uncontrolled combustion, road oiling, and dust control, may return anywhere from 1¢ to 12¢ per gallon more to the waste oil collector than the 2¢ to 7¢ per gallon of raw oil paid to a re-refiner. For example, a collector may take a dust control contract for 10¢ to 15¢ per gallon, laying down the oil directly from his collection truck.

The re-refiner has a very difficult time competing with such uses for waste lubricating oils on a pure price basis, particularly in times of fuel oil shortage. However, both resource and environmental conservation should be important considerations when contemplating alternative methods for waste oil disposal.

#### 6.2.2.3 Wastes Produced in Re-refining--

6.2.2.3.1 Waste Characterization--Re-refining generates three waste streams - sludge, spent clay, and process water. Table 63 gives re-refining process water analysis from five re-refineries in the United States [125]. The re-refineries sampled and their processes are as shown below:

Re-refiner number	Process type
1	Solvent treatment/distillation
2	Acid/clay
3	Acid/clay
4	Distillation/clay
5	Distillation/clay

[125] Booz, Allen and Hamilton, Inc. Preliminary analytical data. Bartlesville Energy Technology Center; U.S. Department of Energy; 1980 March.

TABLE 62. SUMMARY OF WASTE OIL PROCESSES [28]

Process	Primary product	Primary wastes and byproducts	Grass roots economy 5 million gallons/year		Comments
			Investment	Operating cost <sup>a</sup>	
Acid/clay	Lube blending stock	Acid sludge, spent clay	\$1,153,000	21.9¢/gallon lube	Widely used in U.S.
Extraction/acid/clay (IFP process)	Lube blending stock	Acid sludge, spent clay; high ash fuel byproduct	\$1,363,000	18.4¢/gallon lube	One operating plant in Italy.
Distillation/clay (caustic treatment)	Lube blending stock	Spent clay; high ash fuel byproduct	\$1,173,000	17.3¢/gallon lube	At least two plants in U.S.
Distillation/H <sub>2</sub> treating (KTI process)	Lube blending stock	High ash fuel byproduct	\$1,342,000	19.0¢/gallon lube	Under development.
Distillation	Fuel oil (diesel fraction could possibly be recovered)	High ash fuel byproduct	\$ 930,000	14.6¢/gallon fuel oil	Can make high quality fuel but economics questionable.
Controlled combustion	Steam	Ash concentrate	\$ 492,000	80¢/1,000 lb steam	Speculative—fine particle recovery difficult.

<sup>a</sup>Includes 3¢/gallon feed cost and 10%/year depreciation, but excludes return on investment.

TABLE 63. RE-REFINING PROCESS WATER ANALYSES [125]

Refiner No

	1	2	3	4	5		
On Site Tests	Dehyd. 911-039	Combined 911-290	Dehyd. 912-120	Finishing 912-121	Dehyd. 911-148	Finishing 911-145	Combined 912-127
Temperature °C	22.8	15.0	6.5	24.5	31.0	34.5	
pH	2.3	9.8	1.6	4.4	9.6	3.1	3.0
Dissolved Oxygen, mg/L	7.0	1.7	2.6	3.4	3.6	2.2	8.6
Sulfite, mg/L (As SO <sub>3</sub> )	3	62	11400	3943	10	21	200
Oxidation Reduction Potential mv @ °C	+300/22.8	-325/15.0	+183/6.5	-160/24.0	+50/31	-120/34.0	0/27.5
Lab Tests							
Total Nitrogen, mg/L (As N)	220	33	155	19	780	46	74
Ammonia Nitrogen (NH <sub>3</sub> ), mg/L	223	61	163	18	820	68	37
Nitrate (As N), mg/L	33	<1	<1	<1	<1	<1	<1
Nitrite (As N), mg/L	0.09	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01
Cyanide, mg/L	4.6	<1	<1	<1	<1	<1	<1
Phenols, mg/L	0.24	0.15	0.10	0.20	0.85	0.05	0.05
Total Sulfur (As S), mg/L	1890	540	6460	1971	89	58	180
Sulfate (As SO <sub>4</sub> ), mg/L	370	775	2880	230	110	30	67
Sulfide (As S), mg/L	1440	98	44	138	23	21	<1
Organic Chloride, mg/L	<1	3	8	5	10	2	3
Inorganic Chloride, mg/L	14	3	4	8	<1	12	<1
Trivalent Phosphates, mg/L	<0.1	6.0	4.4	0.3	25	8.8	1.8
Grease, mg/L	2.0	0.18	0.18	0.15	0.40	0.08	0.87
Chemical Oxygen Demand, mg/L	7610	2870	28800	3780	46800	1370	1255
Biological Oxygen Demand, mg/L	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
Total Organic Carbon, mg/L	26000	7900	22000	3200	48890	5450	622
Carbonate-Bicarbonate, mg/L	<1	<1	<1	<1	5	<1	<1
Total Acidity/Alkalinity, mg/L	+3000	-5520	+39250	+175	-2397	+925	+175
Total Suspended Solids	8	46	10	10	17	8	1
Total Dissolved Solids	2200	1980	663	751	186	351	83
Total Hardness (As CaCO <sub>3</sub> ), mg/L	59	140	309	282	17	95	157
Metals, Mg/L							
Nickel	2.4	3.6	17.8	1.0	<0.1	<0.1	<0.1
Copper	4.0	<0.02	22.0	1.0	<0.02	<0.02	<0.02
Chromium	0.77	<0.04	8.8	<0.04	<0.04	<0.04	<0.04
Iron	16.6	18.8	157	110	<0.02	41	1.4
Silver	0.14	0.12	1.3	<0.03	<0.03	<0.03	3.6
Cadmium	<0.05	0.62	1.1	<0.05	<0.05	<0.05	<0.03
Calcium	2.0	16.8	0.21	7.0	5.5	6.9	<0.05
Magnesium	0.50	10.0	0.98	10.0	0.11	0.51	43
Zinc	13.5	0.72	5.5	2.3	2.9	<0.005	10.5
Sodium	1.3	75	1.0	104	18.4	5.5	32
Potassium	<0.2	20.1	<0.2	22.0	3.1	1.0	0.75
Manganese	0.36	<0.02	28	0.80	<0.02	0.55	<0.02
Lead	49	1.4	40	0.70	1.4	<0.1	0.1
Tin	<0.5	23	14.3	2.0	3.6	<0.3	4.4
Aluminum	0.6	5.3	2.1	5.9	<0.3	<0.3	0.90
Barium	2	<1	<1	1.0	<1	<1	2
Silicon	4.0	31	52	40	6.0	4.5	2.5
Vanadium	<0.2	<0.2	1.0	<0.2	<0.2	<0.2	<0.2
Arsenic	0.09	0.09	0.68	0.10	0.05	0.35	0.12
Boron	2.3	37.5	54.0	0.50	14.8	8.1	1.9
Mercury	0.009	0.029	0.028	0.015	0.020	0.005	<0.001
Selenium	0.06	0.28	0.06	0.03	0.10	0.58	0.09

TABLE 63 (continued)

Gas Chromatographic/Mass Spectrometer Results  
(Priority Pollutants)  
All values in micrograms/liter except as noted

	Dehyd. 911-039	Combined 911-290	Dehyd. 912-120	Finishing 912-121	Dehyd. 211-148	Finishing 911-145	Combined 912-127
1,2 Dichlorobenzene		60			160		
1,4 Dichlorobenzene				250			13
Hexachlorocyclopentadiene			25				
Nitrobenzene			1100				
Bis(2 Chloroethoxy)Methane			1800				
Isophorone					250	640	
Naphthalene		180		700	470		180
2-Chloronaphthalene	8.8	120					
Fluorene	7.2						
Diethyl Phthalate	7.8		8.5	29		7.2	45
N-Nitrosodiphenylamine	64			270		22	
Anthracene					31		
Di-n-Butyl Phthalate	18	30			14		15
Bis(2 Ethylhexyl)Phthalate		7.6		280	4.7		
Di-n-Octyl Phthalate						1.0	
2 Chlorophenol	38	2200		160	140	60	24
2 Nitrophenol					390		32
Phenol	6000	46000	88000	15000	48000	18000	5100
2,4 Dimethylphenol	2100	800				3300	2600
2,4 Dichlorophenol		130					12
p-Chloro-m-Cresol			1600	170			39
Pentachlorophenol		15					
4-Nitrophenol		98			550	110	87
Methylene Chloride	4.1	68	62	38	52	2.5	110
Trichlorofluoromethane					2.5		47
1,1 Dichloroethane			7.8	24			820
1,2-t-Dichloroethylene							18
Chloroform	11	12		2	100	3.9	18
1,2 Dichloroethane	80			280	290		
1,1,1 Trichloroethane	250	42	980	1800	1900	35	580
Trichloroethylene		23		100	2600	44	910
1,1,2 Trichloroethane			1000	250	180		
Benzene	550	38	24	150	880	290	300
Tetrachloroethylene	18	3.3	700	590	1300	14	160
Toluene	840	120	2500	530	5800	640	630
Chlorobenzene		7.9			500	22	4
Ethylbenzene			530	560	400	90	130
Acrylonitrile	15					28	2.1
Alpha-BHC	<10	<10	<10	<10	<10	<10	<10
Beta-BHC	<10	<10	<10	<10	<10	<10	<10
Gamma-BHC	<10	<10	<10	<10	<10	<10	<10
Delta-BHC	<10	<10	<10	<10	<10	<10	<10
Heptachlor	<10	<10	<10	<10	<10	<10	<10
Aldrin	<10	<10	<10	<10	<10	<10	<10
Heptachlor Epoxide	<10	<10	<10	<10	<10	<10	<10
Chlordane	<10	<10	<10	<10	<10	<10	<10
B-Endosulfan	<10	<10	<10	<10	<10	<10	<10
Dieldrin	<10	<10	<10	<10	<10	<10	<10
4,4'-DDE	<10	<10	<10	<10	<10	<10	<10
Endrin	<10	<10	<10	<10	<10	<10	<10

TABLE 63 (continued)

	<u>#1</u>	<u>#2</u>	<u>#3</u>		<u>#4</u>		<u>#5</u>
	Dehyd. 911-039	Combined 911-290	Dehyd. 912-120	Finishing 912-121	Dehyd. 911-148	Finishing 911-145	Combined 912-127
4,4'-DDD	<10	<10	<10	<10	<10	<10	<10
Alpha-Endosulfan	<10	<10	<10	<10	<10	<10	<10
4,4'-DDT	<10	<10	<10	<10	<10	<10	<10
Endosulfan Sulfate	<10	<10	<10	<10	<10	<10	<10
Endrin Aldehyde	<10	<10	<10	<10	<10	<10	<10
PCB-1242	<10	<10	<10	<10	<10	<10	<10
PCB-1254	<10	<10	<10	<10	<10	<10	<10
PCB-1221	<10	<10	<10	<10	<10	<10	<10
PCB-1232	<10	<10	<10	<10	<10	<10	<10
PCB-1248	<10	<10	<10	<10	<10	<10	<10
PCB-1260	<10	<10	<10	<10	<10	<10	<10
PCB-1016	<10	<10	<10	<10	<10	<10	<10
C1-C8 HC ppm/vol.	4500	4700	6000	1500	6300	6800	3000
Surfactants, mg/L	0.39	0.04	3.6	0.03	1.9	0.31	0.84



This table shows that the process wastewaters contain high concentrations of phenols and other water-soluble compounds. Table 64 shows analytical data on four acid sludges from different sources [126,127]. Variances indicate the difference in additives used in each type of oil. Table 65 shows analytical data on one re-refining caustic/silicate sludge. Table 66 shows analytical data on re-refining process hydrocarbon/sludge/clay from five re-refineries as defined in Table 63. The high metals content, such as aluminum, magnesium, iron, and sodium, among others, reflects high concentrations of these elements in naturally occurring clay. The lead content includes that usually found in the sludge and the clay from processes using pretreatment.

It should be noticed that the analytical data reported here are mostly for lubricating oils and crankcase oils. No data pertaining specifically to metalworking oils were found.

6.2.2.3.2 Ultimate Disposal of Wastes--Re-refining sludges, clays, and untreated wastewaters, particularly that produced by steam stripping during distillation, are considered to be potentially hazardous wastes due to the acid, metals, and hydrocarbon constituents contained in the wastes.

Acid sludge and spent clay can be disposed of by secure landfill. The cost of sludge disposal is at present only a minor contribution to the total cost of re-refining. About 0.1 gallon of sludge is produced per gallon of re-refined oil. Most re-refiners pay less than 0.5¢ per gallon of finished product for sludge disposal. Clay disposal costs are much lower, less than 0.25¢ per gallon of product on the average. Generally, re-refiners depend on local refuse companies for removal of acid sludge and spent clay. In some areas of the country Class I dumps are available for sludge disposal. In other areas, local ordinances prohibiting the disposal of untreated hazardous wastes may force some re-refiners out of business. Acid sludge can be neutralized, but at greatly increased cost. One re-refiner quoted a cost of about 3.5 cents per gallon of product for treatment with calcium carbonate [127].

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[126] Swain, J. W. Assessment of industrial hazardous waste management - petroleum re-refining industry. Washington, DC; U.S. Environmental Protection Agency; 1977 June. 162 p. PB 272 267.

[127] Cukor, P. M.; Keaton, M. J.; and Wilcox, G. A technical and economic study of waste oil recovery. Part III: economic, technical, and institutional barriers to waste oil recovery. Washington, DC; U.S. Environmental Protection Agency; 1973 October. 136 p. EPA-530/SW-90C3. PB 237 620.

TABLE 64. ACID SLUDGE ANALYSES COMPOSITE [126,127]

	Diesel	Stock	Stock	Lubricating oil
Acid, %	47.5	40.8	NA	
Ash sulfate, %	4.45	17.26	NA	
Sulfur, %	14.9	14.1	NA	
Sulfur calculated from percent acid assuming $H_2SO_4$ , %	15.5	13.3	NA	
<u>Elemental analysis, ppm</u>				
Cu	40	40	190	
Al	40	140	560	13
Fe	500	1,100	2,200	796
Si	800	1,400	NA	
Pb	1,000	20,000	10,000	1,491
Ag	14	0	0.8	
Zn	200	2,100	2,100	1,128
Ba	400	1,300	740	PA
Cr	190	50	28	
Ca	12,600	6,400	NA	3,898
Na	200	4,000	NA	9,257
P	1,000	4,300	1,700	1,500
B	40	50	18	NA
Ni	10	30	8	
Sn	35	30	NA	
Hg	70	1,000	NA	1,162
Cd	9	NA	NA	
Mo	18	NA	NA	
Mn	63	NA	NA	
As	45	NA	NA	
Be	0.1	NA	NA	
Co	0.8	NA	NA	
Sr	2.7	NA	NA	
V	18	NA	NA	

TABLE 65. ANALYSIS OF REREFINING CAUSTIC/SILICATE SLUDGE [126]

Element	ppm
Fe	350
Pb	27,500
Cu	48
Cr	18
Al	24
Ni	1
Ag	1
Sn	70
Si	6,250
B	10
Na	1,000
P	1,100
Zn	1,500
Ca	1,000
Be	3,000
S	0.14%

TABLE 66. RE-REFINING PROCESS HYDROCARBON/  
SLUDGE/CLAY ANALYSES [125]

	(1653) Dehyd Light Ends 911-038	(1661) Solvent Sludge 911-301	(1674) Distillation Btms 911-240	(1675) Distillation LN 2 Trap Liquid 911-241
API Gravity @ 60 °F	34.0		18.4	34.1
Specific Gravity @ 60 °F	0.8550		0.9440	0.8545
Viscosity @ 100 cst	2.51		2750	1.62
Viscosity @ 210 cs:	1.13		87.4	N.A.
Viscosity, Index			93	
Acid Base No., mgKOH/gm	0.96	8.74	10.98	25.46
Saponification Number, mgKOH/gm	9.65		36.93	90.95
Pentane Insol., Wt. %	0.122	16.43	0.393	0.093
Benzene Insol., Wt. %	0.328	1.94	0.101	0.093
Aniline Point, °F	133.2		144.0	
Carbon, Wt. %	84.14	70.11	82.04	83.35
Hydrogen, Wt. %	15.00	10.93	12.58	11.27
Nitrogen, Wt. %	0.070	2.69	0.127	0.299
Oxygen, Wt. %	0.10	0.41	0.81	4.72
Sulfur, Wt. %	0.136	0.881	0.850	1.27
Hydrogen Sulfide, ppm wt.	<1		<1	10.2
Mercaptan Sulfur, ppm wt.	<1		226	318
Total Chloride, Wt. %	0.287	1.82	0.123	1.11
Organic Chloride, Wt. %	0.260		0.080	1.11
Total Hydrocarbons, Vol. %				
Water, Wt. %	0.24		<0.05	4.80
Con Carbon, Wt. %	0.242		5.56	0.800
Ash, Wt. %	0.023	19.15	3.14	0.132
Flash Point, (PMCC) °F	+80		+330	<-20
Color, ASTM	3.5			5.5
Copper Strip Corrosion	2C		1A	4C
Pour Point, °F	-45		+30	<-80
Heating Value, BTU/lb.(gross)	19091	14492	18362	12496
Paraffins, L.V. %	34.79			
Naphthenes, L.V. %	25.45			
Aromatics, L.V. %	32.06			
Olefins, L.V. %	7.70			
Non Volatile Residue, Wt. %		91.43		
Distillation: IBP/10	160/289			50/150
(GC) 30/50	375/455			160/215
(ASTM 2887) 70/90	640/721			230/241
FBP	825			465
Metals, ppm wt.				
Aluminum	<1	155	33	7
Barium	<1	243	25	<1
Nickel	6	32	15	<1
Copper	1	70	36	4
Chromium	<1	62	7	1
Iron	11	703	117	57
Silver	<1	2	<1	<1
Cadmium	2	18	20	5
Zinc	1	120	126	50
Magnesium	5	163	535	<1
Calcium	11	828	1715	<1
Sodium	51	202	98	4

TABLE 66 (continued)

	(1653) Dehyd Light Ends 911-038	(1661) Solvent Sludge 911-301	(1674) Distillation Bums 911-240	(1675) Distillation LN 2 Trap Liquid 911-241
Metals, ppm wt.				
Potassium	2	195	12	1
Manganese	5	233	106	1
Lead	3	87600	1090	1
Tin	<1	176	25	<1
Silicon	<1	<1	<1	<1
Vanadium	<1	<1	4	<1
Arsenic	1.0	2.1	0.01	<0.01
Selenium	2.1	2.1	<0.01	0.9
Mercury	<0.01	0.10	<0.01	0.06
Boron	11	2.5	<0.01	62
Phosphorus	211	148	3708	273
Benzene, Wt. %	0.06			<0.02
Total Polychlorinated Biphenyls, ppm wt. (As Arochlor 1242)	<1			N.A.
Polynuclear Aromatic, Wt. % (Max)				
Acenaphthene	0.13			<0.10
Fluoranthene	<0.02			<0.10
Naphthalene	0.19			<0.10
Benzo (a) Anthracene	0.02			<0.10
Benzo (a) Pyrene	<0.02			<0.10
34 Benzo fluoranthene	<0.02			<0.10
Benzo (k) Fluoranthene	<0.02			<0.10
Chrysene	<0.02			<0.10
Acenaphthylene	0.08			<0.10
Anthracene	0.03			<0.10
Benzo (ghi) Perylene	<0.02			<0.10
Fluorene	0.26			<0.10
Phenanthrene	0.15			<0.10
Dibenzo (ah) Anthracene	<0.02			<0.10
Indeno (123cd) Pyrene	<0.02			<0.10
Pyrene	0.04			<0.10
Pesticides, ppm wt.				
Aldrin	<10			<10
Dieldrin	<10			<10
Chlorodane	<10			<10
44'-DUT	<10			<10
44'-DOE	<10			<10
44'-DDD	<10			<10
Endrin	<10			<10
Heptachlor	<10			<10
Heptachlor Epoxide	<10			<10
Alpha-BHC	<10			<10
Beta-BHC	<10			<10
Gamma-BHC	<10			<10
Delta-BHC	<10			<10

TABLE 66 (continued)

	Dehyd Light Ends 911-291	Finishing Light Ends 911-295	Spent Clay 911-299	Acid Sludge 911-298
API Gravity @ 60 °F	36.4	35.3		
Specific Gravity @ 60 °F	0.8428	0.8438		
Viscosity @ 100 cst	4.11	4.61		
Viscosity @ 210 cst	1.49	1.60		
Viscosity, Index				
Acid Base No., mg KOH/gm	0.26	0.45	3.90	140
Saponification Number, mg KOH/gm	4.83	5.41		
Pentane Insol., Wt. %	0.017	0.067	68.01	60.83
Benzene Insol., Wt. %	0.010	0.003	77.39	11.63
Aniline Point, °F	180.3	192.3		
Carbon, Wt. %	83.57	82.36	22.68	83.04
Hydrogen, Wt. %	14.58	14.31	3.56	13.83
Nitrogen, Wt. %	0.017	0.016	0.029	0.190
Oxygen, Wt. %	0.12	0.18		
Sulfur, Wt. %	0.259	0.248	0.131	5.23
Hydrogen Sulfide, ppm wt.	<1	<1		
Mercaptan Sulfur, ppm wt.	181	283		
Total Chloride, Wt. %	0.205	0.200	0.264	0.107
Organic Chloride, Wt. %	0.200	0.180	0.004	
Total Hydrocarbons, Vol. %				
Water, Wt. %	1.10	2.60		
Con Carbon, Wt. %	0.058	0.208		
Ash, Wt. %	0.150	0.088	87.69	4.29
Flash Point, (PMCC) °F	+56	+52		
Color, ASTM	+8	+8		
Copper Strip Corrosion	1B	1A		
Pour Point, °F	-10	0		
Heating Value, BTU/lb. (gross)	19330	19008	3807	11228
Paraffins, L.V. %	41.30	37.86		
Naphthenes, L.V. %	37.15	35.80		
Aromatics, L.V. %	15.45	15.04		
Olefins, L.V. %	6.10	11.30		
Non Volatile Residue, Wt. %			99.74	81.29
Distillation: IBP/10	135/320	125/306		
(GC)	30/50	430/600		
(ASTM 2887)	70/90	715/824		
FBP	920	985		
Metals, ppm wt.				
Aluminum	<1	<1	14400	71
Barium	<1	<1	124	467
Nickel	1	3	42	4
Copper	<1	3	15	20
Chromium	<1	<1	10	<1
Iron	4	14	942	16
Silver	<1	<1	4	2
Cadmium	<1	<1	11	7
Zinc	2	3	76	45
Magnesium	<1	3	1838	18
Calcium	5	9	516	23
Sodium	38	77	1898	12

TABLE 66 (continued)

	Dehyd Light Ends 911-291	Finishing Light Ends 911-295	Spent Clay 911-299	Acid Sludge 911-298
Metals, ppm wt.				
Potassium	3	2	2048	5
Manganese	<1	<1	35	<1
Lead	3	4	<1	9960
Tin	<1	<1	<1	<1
Silicon	<1	<1	11	2
Vanadium	<1	<1	12	<1
Arsenic	<0.01	<0.01	24	4.7
Selenium	<0.01	<0.01	<0.01	<0.01
Mercury	<0.01	<0.01	0.02	0.06
Boron	2	6	113	63
Phosphorus	45	73	189	1668
Benzene, Wt. %	0.05	0.04		
Total Polychlorinated Biphenyls, ppm wt. (As Arochlor 1242)	1.7	1.7		
Polynuclear Aromatic, Wt. % (Max)				
Acenaphthene	0.11	0.09		
Fluoranthene	0.05	0.06		
Naphthalene	0.11	0.09		
Benzo (a) Anthracene	0.04	0.06		
Benzo (a) Pyrene	<0.02	0.06		
34 Benzo(a)fluoranthene	0.07	0.06		
Benzo (k) Fluoranthene	0.07	<0.02		
Chrysene	0.07	0.09		
Acenaphthylene	0.07	0.13		
Anthracene	0.05	0.11		
Benzo (ghi) Perylene	<0.02	<0.02		
Fluorene	0.09	0.09		
Phenanthrene	0.05	0.09		
Dibenzo (ehl) Anthracene	<0.02	<0.02		
Indeno (123cd) Pyrene	<0.02	<0.02		
Pyrene	0.04	0.02		
Pesticides, ppm wt.				
Aldrin	<10	<10		
Dieldrin	<10	<10		
Chlorodane	<10	<10		
44'-DDT	<10	<10		
44'-DDE	<10	<10		
44'-DDD	<10	<10		
Endrin	<10	<10		
Heptachlor	<10	<10		
Heptachlor Epoxide	<10	<10		
Alpha-BHC	<10	<10		
Beta-BHC	<10	<10		
Gamma-BHC	<10	<10		
Delta-BHC	<10	<10		

TABLE 66 (continued)

	Dehyd Light Ends <u>912-122</u>	Finishing Light Ends <u>912-123</u>	Spent Clay <u>912-124</u>	Acid Sludge <u>912-125</u>
API Gravity @ 60 °F	38.4	35.4		
Specific Gravity @ 60 °F	0.8323	0.8478		
Viscosity @ 100 cst	0.74	1.69		
Viscosity @ 210 cst	N.A.	0.81		
Viscosity, Index				
Acid Base No., mg KOH/gm	1.96	0.25	5.89	282
Saponification Number, mg KOH/gm	4.75	26.06		
Pentane Insol., Wt. %	0.003	0.026	33.15	60.12
Benzene Insol., Wt. %	0.004	0.017	37.61	40.61
Aniline Point, °F	102.7	133.3		
Carbon, Wt. %	72.17	80.37	59.93	41.93
Hydrogen, Wt. %	13.01	14.41	9.82	6.99
Nitrogen, Wt. %	0.029	0.011	0.032	0.142
Oxygen, Wt. %	0.35	0.10		39.56
Sulfur, Wt. %	0.156	0.130	0.199	3.52
Hydrogen Sulfide, ppm wt.	42	<1		
Mercaptan Sulfur, ppm wt.	80	1.2		
Total Chloride, Wt. %	13.67	4.93	0.105	0.209
Organic Chloride, Wt. %	10.60	0.25	0.060	
Total Hydrocarbons, Vol. %				
Water, Wt. %	0.05	0.05		
Con Carbon, Wt. %	0.159	0.007		
Asb, Wt. %	0.56	0.002	44.32	8.64
Flash Point, (PMCC) °F	<-20	+78		
Color, ASTM	L2	L3		
Copper Strip Corrosion	3B	2C		
Pour Point, °F	<-80	<-80		
Heating Value, BTU/lb. (gross)	17228	18454	11230	9275
Paraffins, L.V. %	51.54	42.89		
Naphthenes, L.V. %	30.84	34.97		
Aromatics, L.V. %	17.62	14.54		
Olefins, L.V. %	<0.10	7.60		
Non Volatile Residue, Wt. %			89.03	58.97
Distillation: IBP/10	55/185	161/297		
(GC) 30/50	270/314	346/415		
(ASTM 2887) 70/90	345/385	535/636		
FEF	498	865		
Metals, ppm wt.				
Aluminum	3	2	12200	1349
Barium	<1	<1	<1	544
Nickel	2	<1	25	23
Copper	<1	<1	18	170
Chromium	<1	<1	18	14
Iron	8	19	467	381
Silver	<1	<1	1	2
Cadmium	<1	<1	12	8
Zinc	3	<1	68	64
Magnesium	<1	<1	891	1320
Calcium	?	3	30	1149
Sodium	3	11	273	41

TABLE 66 (continued)

	Dehyd Light Ends <u>912-122</u>	Finishing Light Ends <u>912-123</u>	Spent, Clay <u>912-124</u>	Acid Sludge <u>912-125</u>
Metals, ppm wt.				
Potassium	1	<1	1822	4
Manganese	<1	<1	88	62
Lead	1	<1	<1	2265
Tin	<1	<1	<1	<1
Silicon	<1	<1	17	8
Vanadium	<1	<1	35	4
Arsenic	13	<0.01	3	0.07
Selenium	<0.01	<0.01	<0.01	0.02
Mercury	0.12	0.14	0.04	0.10
Boron	2	69	26	<1
Phosphorus	2	18	173	42
Benzene, Wt. %	0.29	0.02		
Total Polychlorinated Biphenyls, ppm wt. (As Arochlor 1242)	N.A.	<1		
Polynuclear Aromatic, Wt. % (Max)				
Acenaphthene	0.12	0.12		
Fluoranthene	<0.03	<0.02		
Naphthalene	0.21	1.17		
Benzo (a) Anthracene	<0.03	<0.02		
Benzo (a) Pyrene	<0.03	<0.02		
34 Benzofluoranthene	<0.03	<0.02		
Benzo (k) Fluoranthene	<0.03	<0.02		
Chrysene	<0.03	<0.02		
Acenaphthylene	0.20	0.11		
Anthracene	<0.03	0.03		
Benzo (ghi) Perylene	<0.03	<0.02		
Fluorene	0.09	0.02		
Phenanthrene	0.04	<0.02		
Dibenzo (ah) Anthracene	<0.03	<0.02		
Indeno (123cd) Pyrene	<0.03	<0.02		
Pyrene	<0.03	<0.02		
Pesticides, ppm wt.				
Aldrin	<10	<10		
Dieldrin	<10	<10		
Chlorodane	<10	<10		
44'-DDT	<10	<10		
44'-DDE	<10	<10		
44'-DDD	<10	<10		
Endrin	<10	<10		
Heptachlor	<10	<10		
Heptachlor Epoxide	<10	<10		
Alpha-BHC	<10	<10		
Beta-BHC	<10	<10		
Gamma-BHC	<10	<10		
Delta-BHC	<10	<10		



TABLE 66 (continued)

	Dehyd Light Ends 911-149	Finishing Light Ends 911-146	Spent Clay 911-147	Distillation Bums 911-150
API Gravity @ 60 °F	42.4	35.6		20.7
Specific Gravity @ 60 °F	0.8137	0.8463		0.9297
Viscosity @ 100 cst	1.05	2.18		626
Viscosity @ 210 cst	0.58	0.96		42.3
Viscosity, Index				110
Acid Base No., mgKOH/gm	0.09	1.42	6.31	2.72
Saponification Number, mgKOH/gm	12.54	16.58		40.87
Pentane Insol., Wt. %	0.039	0.001	46.40	1.52
Benzene Insol., Wt. %	0.003	0.009	59.28	1.35
Aniline Point, °F	127.6	153.1		212.0
Carbon, Wt. %	82.66	83.80	64.49	82.84
Hydrogen, Wt. %	15.06	14.90	10.50	12.89
Nitrogen, Wt. %	0.018	0.022	0.039	0.146
Oxygen, Wt. %	0.10	0.14	N.A.	0.49
Sulfur, Wt. %	0.107	0.789	0.178	0.668
Hydrogen Sulfide, ppm wt.	<1	596		<1
Mercaptan Sulfur, ppm wt.	<1	1390		95
Total Chloride, Wt. %	1.97	0.279	0.009	0.226
Organic Chloride, Wt. %	1.85	0.160	0.001	0.100
Total Hydrocarbons, Vol. %				
Water, Wt. %	0.05	0.05		0.05
Con Carbon, Wt. %	0.045	0.006		5.98
Ash, Wt. %	0.035	0.022	52.47	3.90
Flash Point, (PMOC) °F	+54	+62		+270
Color, ASTM	L2	L2		
Copper Strip Corrosion	1A	2C		1A
Pour Point, °F	<-80	-60		0
Heating Value, BTU/lb. (gross)	19039	19120	10478	18488
Paraffins, L.V. %	37.94	36.02		
Naphthenes, L.V. %	35.20	33.99		
Aromatics, L.V. %	19.96	21.39		
Olefins, L.V. %	6.90	8.60		
Non Volatile Residue, Wt. %			96.79	
Distillation: IEP/10	131/250	146/325		
(GC) 30/50	321/357	374/446		
(ASTM 2887) 70/90	383/460	537/675		
FEP	639	830		
Metals, ppm wt.				
Aluminum	<1	12	20400	75
Barium	<1	<1	<1	6
Nickel	5	5	19	6
Copper	<1	2	6	87
Chromium	<1	<1	5	11
Iron	2	6	360	283
Silver	<1	<1	1	1
Cadmium	<1	<1	7	9
Zinc	2	<1	52	85
Magnesium	2	1	380	365
Calcium	4	<1	9	1306
Sodium	12	1	195	4763

TABLE 66 (continued)

	Dehyd Light Ends 911-149	Finishing Light Ends 911-146	Spent Clay 911-147	Distillation Bums 911-150
Metals, ppm wt.				
Potassium	3	<1	671	113
Manganese	<1	<1	14	11
Lead	107	2	<1	4235
Tin	<1	<1	<1	<1
Silicon	<1	<1	14	1
Vanadium	<1	<1	7	6
Arsenic	<0.01	<0.01	3.7	1.0
Selenium	0.90	1.0	<0.01	0.90
Mercury	0.04	0.04	0.06	<0.01
Boron	39	8	16	38
Phosphorus	16	149	67	1346
Benzene, Wt.%	0.20	<0.02		
Total Polychlorinated Biphenyls, ppm wt. (As Arochlor 1242)	<1	1.8		
Polynuclear Aromatic, Wt.% (Max)				
Acenaphthene	0.01	0.21		
Fluoranthene	<0.01	<0.02		
Naphthalene	0.16	0.05		
Benzo (a) Anthracene	<0.01	<0.02		
Benzo (a) Pyrene	<0.01	<0.02		
34 Benzo(a)fluoranthene	<0.01	<0.02		
Benzo (k) Fluoranthene	<0.01	<0.02		
Chrysene	<0.01	<0.02		
Acenaphthylene	<0.01	0.13		
Anthracene	<0.01	0.06		
Benzo (ghi) Perylene	<0.01	<0.02		
Fluorene	0.03	0.24		
Phenanthrene	<0.01	0.09		
Dibenzo (ah) Anthracene	<0.01	<0.02		
Indeno (123cd) Pyrene	<0.01	<0.02		
Pyrene	<0.01	0.03		
Pesticides, ppm wt.				
Aldrin	<10	<10		
Dieldrin	<10	<10		
Chlorocane	<10	<10		
44'-DDT	<10	<10		
44'-DDE	<10	<10		
44'-DDD	<10	<10		
Endrin	<10	<10		
Heptachlor	<10	<10		
Heptachlor Epoxide	<10	<10		
Alpha-BHC	<10	<10		
Beta-BHC	<10	<10		
Gamma-BHC	<10	<10		
Delta-BHC	<10	<10		

TABLE 66 (continued)

	Combined Light Ends 912-126	Spent Clay 912-128	Distillation Btms 912-129
API Gravity @ 60 °F	30.9		9.1
Specific Gravity @ 60 °F	0.8713		1.0064
Viscosity @ 100 cst	9.26		11768
Viscosity @ 210 cst	2.38		1099
Viscosity, Index			123
Acid Base No.,mgKOH/gm	2.38	11.95	8.17
Saponification Number,mgKOH/gm	10.48		69.22
Pentane Insol., Wt.%	0.014	69.87	6.92
Benzene Insol., Wt.%	0.136	65.43	1.86
Aniline Point, °F	183.0		227.7
Carbon, Wt.%	82.68	35.78	77.17
Hydrogen, Wt.%	14.20	5.44	11.26
Nitrogen, Wt.%	0.035	0.032	0.348
Oxygen, Wt.%	0.24		
Sulfur, Wt. %	0.295	0.266	1.17
Hydrogen Sulfide, ppm wt.	15		<1
Mercaptan Sulfur, ppx wt.	30		105
Total Chloride, Wt.%	0.413	0.222	0.304
Organic Chloride, Wt.%	0.180	0.005	0.18
Total Hydrocarbons, Vol.%			
Water, Wt.%	2.10		0.05
Con Carbon, Wt.%	0.015		6.91
Ash, Wt.%	0.034	59.41	8.19
Flash Point, (PMCC) °F	+78		+310
Color, ASTM	+8		
Copper Strip Corrosion	1A		4B
Pour Point, °F	0		+75
Heating Value, BTU/lb.(gross)	18851	8357	17050
Paraffins, L.V.%	34.20		
Naphthenes, L.V. %	35.52		
Aromatics, L.V. %	19.78		
Olefins, L.V. %	10.50		
Non Volatile Residue, Wt.%		95.95	
Distillation: IEP/10	178/325		
(GC) 30/50	573/680		
(ASTM 2887) 70/90	762/855		
FEP	1012		
Metals, ppm wt.			
Aluminum	5	27800	378
Barium	<1	<1	940
Nickel	<1	36	45
Copper	1	6	262
Chromium	<1	17	63
Iron	4	750	780
Silver	<1	3	6
Cadmium	<1	13	29
Zinc	4	60	133
Magnesium	15	2698	174
Calcium	28	113	879
Sodium	4	64	432

TABLE 66 (continued)

	Combined Light Ends 912-126	Spent Clay 912-128	Distillation Btms 912-129
Metals, ppm wt.			
Potassium	2	809	439
Manganese	<1	71	169
Lead	<1	<1	10300
Tin	<1	<1	28
Silicon	<1	7	<1
Vanadium	<1	17	6
Arsenic	<0.01	15	15
Selenium	<0.01	<0.01	<0.01
Mercury	0.01	0.02	<0.01
Boron	4	51	109
Phosphorus	373	485	3390
Benzene, Wt. %	<0.02		
Total Polychlorinated Biphenyls, ppm wt. (As Arochlor 1242)	9.7		
Polynuclear Aromatic, Wt. % (Max)			
Acenaphthene	0.10		
Fluoranthene	0.10		
Naphthalene	0.02		
Benzo (a) Anthracene	<0.02		
Benzo (a) Pyrene	<0.02		
3,4 Benzofluoranthene	0.19		
Benzo (k) Fluoranthene	0.14		
Chrysene	<0.02		
Acenaphthylene	0.05		
Anthracene	0.10		
Benzo (ghi) Perylene	0.04		
Fluorene	0.07		
Phenanthrene	0.10		
Dibenzo (ah) Anthracene	0.10		
Indeno (1,2,3cd) Pyrene	<0.02		
Pyrene	0.04		
Pesticides, ppm wt.			
Aldrin	<10		
Dieldrin	<10		
Chlorodane	<10		
4,4'-DDT	<10		
4,4'-DDE	<10		
4,4'-DDD	<10		
Endrin	<10		
Heptachlor	<10		
Heptachlor Epoxide	<10		
Alpha-BHC	<10		
Beta-BHC	<10		
Gamma-BHC	<10		
Delta-BHC	<10		

Acid sludge can be burned by use of equipment and methods, such as incinerators, reverberatory furnaces, fluidized bed furnaces, and pyrolysis. The major problem in burning acid sludge is achieving a homogeneous mixture with a viscosity reducer such as re-refinery-produced distillate. Heater or boiler materials of construction must also be considered because of the potential corrosion and erosion possibilities. Since metallic and chemical impurities remain in the acid sludge, it can also result in the release of toxic air pollutants unless adequate control measures are implemented [126].

Resource recovery of acid sludge is a feasible goal. The processed sludge is used as an asphalt product extender and plasticizer [126]. The Peak Oil Company of Tampa, Florida, in cooperation with the United States Department of Energy, has completed a study for the incorporation of acid sludge derived from the re-refining of used lubricating oil into a useful and salable building material. Both bricks and paving materials have been produced using a formulation developed by Peak [128].

Clay presents a less difficult disposal problem. First, the hazardous constituents are present in greatly reduced quantities. Second, a large part of the hazardous constituents can be removed by washing with solvents and even a water/detergent mixture. A final burning in a kiln to remove occluded materials provides a reclaimed and reusable material [126].

Steam stripping water, after oil (hexane solubles) removal can be treated by well established wastewater treatment methods, such as coagulation, flocculation, air flotation, and filtration. Such water can be reused in boilers or discharged. Minimal treatment of the water from steam stripping allows the water to be reused for cooling if not as boiler feed water [126].

It is not impossible, difficult, or even too expensive to achieve zero discharge with complete recycling. Sludge and solids from adequate water treatment are of small quantity compared to pre-treatment sludge and spent clay.

### 6.3 DISPOSAL AND RECLAMATION OF FATTY OILS

Fatty oils have three major applications in metalworking: (1) as emulsified rolling lubricant, particularly for rolling of thin strips of steels; (2) compounded as straight oils, mixtures of fatty oils, and mineral oils; and (3) as raw materials for the manufacture of fatty additives.

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[128] Suarez, M.; Morris, D.A.; and Morris, R. C. Acid sludge utilization. Bartlesville, OK; U.S. Department of Energy; 1980 September. 31 p. Contract No. DE-AC-19-79BC/0089.

Emulsified rolling oils from the steel industry are usually recovered from the steel mill wastewater treatment plant. A number of types of mineral oils are mixed together with animal and vegetable fats and greases, and these oils accumulate on top of the skimming tanks. These mixed fatty oils and mineral oils have been used as fuels, but future use will be limited by EPA regulation on burning of waste oils. The large percentage of fatty oils used in rolling oils makes more difficult the separation and refining of the petroleum-based oil.

Some fatty oils recovered from wastewater may be purified for use in soapmaking. Recovery requires process steps similar to those discussed in the section on emulsified oils [28]. Since fatty oils are prone to oxidation and rapid deterioration, some fatty oils are not recoverable and must be disposed of.

Effective techniques for recovery or disposal of fatty oils are chemical coagulation, air flotation, and biological treatment [28]. This is demonstrated at Swift and Company's high-volume edible fat and oil refining plant at Bradley, Illinois [129]. The plant uses skimming, chemical treatment, and centrifugal separation to upgrade the quality of the removed fatty materials. A simplified process flow diagram for both the wastewater clarification and the oil recovery systems is shown in Figure 63. An overall economic evaluation indicated the 7,000 pounds of oil recovered (99 percent ether-soluble), valued at 4-1/4 to 4-5/8 cents per pound, would offset 60 percent of the total daily direct operating costs for the waste treatment systems, including the oil reclaiming system.

In compounded oils, the fatty oils act as emulsifying agents in high-moisture environments, incorporating accumulated water into the body of the oil in the form of a water-in-oil emulsion. Recovery of compounded oils necessitates removal of any water emulsified in the oil. Then the same techniques applicable to the mixed fatty and mineral oils separated from plant wastewater are suitable for compounded oils.

The fatty oil additives in metalworking fluids add to the complexity of the problem of re-refining and reuse. The re-refining process may be adversely affected by the additives in the waste oil, or fatty oil. If the additives are successfully separated from the waste oil in the refining process, they present a disposal problem. Instead of recovery of the additives from waste oils, the current practice is reconditioning, that is, addition of a new additive package to bring the refined oil properties up to specifications.

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[129] Seng, C. Recovery of fatty materials from edible oil refinery effluents. U.S. Environmental Protection Agency; 1973 December. 148 p. EPA-600/2-73-015. PB 231 268.

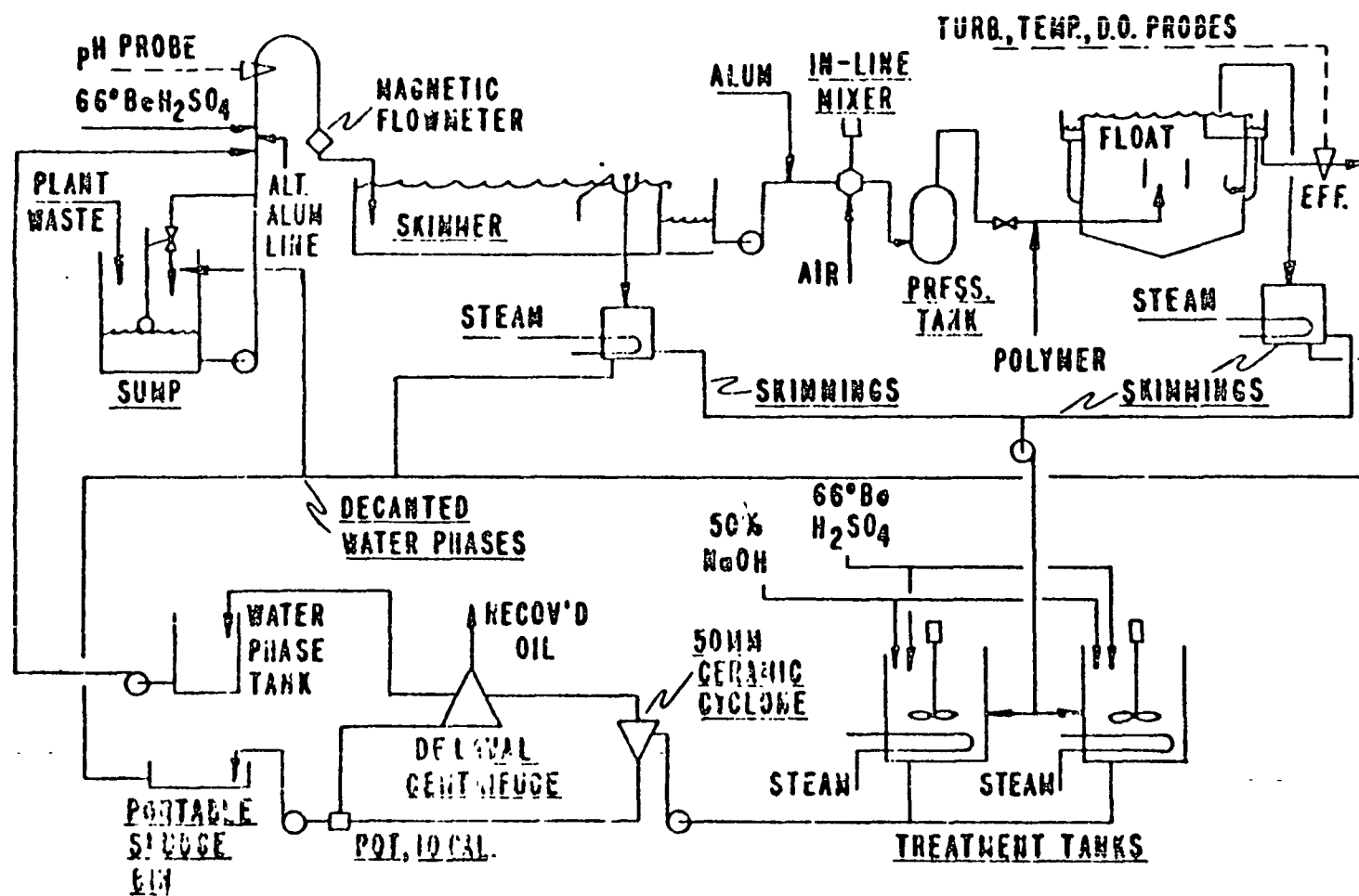


Figure 63. Bradley waste treatment flow diagram [129].

#### 6.4 RECLAMATION, TREATMENT, AND DISPOSAL OF SYNTHETIC FLUIDS

Only limited information is available about treatment and reclamation of waste metalworking synthetic fluids. Some recyclers claim that no feasible technology is currently available for waste synthetic fluid treatment or reclamation. Others say that it is possible but only after extensive work with arm-twisting of the fluid manufacturer. Many large companies currently will not use synthetic fluids if the manufacturer does not offer a method of breakdown and disposal. Some manufacturers do accept waste synthetic oils for reprocessing.

Synthetics will commonly last a year but longevity depends upon how effectively the in-plant recycling system operates. Some elaborate systems can minimize microbial spoilage of fluid and keep the fluids very clean. Those with less elaborate systems are often forced to pour the fluids down the drain if the manufacturer will not be of assistance or if no method really exists for destabilizing waste synthetic fluids.

Also, by setting up a periodic synthetic fluid analysis and biocide treatment schedule, synthetic fluid and metalworking tool life can be extended, and production efficiency greatly improved. The costs and time involved for such a program are more than offset by reduced fluid purchases and tool reworking, with the bonus being greater production efficiency. Not surprisingly, this production bonus can have a tremendous impact on bottom line profits.

Waste synthetic oils should be segregated and recycled where possible, because of their high cost and because they may contaminate otherwise recyclable oils [28]. Good filtration equipment in the in-plant fluid recycling system will greatly extend fluid and metalworking tool life by removing metal fines and chips. This will result in better product, and increase productivity by reducing downturns.

It has been reported that flash distillation and chemical adsorption are the two most common processes used for reclamation of synthetic fluids formulated without polar additives. These processes are described in detail in Section 6.2.1.

Some waste synthetic fluids exhibit susceptibility to biodegradation and can be disposed of by biological treatment [130]. A biodegradable synthetic fluid can undergo destruction by microorganisms. To be biodegradable it must consist of materials which are nontoxic to life and are not considered to be dangerous pollutants. In addition to readily passing through conventional

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[130] Bennett, E. O. The disposal of metal cutting fluids. Lubrication Engineering. 300-307, 1973 July.



disposal systems, a degradable product should produce no persistent intermediate residues, it should have no objectionable effects on the receiving water or its subsequent reuse, it should not taint fish flesh, and it should not produce objectionable growths in the marine environment.

Consideration must always be given to the time required for the process to take place. Many materials are biodegradable if detained long enough in a disposal system. Thus, one biodegradable fluid may require only a few hours while another may require several days. A company purchasing a biodegradable product must consider this factor and must make sure that the product will be degraded in the disposal plant during the normal retention period.

In a study conducted by the University of Houston, eight synthetic fluids were subjected to biodegradation under the most ideal conditions for a period of four weeks. The result of this study is presented in Table 67 [130]. The results show that some fluids exhibit greater susceptibility to biodegradation than others.

TABLE 67. BIODEGRADATION OF SYNTHETIC FLUIDS [130]

Synthetic fluids	
Fatty acids	Percent degraded
A	68
B	100
C	100
D	100
E	53
F	100
G	100
H	100

Many synthetic fluids contain glycols. The higher viscosity (higher molecular weight) polyalkylene glycols are resistant to rapid bio-oxidation [37]. Thus, under the customary five-day test for biodegradability, a very small value of BOD would be obtained. Nevertheless, under longer-term exposure, such as might occur in a river, the products would biodegrade slowly.

The rate of biodegradation of polyglycols is influenced by molecular weight with higher viscosity members of the family showing slower degradation. Because of the low BOD values, only a portion of the polyglycol would be removed in a waste treatment plant. At low concentrations (high dilutions), the products should not adversely affect the biological oxidation in the waste treatment plant. Furthermore, studies to date indicate a low order of toxicity with aquatic life.

Because of their complete water solubility, the polyglycols never produce an "oil film." However, despite complete water solubility, local, state or federal regulations may preclude the discharge of any major quantity of used polyglycol lubricant to the waste water stream. Under these conditions, incineration is an option.

Waste synthetic fluids can be disposed of by incineration or landfilling. However, it is sometimes economical to reduce the bulk volume prior to disposal, using techniques such as reverse osmosis or ultrafiltration.

Osmosis is the passage of solvent, in this case water, from a dilute to a more concentrated solution through a semi-permeable membrane. The flow of solvent continues until the pressure is high enough to prevent further transfer. This equilibrium pressure is known as the osmotic pressure. If a pressure greater than the osmotic pressure is applied to the concentrated solution, solvent will flow as a "pure" solvent. This principle can be applied to remove water from used synthetic cutting fluids (Figure 64). The permeate stream produced is substantially purified water, although it contains low concentrations of organic and inorganic matter. Colloidal, particulate, and microbial contaminants are retained in the concentrate.

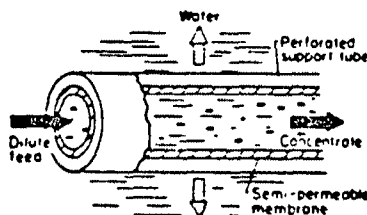


Figure 64. Reverse osmosis can be used to reduce the water content of synthetics [131].

Ultrafiltration, sometimes called molecular filtration, is another membrane separation process. The membrane is porous and the constituents are separated on the basis of molecular size. The separation efficiency is determined by the pore size.

There are two features which distinguish between the processes, operating pressure and the separation. Reverse osmosis uses pressures in the order of 500-1,000 psi while the pressures in ultrafiltration are usually about 10-50 psi. In ultrafiltration small dissolved molecular species, such as organic salts are

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[131] Evans, C. Treatment of used cutting fluids and swarf. Tribology International. 33-37, 1977 February.

passed through the membrane, while in reverse osmosis only the solvent is transferred.

There are more exotic synthetic fluids coming into the market. Reclamation, treatment, and disposal aspects of these expensive fluids will likely be evaluated prior to their usage. Products that can be discarded with a minimum of difficulty have an economic advantage over fluids that must be subjected to complicated treatment during the disposal process.

## 6.5 DISPOSAL AND RECLAMATION OF ORGANIC SOLVENTS

Contaminated organic solvents generated in various metal finishing operations such as degreasing or metal cleaning, coating and painting are commonly subjected to reclamation and reuse. They include a wide range of aliphatic, aromatic, and halogenated hydrocarbons, alcohols, ketones, and esters. This section describes organic solvent reclamation technology as an adjunct of metal finishing operations as well as by independent operations contracted to collect and distill waste material. The economics of on-site reclamation are compared with those of off-site processing. Future trends, developments of such technology, and alternative disposal technology are also discussed.

### 6.5.1 On-Site Reclamation

Organic solvents used in metal cleaning and metal painting become contaminated with oils, water, pigments, or other undissolved solids. Basically, five types of reclamation technology have been applied to waste solvents generated from metal finishing operations [81], namely, (1) adsorption, (2) condensation c. refrigeration, (3) absorption, (4) distillation, and (5) evaporation. These are discussed in detail in the following subsections. However, the discussion does not include undissolved solids and water which are removed from liquid waste solvent by initial treatment through mechanical separation such as decanting, filtering, draining, settling, and use of a centrifuge.

#### 6.5.1.1 Adsorption--

6.5.1.1.1 Description [7,81,132,133]--Adsorption is the process by which components of a solvent vapor are retained on the surface of granular solids. There are many types of solid adsorption

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[132] Larson, D. M. Activated carbon adsorption for solvent recovery in vapor degreasing. Metal Finishing. 42-45, 1974 October.

[133] Control techniques for volatile organic emissions from stationary sources. Research Triangle Park, NC; U.S. Environmental Protection Agency; 1978 May. 578 p. EPA-450/2-78-022. PB 284 804.

media available; the most commonly used is activated carbon. Carbon adsorption systems for solvent vapor recovery can be added to most vapor degreasers by direct connection downstream of the adsorption unit.

The two main functions of a carbon adsorption system are that of collection and cleaning, commonly referred to as adsorption and desorption [132]. A typical carbon adsorption system consists of two vessels filled with activated carbon, a solvent-laden air inlet and outlet, a blower and filter, a steam inlet and outlet source, and a condenser and decanter. Automatic operation is most common, although manually operated systems are available. Operational sequence is straightforward. The solvent-laden air is passed over the bed of activated carbon. The carbon collects the organic solvents and passes the clean air out the exhaust. Once the carbon has collected its capacity of organic solvents, it must be cleaned free of the solvents in order to prepare for the next adsorption cycle. Some typical working carbon bed capacities are shown in Table 68.

TABLE 68. WORKING BED CAPACITIES [39]

Solvent	Percent of carbon bed weight
Acetone	8
Heptane	6
Isopropyl alcohol	8
Methylene chloride	10
Perchloroethylene	20
Stoddard solvent	2-7
1,1,1-Trichloroethane	12
Trichloroethylene	15
Trichlorotrifluoroethane	8
VM&P Naphtha	7

At the end of the adsorption period the carbon adsorption system will automatically cycle itself, rotating one bed off adsorption (in a two-bed system) and into a cleaning cycle. The cleaning of the carbon is referred to as desorption or regeneration. Most carbon adsorption systems installed on vapor degreasers consist of dual vessels which permit continuous operation by maintaining one carbon bed on the adsorption cycle at all times. The regeneration cycle is usually performed automatically by injecting low pressure steam into the carbon bed. This input of energy releases the solvent from the carbon. The resulting steam-solvent mixture is then fed into a condenser where the solvent and steam are condensed, and then into a decanter, where the solvent and water are then separated by simple mechanical decantation. Because degreasing

solvents are not water soluble, no further equipment is required. Figure 65 is a typical flow diagram for a carbon adsorption system. In the case of a water-miscible solvent the decanter is not used. The condensate flows directly (via intermediate storage) to a stripper where water is separated from the solvent. In many cases, solvents are recovered as a mixture. The separation of these solvents and dehydration of the water-soluble components usually involves several separation techniques depending on the physical and chemical characteristics of the solvents [134]. An alternative to recovery is the addition of an incinerator for combustion of the desorbed effluent during stripping (adsorption-incineration system).

A properly sized carbon adsorption system installed on the vapor degreaser will remove 95 to 100 percent of the solvent vapors. However, total solvent emissions are only reduced 40 to 65 percent. This is because the ventilation apparatus of the control system cannot capture all solvent vapors and deliver them to the adsorption bed [133]. The major loss areas are dragout on parts, leaks, spills, and disposal of waste solvent. Carbon adsorption systems are available in a series of sizes which handle ventilation rates between 600 and 10,000 cfm.

The total amount of solvent recovery is dependent on the types of parts being cleaned, proper design of the degreaser, and the actual operation of the degreaser. The most important factor is the actual operation of the degreaser. If the degreasers are properly operated, solvent savings consistently above 85 percent can be expected [132].

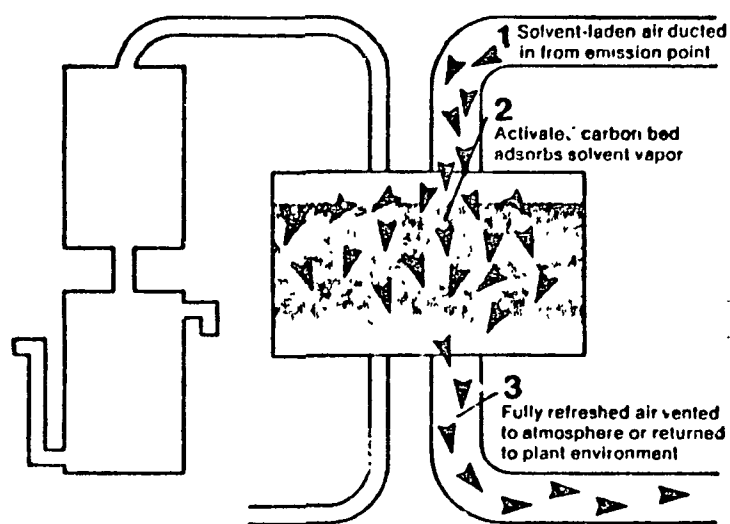
Activated carbon adsorption systems, operated on stabilized chlorinated solvents for vapor degreasing, do not substantially deplete the stabilizer level in the solvent, with the exception of 1,1,1-trichloroethane. This solvent has water-soluble stabilizers which are completely removed when the solvents are steam-stripped from the carbon bed. When these stabilizers are removed, highly corrosive conditions, greater than with the other degreasing solvents, can be present [132]. Thus, special metals are required to handle this solvent in the recovery system. Systems are currently available as complete packages to handle adsorption, desorption, drying, neutralization, and restabilization of 1,1,1-trichloroethane [132].

In steam stripping of other chlorinated solvents, such as perchloroethylene, trichloroethylene, and methylene chloride, quantities of hydrochloric acid are generated in the carbon bed.

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[134] Davis, W. L.; and Kovack, J. L. Solvent recovery by carbon adsorption for the coating industry. Technical Association of the Pulp and Paper Industry; 1980 Paper Synthetic Conference, 1980.

Here is the adsorption phase of a recovery tank in a solvent recovery system.



In the desorption phase, the same tank reverses its function to initiate solvent recovery.

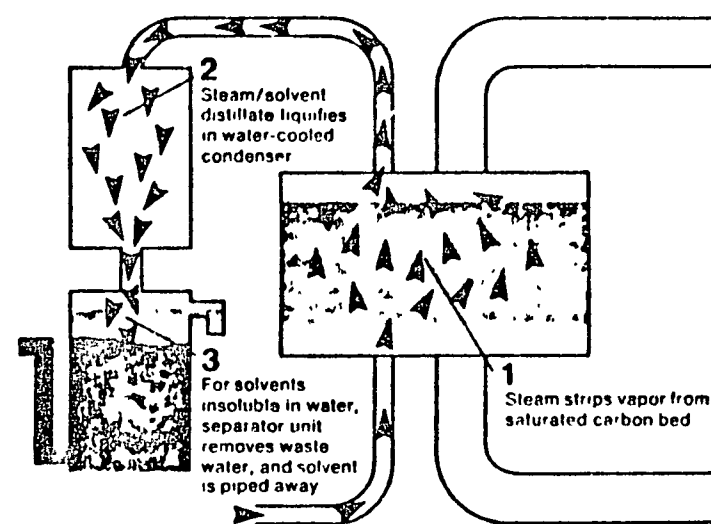


Figure 65. Carbon adsorption principle of operation[31].

Therefore, materials of construction for the system must be designed to provide suitable corrosion resistance. Baked phenolics, acid-resistant coatings, and certain alloy materials are the most suitable [132].

6.5.1.1.2 Cost Analysis [133-135]--Costs for adsorption systems vary with: (1) the nature of contaminants in the waste vapor, (2) the concentrations of organics in the vapor, (3) the adsorbent, (4) the regeneration technique, (5) the type of adsorber, and (6) the vapor volume flow rate.

Adsorption capital costs include costs of the basic equipment, auxiliary equipment, equipment installation, and interest charges on investment during construction. The capital costs for a fixed-bed adsorber system with recovery of desorbed vapors are shown in Figure 66. All costs are indexed to June 1976. Costs for moving and fluidized bed adsorbers are slightly lower than those for fixed-bed systems. Capital costs for adsorption incineration systems with no heat recovery are approximately 20 to 30 percent higher than adsorption recovery systems handling comparable flows.

Annualized costs include labor and maintenance costs, utilities and materials costs, capital-related charges, and credit for solvent recovery. Table 69 shows typical components of such costs for carbon adsorption systems with assumptions in the footnotes. When recovered organics are credited at their market values, the adsorption operation shows a capital return. Most installations attain complete return on capital within one to three years relative to an operating life of at least 15 years for the system. Reuse of the recovered solvents, however, is not usually practical when more than one solvent is involved. Product separation is normally too costly to warrant recovery for reuse in the process. Annualized costs for the adsorption-incineration system are comparable to those for the adsorption-recovery system except that no credit is allowed for solvent recovery.

6.5.1.1.3 Applicability and Feasibility [133, 135]--Metal finishing operations that can be controlled by adsorption include degreasing or metal cleaning, paint spraying, tank dipping, and metal foil coating.

Adsorption is not normally practiced at organic concentrations of greater than 25 percent of the lower explosive limit because the heat released by adsorption cycle may raise the temperature of

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[135] Grandjacques, B. Carbon adsorption can provide air pollution control with savings. Pollution Engineering. 28-31, 1977 August.

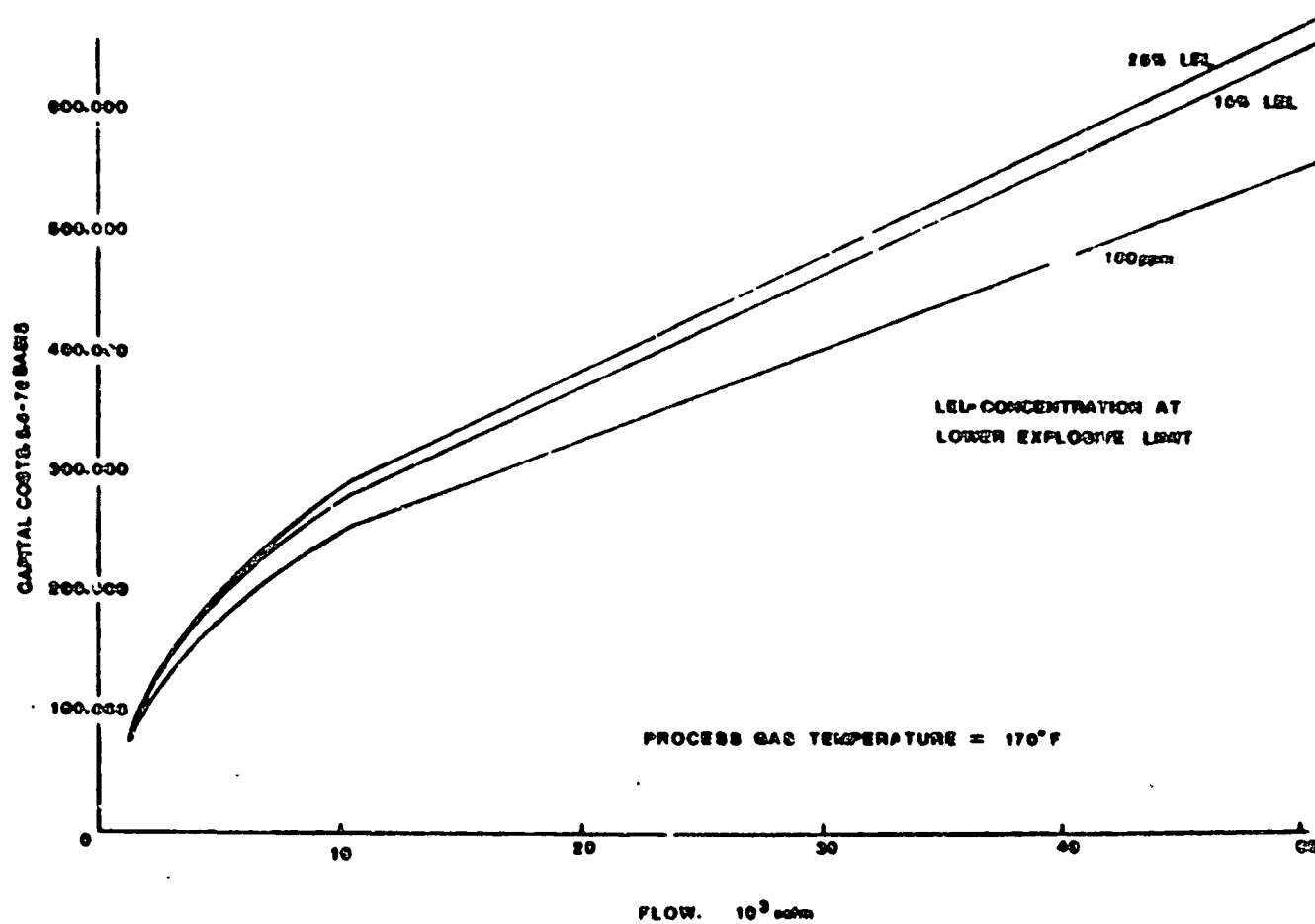


Figure 66. Adsorption capital costs [133].



TABLE 69. TYPICAL COMPONENTS OF ANNUALIZED COSTS FOR CARBON ADSORPTION SYSTEMS [7]

Configuration

1. Dual fixed-bed adsorber operating at 100°F (38°C)
2. Solvent recovery with condenser and decanter

Gas stream characteristics

Flow	20,000 scfm (9.4 m <sup>3</sup> /s)
Concentration	25% LEL
Process gas temperature	170°F (77°C)

Component	Annual cost
Direct operating costs	
Utilities	\$ 48,700 <sup>a</sup>
Direct labor	3,000 <sup>b</sup>
Maintenance	15,400 <sup>c</sup>
Carbon replacement	11,500 <sup>d</sup>
Capital charges	80,850 <sup>e</sup>
Recovery (credits)	(297,000) <sup>f</sup>
Total net annualized costs (credits)	\$(137,500) <sup>g</sup>

<sup>a</sup>Cooling water at \$0.045/1,000 gallon (\$0.012/m<sup>3</sup>), steam at \$2/1,000 lb (\$0.53/m<sup>3</sup>), electricity at \$0.033/kWh (\$9.17/GJ).

<sup>b</sup>Labor at \$8.25/hr.

<sup>c</sup>Maintenance as 4% of the capital cost.

<sup>d</sup>Carbon at \$0.72/lb (\$1.58/kg) with 20% of carbon replenished each year.

<sup>e</sup>Capital charges include as percent of capital cost: depreciation, 12%; taxes, insurance, and overhead, 4%; interest, 5%.

<sup>f</sup>Benzene credited at \$0.75/gallon, hexane at \$0.47/gallon.

<sup>g</sup>Net costs calculated as capital charges + direct operating costs - recovery credits.

the carbon bed high enough to cause carbon combustion. For safe and efficient operation, the inlet gas temperature is limited to less than 100°F (40°C) and the solvent concentration to less than 25 percent of the lower explosive limit. For high organics concentration, (larger than 25 percent), using incineration technology becomes attractive.

6.5.1.1.4 Environmental Impacts [133]--Air and water pollution may occur in the adsorption system. If a steam desorption cycle is employed in the system and the recoverable solvents are soluble in water, then some form of water treatment or separation process is required to minimize the organic concentration in the wastewater.

If an incinerator is used to destroy the exit stream from the adsorber, the type and amount of air emission are also of concerned.

The disposal of spent adsorbent is another environmental concern, but this may be necessary only once in three to five years.

6.5.1.2 Refrigeration or Condensation--

6.5.1.2.1 Description [7,39,133]--A simple refrigeration device called a "refrigerated chiller" or "cold-trap" system is used on vapor degreasers [7,39]. The vapors created within a vapor degreaser are prevented from overflowing out of equipment by means of condenser coils and a freeboard water jacket to produce a cold blanket across the surface of the vapor. The cold blanket condenses the rising fumes to the saturation level where they become droplets and fall back into the tank below.

Refrigerated freeboard chillers are a more dedicated system. In appearance, they seem to be a second set of condenser coils located slightly above the primary condenser coils of the degreaser (Figure 67) [136]. Functionally, they achieve a different purpose. Primary condenser coils control the upper limit of the vapor zone, while refrigerated freeboard chilling coils impede diffusion of solvent vapors from the vapor zone into the work atmosphere. This is accomplished by chilling the air immediately above the vapor zone and creating a cold air blanket. This blanket also reduces mixing of air and solvent vapors by reducing the air/vapor mixing zone, which results from a sharper temperature gradient. In addition, chilling decreases the upward convection of warm, solvent-laden air.

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[136] Chemical Engineer's Handbook. Fifth Edition. J. H. Perry and C. H. Chilton, eds. New York, McGraw-Hill Book Company, 1973.

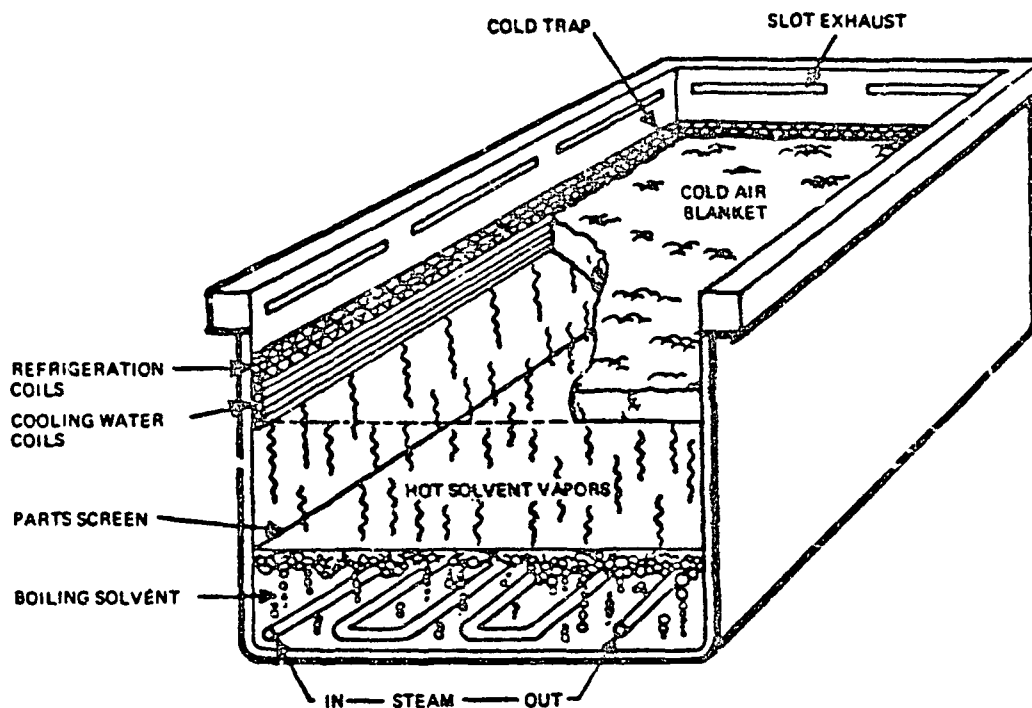


Figure 67. Schematic representation of degreaser with cold trap installed [136].

Patent coverage of the "cold trap" is limited to designs that control the refrigerant temperature at  $0^{\circ}\text{C}$  or colder [137]. Manufacturers operating within this patent recommend a heat exchange temperature of  $-23^{\circ}\text{C}$  to  $-30^{\circ}\text{C}$ . Commercial systems operating between  $1^{\circ}\text{C}$  to  $5^{\circ}\text{C}$  are also available. Most major manufacturers of vapor degreasing equipment offer both types of refrigerated freeboard chillers.

These systems are designed with a timed defrost cycle to remove ice from the coils and to restore heat exchange efficiency. Although liquid water formed during the defrost cycle is directed to the water separator, water contamination of the degreasing solvent is not uncommon.

Although water contamination of vapor degreasing solvents has an adverse effect on the stabilizer systems, major stabilizer depletions from this source are unusual. Water is a major source of equipment corrosion and can diminish the working life of the equipment.

[137] Control of volatile organic emissions from organic solvent metal cleaning. Research Triangle Park, NC; U.S. Environmental Protection Agency; 1978 April. EPA-450/2-77-022.

A third type of refrigerated chiller is the refrigerated condenser coil. Rather than provide an extra set of chilling coils as the freeboard chillers do, refrigerated condenser coils replace primary condenser coils. If coolant in the condenser coils is sufficiently refrigerated, it will create a layer of cold air above the air/vapor interface. Refrigerated condenser coils are normally used only on small, open-top vapor degreasers because energy consumption may be too great for larger open-top vapor degreasers. The refrigerated condenser coil offers portability of the open-top degreaser by excluding the need for plumbing to cool condenser coils with tap water.

When a rise in the boiling temperature indicates an accumulation of oils and other soils, the degreaser must be cleaned. At this time, the used solvent and oil mixture is removed and taken away by a reclaiming service or run through the plant's own still for purification [138]. It is wise to check acid acceptance at this time and correct it as directed by the solvent manufacturer.

6.5.1.2.2 Cost Analysis [133]--The costs for refrigeration units depend on the following: (1) the nature and concentrations of the vapors in the exhausted gas; (2) the mean temperature difference between gas and coolant; (3) the nature of the coolant; (4) the desired degree of condensate subcooling; (5) the presence of noncondensable gases in the exhausted gas; and (6) the build-up of particulate matter on heat exchange surfaces.

Annualized and capital costs for refrigeration vapor recovery units have been developed by the EPA [139]. These costs are shown in Figures 68 and 69 as a function of the hydrocarbon vapor flow rate. All costs are indexed to June 1976.

Capital cost estimates represent the total investment required to purchase and install a refrigeration unit. New installations are assumed, but retrofitting at existing installations is expected to be only slightly higher.

An example of annualized cost components for a refrigeration unit is shown in Table 70. Utilities costs will vary depending on the inlet concentration of the solvent vapor. Solvent credits help offset about 35 to 75 percent of the annualized expenses. At higher flow rates, solvent credits appear to offset operating expenses and capital charges, resulting in a net savings by recovering the vapors.

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[138] Monahan, R. Vapor degreasing with chlorinated solvents. Metal Finishing. 26-31, 1977 November.

[139] Control of hydrocarbons from tank truck gasoline loading terminals. Research Triangle Park, NC; U.S. Environmental Protection Agency; QAQPS; 1977 May. Draft copy.

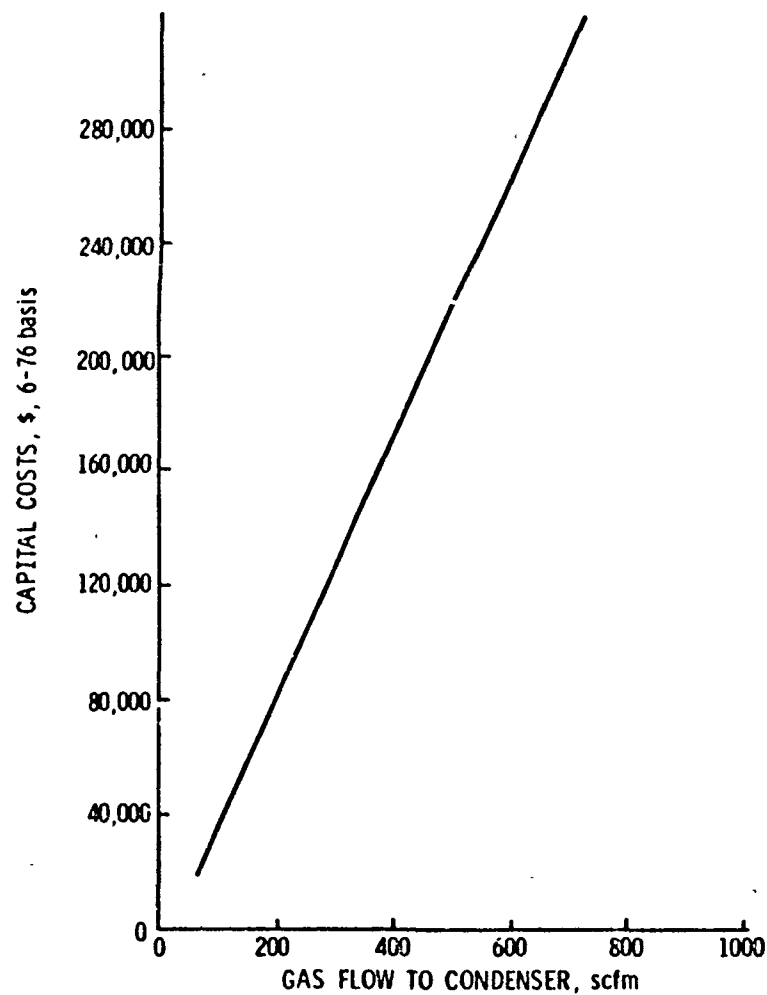


Figure 68. Capital costs for refrigeration vapor recovery units [133].

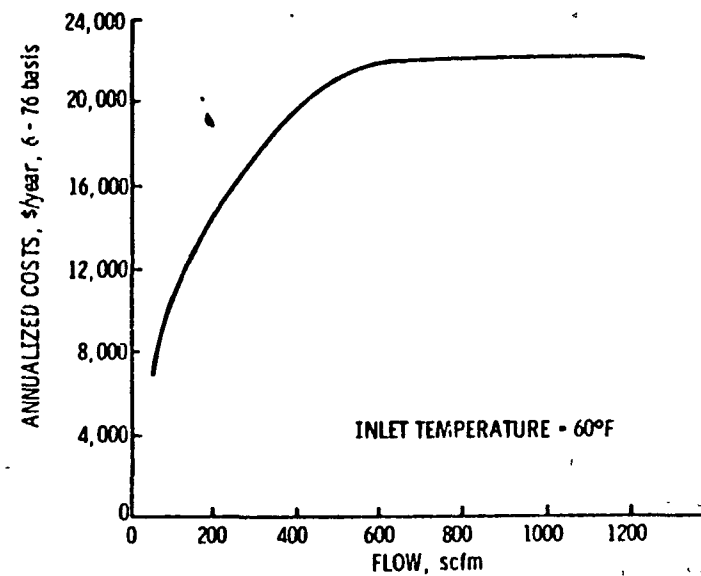


Figure 69. Annualized costs for refrigeration vapor recovery units [133].

TABLE 70. COMPONENTS OF ANNUALIZED COSTS FOR A  
REFRIGERATION VAPOR RECOVERY UNIT [133]

Gas stream characteristics	
Flow	420 scfm (12 m <sup>3</sup> /min)
Concentration	20% (by volume) hydrocarbons
Inlet temperature	60°F (16°C)
Direct operating costs	
Utilities	\$ 6,000 <sup>a</sup>
Maintenance	5,300 <sup>b</sup>
Capital charges	30,000 <sup>c</sup>
Gasoline recovery (credit)	<u>(21,400)<sup>d</sup></u>
Net annualized costs	\$ 19,900 <sup>e</sup>

<sup>a</sup>Electricity at \$0.04/kWh (\$11.11/GJ).

<sup>b</sup>Maintenance as 3% of the capital costs.

<sup>c</sup>Calculated at 10% for 15 years plus 4% for taxes, insurance, and administration.

<sup>d</sup>Gasoline valued at \$0.40/gallon (\$0.10/L) F.O.B. terminal before tax.

<sup>e</sup>Computed as operating costs + capital charges - gasoline recovery credits.

6.5.1.2.3 Applicability and Feasibility [81,133]--Refrigeration has been used successfully in controlling organic emissions from metal cleaning or degreasing operations. However, it will not remove all the vapor from the air. Because of its lower efficiency and other disadvantages, it is not used widely for solvent recovery in industry. The yield from refrigeration is necessarily lower than that from adsorption and absorption systems, but this may be offset by lower costs.

In general, refrigeration systems are uneconomical as the sole means of emission control unless the gas contains high concentrations of valuable organic vapors. The refrigeration operation can recover only those constituents above the saturating concentration at the condensing temperature. Therefore, it is only practical at concentrations well above 10,000 to 20,000 ppm [140].

[140] Harvin, R. L. Recovery and reuse of organic ink solvents. Louisville, KY; C&I Girdler, Inc.; 1975 September. 25 p.

6.5.1.2.4 Environmental Impact [133]--A condenser seldom creates secondary environmental problems when the condensation process is considered by itself. Problems that do arise include disposal of noncondensibles in refrigeration systems. The noncondensable gas effluent from the surface condenser is either vented to the atmosphere or further processed (e.g., via incineration), depending on the effluent composition. The coolant never contacts the vapors or condensate in a condenser; therefore, the recovered organic solvents are usually reusable.

#### 6.5.1.3 Absorption--

6.5.1.3.1 Description [81,133]--Absorption is a well known process in which a liquid medium is used to extract a soluble vapor from a gas stream. Absorption recovers vaporized solvents by close contact with a liquid absorbent at the proper temperature. In general, absorption is most efficient under the following conditions [141]: (1) the organic vapors are quite soluble in the absorbent; (2) the absorbent is relatively nonvolatile; (3) the absorbent is noncorrosive; (4) the absorbent is inexpensive and readily available; (5) the absorbent has low viscosity; and (6) the solvent is nontoxic, nonflammable, chemically stable, and has a low freezing point.

The solvent-laden absorbent stream may be stripped of solvents and recycled. Some absorbent will be lost with the stripped solvent and must be replaced. The rate of mass transfer between the gas and the absorbent is largely determined by the amount of surface area available for absorption. Other factors governing the absorption rate, such as the solubility of the gas in the absorbent and the degree of chemical reaction, are characteristics of the constituents involved and are independent of the equipment used.

Absorption equipment must be designed to provide adequate contact between the gas and the absorbent liquid to permit interphase diffusion of the organic vapors. Contact is provided by several types of equipment such as plate towers, packed towers, spray towers, and venturi scrubbers. The fluid is usually pumped to the top of the tower, distributed and drained by gravity counter-current to the gas stream being treated. With proper tower conditions and fluid choice, removal of the dilute solvent vapors from air can be effectively accomplished.

6.5.1.3.2 Cost Analysis [133]--Absorption costs vary widely and depend upon the following factors: (1) the type of absorber; (2) the kind of contacting media; (3) the nature and amounts of

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[141] Treybal, R. E. Mass Transfer Operations. New York, McGraw-Hill Book Company, 1968. pp. 129, 154, 225-226.

organic vapors in the gas; (4) the absorbent used; (5) the value of recovered solvents or of the absorbent-dissolved organics solution; (6) the design removal efficiency; and (7) the gas volume flow rates.

Capital costs for newly installed packed tower absorbers are depicted in Figure 70. These costs include the cost of the basic equipment, the cost of any auxiliary equipment, and the costs associated with equipment installation and site preparation. Retrofits may cost up to two times the illustrated values. Corrosive properties of certain organic streams require special construction materials which increase capital costs. Absorption systems using absorbents with poor absorption capabilities for organic vapors would have larger capital costs associated with the need for larger absorption towers. Regenerative absorption systems also have increased capital costs because of additional equipment needed for absorbent regeneration.

Annualized costs for a cross-flow packed scrubber are presented in Figure 71. Utilities include power costs for the recirculating pump and fan. Process water costs are small in this case since recirculation is assumed. Treatment costs, although not included in Figure 71, should be taken into consideration when evaluating absorption system costs. Maintenance costs appear to average five percent of the capital investment. Relatively low capital investments for absorption systems help minimize capital charges.

6.5.1.3.3 Applicability and Feasibility [133]--Absorption has been used to control and recover organic vapors in surface coating and degreasing operations. Commonly used absorbents for organic vapors are water, mineral oil, and nonvolatile hydrocarbon oils. For example, trichloroethylene vapors in air can be reduced by absorption in mineral oil. However, at ambient temperature the air stream leaving the column can contain about 120 ppm mineral oil. Thus, this process can result in controlling one hydrocarbon but emitting another. Also, solvent stabilizer is not recovered during the process. Restabilization of the recovered solvent will be needed.

It appears that absorption is good for high concentrations of solvent vapor in air, valuable vapors, or highly toxic chemical vapors. The recovery of solvents is not economically achieved by absorption in dilute gas mixtures (<1%).

The use of absorption may be feasible where chlorinated solvents are absorbed in metal cutting lubricant oils. The presence of the chlorinated solvent in cutting oils increases tool cutting speed and tool life. This practice lessens the energy needed for distillation but results in slow re-release of solvent vapors to the atmosphere during use as a metal cutting lubricant.



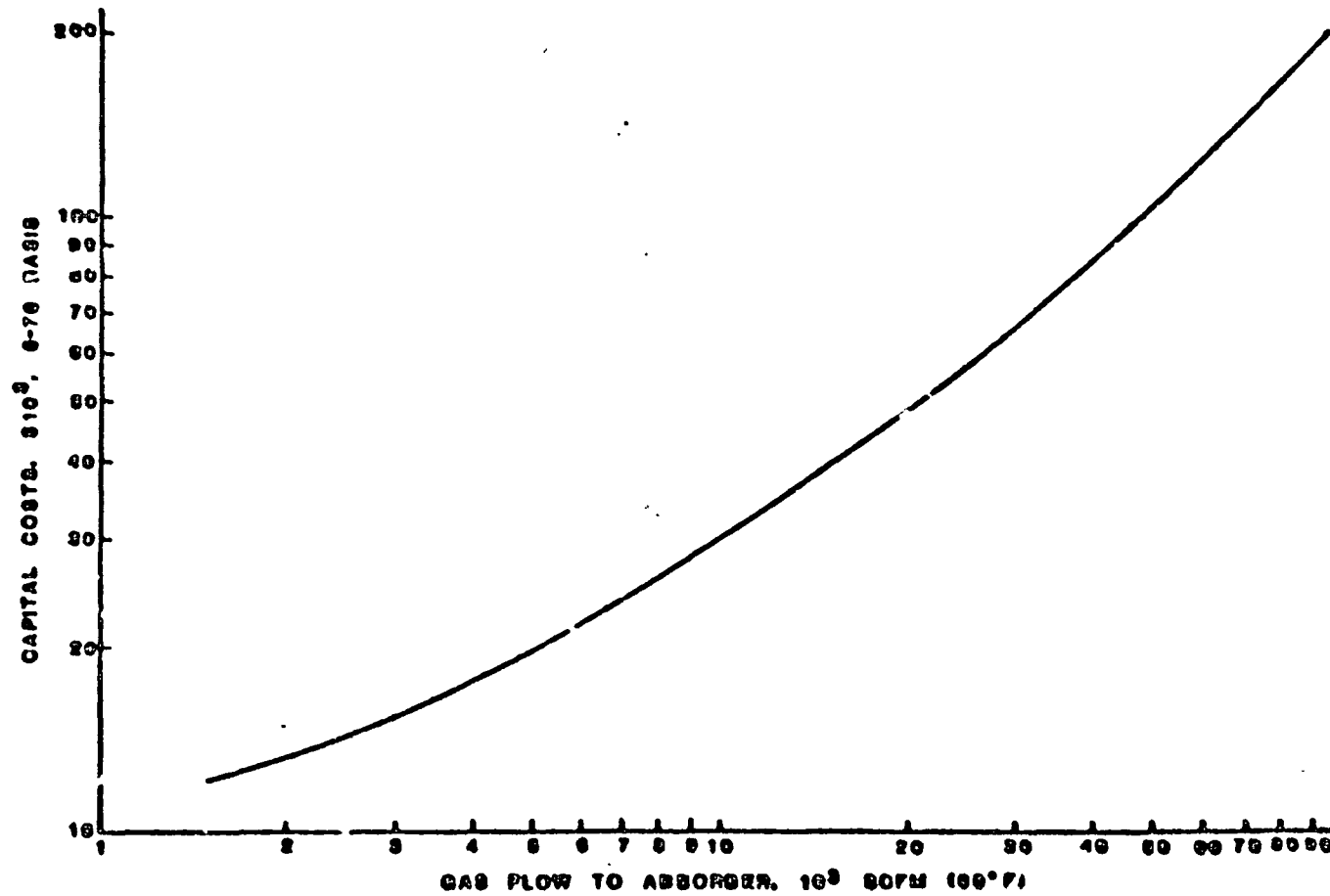


Figure 70. Capital costs for packed tower absorbers (new installations) [133].

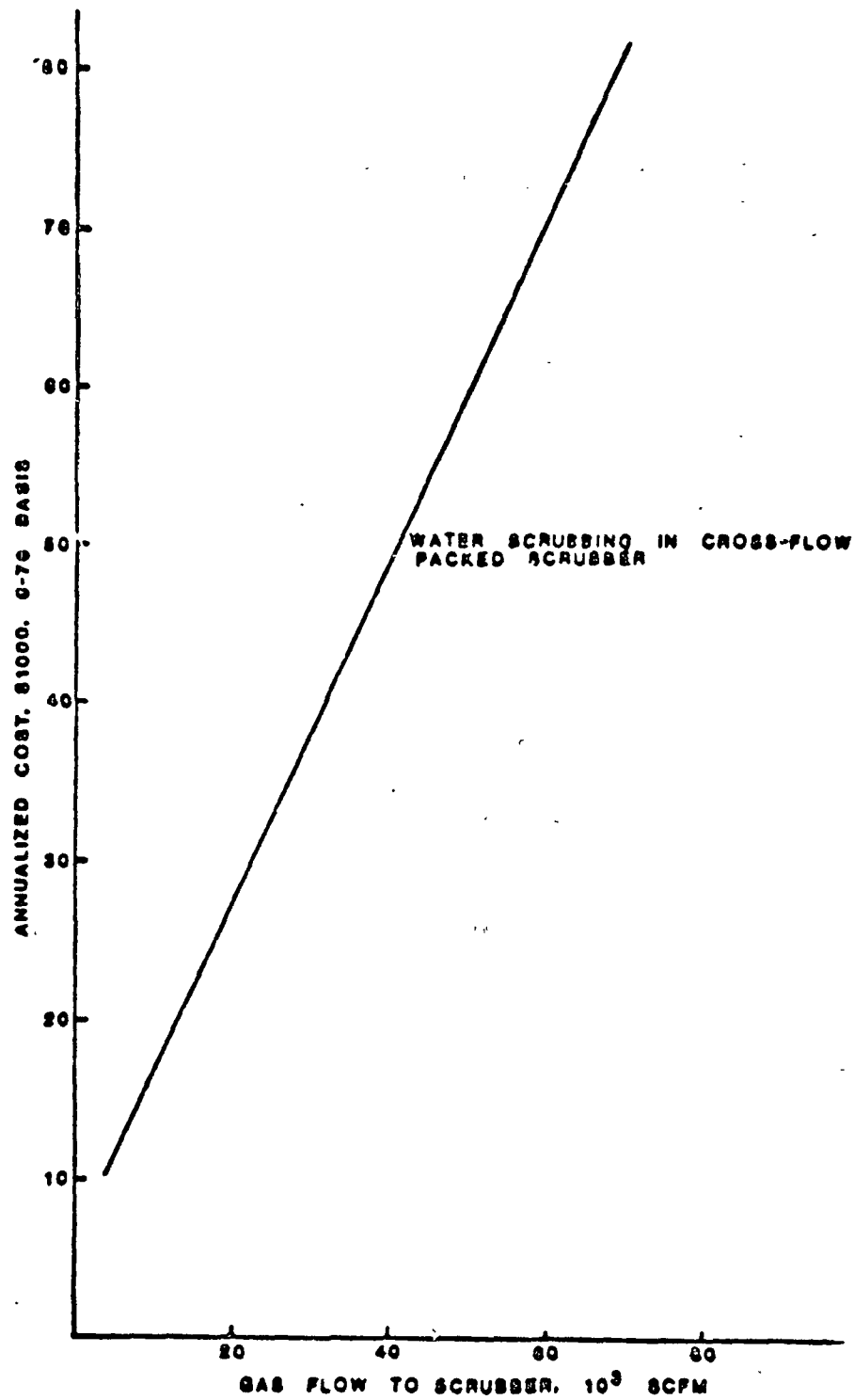


Figure 71. Annualized costs for a cross<sup>2</sup>-flow packed scrubber [133].

6.5.1.3.4 Environmental Impact--Adverse environmental effects which can result from the operation of an absorber include improper disposal of the organic-laden liquid effluent, undesired emissions from the incineration of the regenerated waste gas, and loss of absorbent to the atmosphere.

The liquid effluent from an absorber can frequently be used elsewhere in the process. When this is not possible, the nonregenerated absorbent effluent should be treated to provide good water quality. Such treatment may include a physical separation process (decanting or distilling) or a chemical treating operation.

Regeneration consists of heating the liquid effluent stream to reduce the solubility of the absorbed organics and separate them from the absorbent. These concentrated organics can then be oxidized in an afterburner. Emissions of  $\text{SO}_x$ ,  $\text{NO}_x$ , and other incomplete oxidation products may be a result, depending on the nature of the regenerated gas stream.

#### 6.5.1.4 Distillation--

6.5.1.4.1 Description [81,142]--Distillation is the process of partial vaporization of a liquid mixture and condensation of vapor for the purpose of separating the components. Usually, in metal cleaning operations distillation is employed to recover contaminated solvents. Figure 72 schematically illustrates a typical continuous fractional distillation column [143]. Contaminated solvents with dissolved materials which cannot be settled or filtered out, is continuously fed into the distillation column where it is cycled through the reboiler and heated by steam flowing through coiled tubes. Vaporized components return to the distillation columns for separation, and the less volatile residual liquids or tars (bottom products) are removed from the system for reuse or disposal. In fractional distillation, the vapors pass up through the column and are partitioned, according to their relative volatilities, throughout the sieve and valve tray packings. The vapors are drawn off, condensed, and stored in the accumulator. From the accumulator, a portion of the isolated fraction is returned to the column for refluxing, and the remainder is collected (overhead product) for reuse or disposal.

Distillation is available as atmospheric or vacuum units. For atmospheric distillations, the pressure is set at the pressure that the overhead product can be at least partially condensed

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[142] Hengstebeck, R. J. Distillation. Principles and Design Procedures. New York, Reinhold Publishing Corporation, 1961.

[143] Hansen, W. G.; and Rishel, H. L. Cost comparisons of treatment and disposal alternatives for hazardous wastes; volume I. Cincinnati OH; U.S. Environmental Protection Agency; 1980 December. 272 p. EPA-600/2-80-188. PB 81 128514.

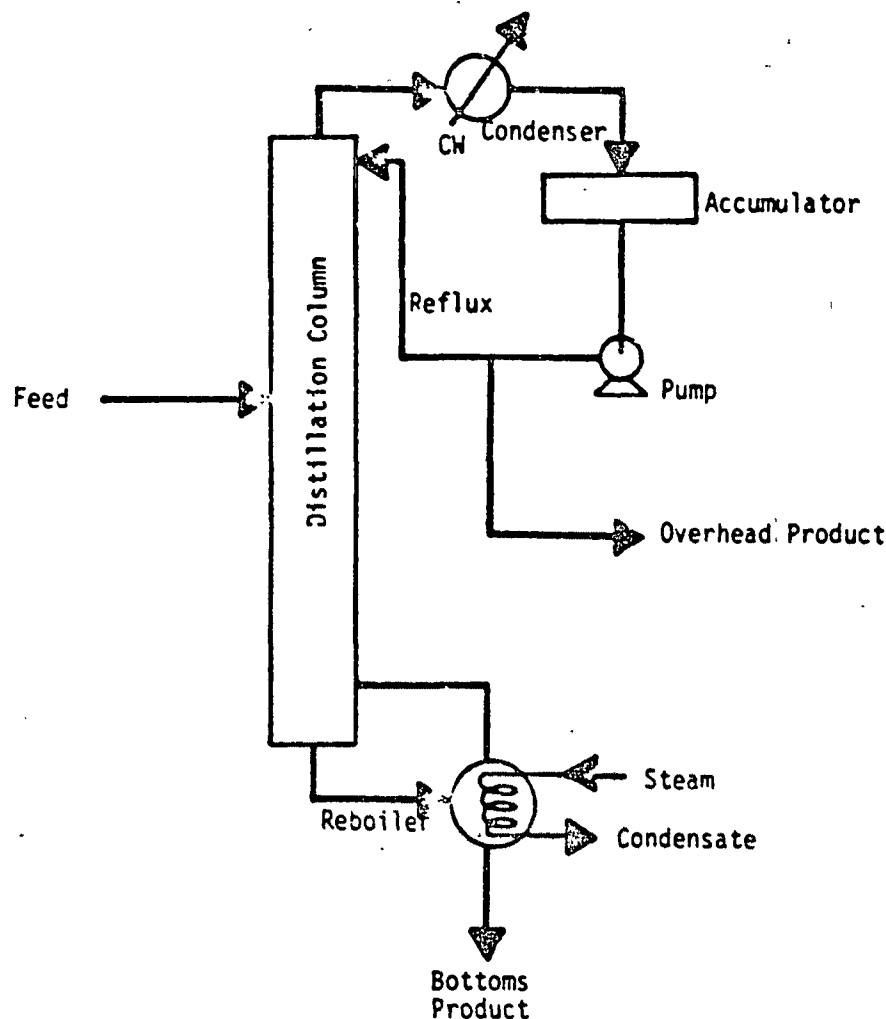


Figure 72. Continuous fractional distillation column [143].

by heat exchange with a convenient cooling medium, and liquid from the bottom stage can be partially vaporized by exchange with a convenient heating medium; otherwise refluxing and reboiling would not be readily achievable. When both conditions cannot be met simultaneously, refrigeration may be used to condense the overhead, or a furnace may be used for reboiling. When the feed contains high-boiling materials that are too heat-sensitive to be distilled at atmospheric pressure, distillations are carried out under vacuum to reduce column temperatures. Because temperatures are highest at the bottom of a column, the properties of the bottom product usually determine whether vacuum must be used [143].

The contaminants accumulate in the bottom of the still during the distillation cycle. Solvent incinerators are generally used to burn the still bottoms. The still bottoms can also be disposed of by landfill and deep well injection. However, the still bottoms which contain less than a few hundred parts of solvent per million parts of water can also be drained to a sewer [144].

Distillation column capacity requirements depend on the waste input rate and volatiles of the constituents to be separated.

Descriptions of the method for calculating column diameter and height is available in the literature [145-147]. If the maximum diameter and height cannot accommodate the liquid flow, two or more equal-sized columns are used to treat the waste solvents. In actual systems there are many possible combinations of reflux ratio, column pressure, column height, column diameter, and contacting intervals.

6.5.1.4.2 Cost Analysis [143]--The capital costs for distillation include costs of the basic and auxiliary equipment, equipment installation, and building costs. Operating costs include labor and maintenance costs, utilities and materials costs, and capital related charge. The breakdown of capital and operating costs are shown in Tables 71 and 72, respectively. The change in the total capital costs (exclusive of land cost) according to the scale of separation is shown in Figure 73. Labor and equipment maintenance costs are shown in Figure 74. All costs are adjusted for inflation to mid-1978 values and are based on charges as they exist in Chicago, Illinois. The direct and indirect operating costs (including debt service and amortization) are used to calculate the average cost over the 5-year life cycle of the example, a 1,000 gpm distillation facility. The life cycle average cost is \$13.02/1,000 gallons. This result is shown in Table 73.

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- [144] Reynen, F.; and Kuncel, K. L. Solvent recovery systems nets plant approximately \$50,000/yr savings. *Chemical Processing*. 38(9):19, 1975.
- [145] Robinson, C. S.; and Gilliland, E. R. *Elements of fractional distillation*. New York, McGraw-Hill Book Company, 1950. 492 p.
- [146] Fair, J. R.; and Bolles, W. L. Modern design of distillation columns. *Chemical Engineering*. 75(8):156-178, 1968.
- [147] Colley, Forster, and Stafford (eds). *Treatment of industrial effluents*. New York, John Wiley and Sons, 1976. 378 p.

TABLE 71. SUMMARY OF CAPITAL COSTS FOR DISTILLATION<sup>a</sup> [143]

Capital cost category module	Costs <sup>b</sup>					Quantities		
	Site Preparation	Structures	Mechanical equipment	Electrical equipment	Land	Total	Land, ft <sup>2</sup>	Other steam, lb/hr
Steam generator	\$ 70	\$ 6,490	\$414,400	\$ --	\$ 697	\$ --	937	120,000
Distillation column	120	4,540	232,730	11,637	768	--	1,032	--
Accumulator	389	2,130	2,840	--	321	--	432	--
Waste pump	--	--	2,950	--	--	--	--	--
Piping	675	--	39,300	--	--	--	--	--
Total	1,254	13,160	692,220	11,637	1,786	--	2,401	120,000
Supplemental capital costs	--	97,323 <sup>c</sup>	--	--	--	--	--	--
Subtotal of capital costs	--	--	--	--	--	817,380	--	--
Working capital <sup>d</sup>	--	--	--	--	--	179,166	--	--
AFDC <sup>e</sup>	--	--	--	--	--	40,869	--	--
Grand total of capital costs	--	--	--	--	--	779,403	--	--

<sup>a</sup>Scale = 1,000 gpm; liquid density = 62 lb/ft<sup>3</sup>; vapor density = 50 lb/ft<sup>3</sup>.<sup>b</sup>Mid-1978 dollars.<sup>c</sup>Building.<sup>d</sup>At one month of direct operating costs.<sup>e</sup>Allowance for funds during construction at 5% of capital costs.

TABLE 72. SUMMARY OF FIRST YEAR OPERATING COSTS FOR DISTILLATION<sup>a</sup> [143]

O&M Cost category module	Costs <sup>b</sup>						Quantities		
	Labor			Energy electrical (\$0.035/kWh)	Maintenance costs	Chemical costs	Total	kWh/ yr	Natural gas, ft <sup>3</sup> /yr
	Type 1 Operator 1 (\$7.77/hr)	Type 2 Operator 2 (\$9/19/hr)	Type 3 laborer (\$6.76/hr)						
Steam generator	\$ 1,179	\$ 209	\$15,586	\$956,000	\$2,798	\$120,000	\$ --	--	2.48 x 10 <sup>9</sup>
Distillation column	17,703	10,406	20,513	--	1,602	--	--	--	--
Accumulator	--	--	--	--	398	--	--	--	--
Waste pump	--	--	--	1,730	--	--	--	49,429	--
Piping	--	--	179	--	276	--	--	--	--
Total	18,882	10,615	36,278	957,730	5,074	120,000	--	49,429	2.48 x 10 <sup>9</sup>
Supplemental O&M costs	--	--	--	--	1,348	--	--	--	--
Subtotal of direct O&M costs	--	--	--	--	--	--	1,149,927	--	--
Administrative overhead <sup>c</sup>	--	--	--	--	--	--	229,985	--	--
Debt service and amortization <sup>d</sup>	--	--	--	--	--	--	273,668	--	--
Real estate taxes and insurance <sup>e</sup>	--	--	--	--	--	--	20,748	--	--
Total first year operating costs	--	--	--	--	--	--	1,674,328	--	--

<sup>a</sup>Scale = 1,000 gpm.<sup>b</sup>Mid-1978 dollars.<sup>c</sup>At 20% of direct operating costs.<sup>d</sup>At 10% interest over 5 years.<sup>e</sup>At 2% of total capital

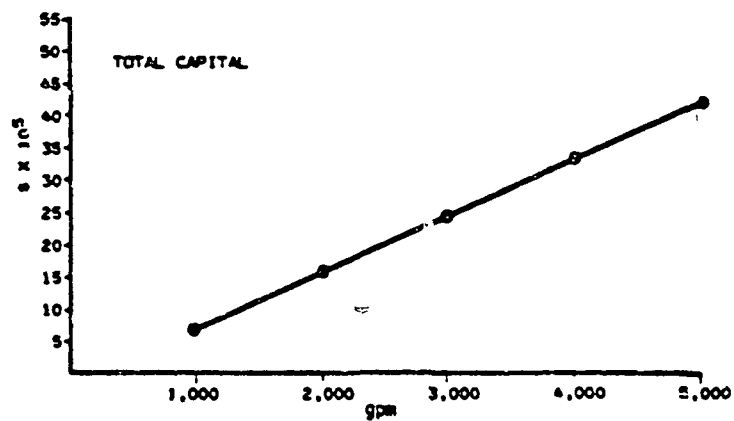


Figure 73. Distillation: changes in total capital costs with scale [143].

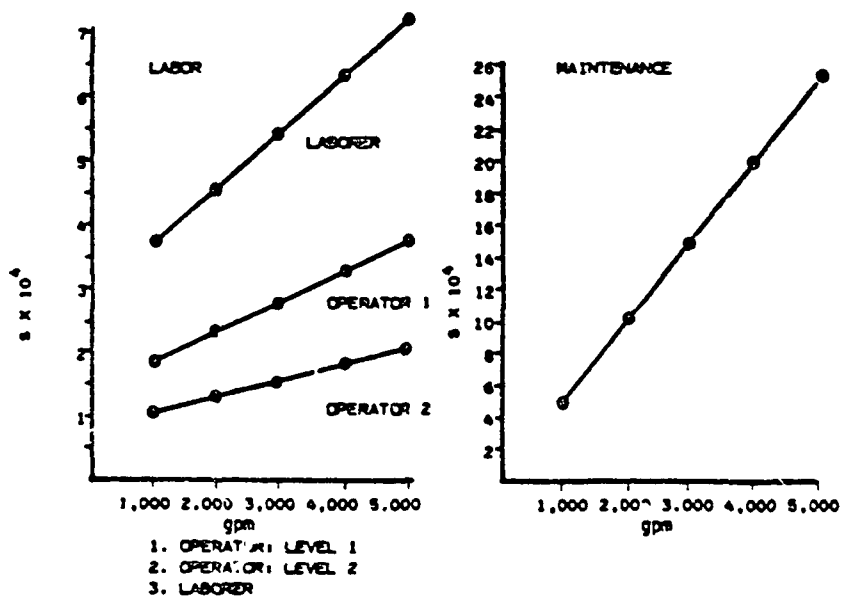


Figure 74. Distillation: changes in O&M requirements with scale [143].



TABLE 73. COMPUTATION OF LIFE CYCLE AVERAGE COST FOR IMPLEMENTING DISTILLATION (LIFETIME - 5 YEARS) [143]

Item	Direct operating costs <sup>a</sup>	Indirect operating costs <sup>b</sup>	Sum operating costs	Present value annualized costs <sup>c</sup>	Annual quantity of throughput <sup>d</sup> (x 1,000 gal)
Year 1 <sup>e</sup>	\$1,149,927	\$524,401	\$1,674,328	\$1,674,328	124,800
Year 2	1,264,920	547,399	1,812,319	1,647,579	124,800
Year 3	1,391,412	572,698	1,964,110	1,623,140	124,800
Year 4	1,530,553	600,526	2,131,079	1,601,080	124,800
Year 5	1,683,608	631,137	2,314,745	1,580,971	124,800
Totals			9,896,581	8,127,098	624,000
Simple average (per 1,000 gallon)			\$15.86		
Simple average (per cubic meter)			\$ 4.19		
Life cycle average (per 1,000 gallon)				\$13.02	
Life cycle average (per cubic meter)				\$ 3.44	

<sup>a</sup> Assumes 10% annual inflation.

<sup>b</sup> Inflation increases the administrative overhead only.

<sup>c</sup> Assumes a 10% interest/discount rate to the beginning of the first year of operation.

<sup>d</sup> 1,000 gpm x 60 min x 3 hrs/day x 260 days/yr.

<sup>e</sup> First year costs in mid-1978 dollars - for Chicago example.

6.5.1.4.3 Applicability and Feasibility [81,143]--Distillation is a feasible method of recovering contaminated solvents with high boiling points used in metal cleaning operations. It can either be a single operation or part of a treatment sequence for recovering solvents used in metal cleaning, coating, and painting. Some private contractors also use distillation in reclamation services.

6.5.1.4.4 Environmental Impact--In distillation columns, emissions can result from column and tank vents and from the steam ejector of vacuum distillation. Uncondensed vapors are released from these columns. Most columns, however, employ some type of vapor recovery system.

Conditions causing excessive carryover of contaminants are the result of an excessive distillation rate. Excessive emissions can also be caused by inability of distillation to maintain a reasonable vacuum.

Leaks in the head and side sheets of vertical tubes, excess water in the condenser tube bundle, malfunction in float level control, worn and leaking vacuum pump system, and foaming of still contents causing capacity losses will further create excessive emission levels.

The final residue from distillation operations is unsuitable for reclamation and requires proper disposal. Incineration, landfill, and deep-well injection are common disposal methods.

#### 6.5.1.5 Evaporation--

6.5.1.5.1 Description [81,142,148]--Evaporation refers to the removal of a volatile liquid from solvent solutions by vaporization and concentration of nonvolatile dissolved or suspended solids or liquids. The process and the equipment are similar to that of distillation units, except that in evaporation, no attempt is made to separate components of the vapor. As shown in Figure 75, evaporation technology includes the evaporator unit, the external separator, and a condenser [81]. The waste is introduced at the product inlet, vaporized, and passed into the separator. The volatile component is captured in the condenser and may be incinerated, reclaimed, or disposed.

The concentrated nonvolatile component is removed at the product discharge and then is disposed of by landfill or incineration.

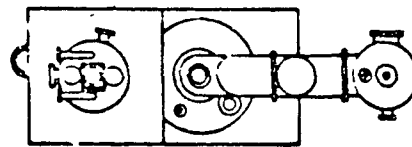
Single-pass, climbing-film type evaporators are widely used. They consist of a long tube bundle combined with a disengaged chamber. The solution is evaporated as it passes through the tubes. The tubes are heated by contact with steam. In the external separator, the liquid is separated and flows to the bottom, while the vapor goes to a condenser.

Agitated thin-film or wiped-film evaporators utilize a tall vertical cylinder surrounded by a heating jacket [149]. With this design, solvent is forced into a thin film along the heated evaporator walls by rotating blades. These blades agitate the solvent while maintaining a small clearance from the evaporator wall to prevent contaminant buildup on heating surfaces.

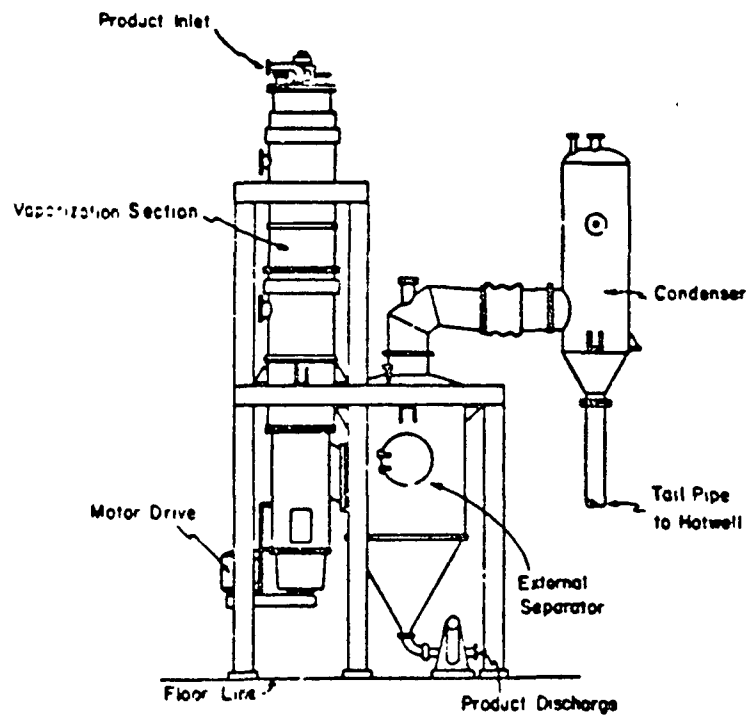
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[148] Tierney, D. R.; and Hughes, T. W. Source assessment: reclaiming of waste solvents, state of the art. Cincinnati, OH; U.S. Environmental Protection Agency; 1978 April. 53 p. EPA-600/2-78-004f.

[149] Reay, W. H. Recent advances in thin-film evaporation. London England, Luwa (U.K.) Ltd, 1963 June. Represented from the Industrial Chemist. 5 p.



Plan View



Elevated View

Figure 75. Detail of single evaporator showing associated equipment included in the evaporator module [143].

6.5.1.5.2 Cost Analysis [143]--Capital costs for climbing-film evaporators are itemized in Table 74. The most costly elements are the evaporator (including the external separator), and the steam generator. Table 75 summarizes the first year operating costs. Ninety percent of these costs are attributable to energy, water, and chemical requirements for the steam source. All costs are indexed to mid-1978.

Figures 76 and 77 show the capital costs (excluding land costs) and operating costs for five scales of operation, respectively. The capital and operating cost data indicate economics of scale. The life cycle average cost for a 1,000-gpm facility is \$8.48/1,000 gallons.

6.5.1.5.3 Applicability and Feasibility--Evaporation is a feasible method of recovering various contaminated solvents from metal finishing operations. Owing to its high cost, it is usually adopted by private contractors for solvent recovery service.

6.5.1.5.4 Environmental Impact--Evaporation units often discharge vapors to a condenser or fractionating tower. Hydrocarbons from these units are thus emitted through the vents of the subsequent control equipment.

The final residue from evaporation is unsuitable for reclamation. It can be disposed of by landfill, incineration, or deep-well injection.

## 6.5.2 Reclamation by Private Contractor [46]

### 6.5.2.1 Description--

Contract solvent reprocessing operations vary considerably in size, materials handled, and technology used. Batch stills, coil stills, scraped surface stills, or agitated thin-film evaporators are commonly employed to purify waste solvents.

Two major classes of materials are reprocessed. One is halogenated hydrocarbons such as methylene chloride, trichloroethylene, perchloroethylene, and 1,1,1-trichloroethane. These spent solvents derive primarily from degreasing and metal cleaning. The other category includes a wide range of solvents such as aliphatic hydrocarbons, aromatic and naphthenic hydrocarbons, alcohols, ketones, and esters. These waste solvents are generated by the chemical process industry, solvent manufacture and distribution, metal cleaning and coating, industrial paint use, printing operations, and paint manufacture.

Most of the larger contractors handle both halogenated hydrocarbons and miscellaneous solvents of the types listed above while some of the smaller operations process only the more valuable halogenated hydrocarbons.

TABLE 74. SUMMARY OF CAPITAL COSTS FOR EVAPORATION<sup>a</sup> [143]

Capital cost category module	Costs <sup>b</sup>						Quantities	
	Site Preparation	Structures	Mechanical equipment	Electrical equipment	Land	Total	Land, ft <sup>2</sup>	Other steam, lb/hr
Evaporator	\$410	\$31,100	\$216,250	\$10,813	\$1,370	\$ --	1,840	--
Steam generator	38	1,865	148,500	--	353	--	475	40,000
Waste pump	--	--	2,950	--	--	--	--	--
Sludge pump	--	--	798	--	--	--	--	--
Yard piping	225	--	1,130	--	--	--	--	--
Total	673	32,965	369,628	10,813	1,723	--	2,315	40,000
Supplemental capital costs	--	97,324 <sup>d</sup>	--	--	--	--	--	--
Subtotal of capital costs	--	--	--	--	--	\$513,126	--	--
Working capital <sup>d</sup>	--	--	--	--	--	63,615	--	--
AFDC <sup>e</sup>	--	--	--	--	--	25,656	--	--
Grand total of capital costs	--	--	--	--	--	602,397	--	--

<sup>a</sup>Scale = 1,000 gpm.<sup>b</sup>Mid-1978 dollars.<sup>c</sup>Building.<sup>d</sup>At one month of direct operating costs.<sup>e</sup>Allowance for funds during construction at 5% of capital costs.

TABLE 75. SUMMARY OF FIRST YEAR O&M COSTS FOR EVAPORATION<sup>a</sup> [143]

O&M Cost category module	Costs <sup>b</sup>						Quantities		
	Labor			Energy electrical (\$0.035/kWh)	Maintenance costs	Chemical costs	Total	kWh/yr	Natural gas, ft <sup>3</sup> /yr
	Type 1 Operator 1 (\$7.77/hr)	Type 2 Operator 2 (\$9.19/hr)	Type 3 laborer (\$6.76/hr)						
Evaporator	\$17,703	\$10,476	\$20,513	\$ --	\$1,125	\$ --	\$ --	--	--
Steam generator	1,179	209	15,586	319,000	1,807	372,000	--	--	44,120
Waste pump	--	--	--	1,730	--	--	--	49,429	--
Sludge pump	--	--	--	173	--	--	--	4,943	--
Yard piping	--	--	103	--	6	--	--	--	--
Total	18,882	10,685	36,202	320,903	2,938	372,000	--	54,372	44,120
Supplemental O&M costs	--	--	--	--	1,770	--	--	--	--
Subtotal of direct O&M costs	--	--	--	--	--	--	\$ 763,380	--	--
Administrative overhead <sup>c</sup>	--	--	--	--	--	--	152,676	--	--
Debt service and amortization <sup>d</sup>	--	--	--	--	--	--	158,911	--	--
Real estate taxes and insurance <sup>e</sup>	--	--	--	--	--	--	12,048	--	--
Total first year operating costs	--	--	--	--	--	--	1,087,015	--	--

<sup>a</sup>Scale = 1,000 gpm

<sup>b</sup>Mid-1978 dollars.

<sup>c</sup>At 20% of direct operating costs.

<sup>d</sup>At 10% interest over 5 years.

<sup>e</sup>At 2% of total capital.

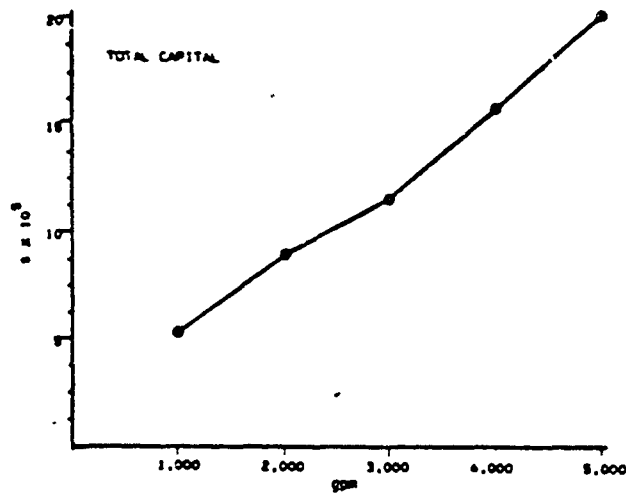


Figure 76. Evaporation: changes in total capital costs with scale [143].

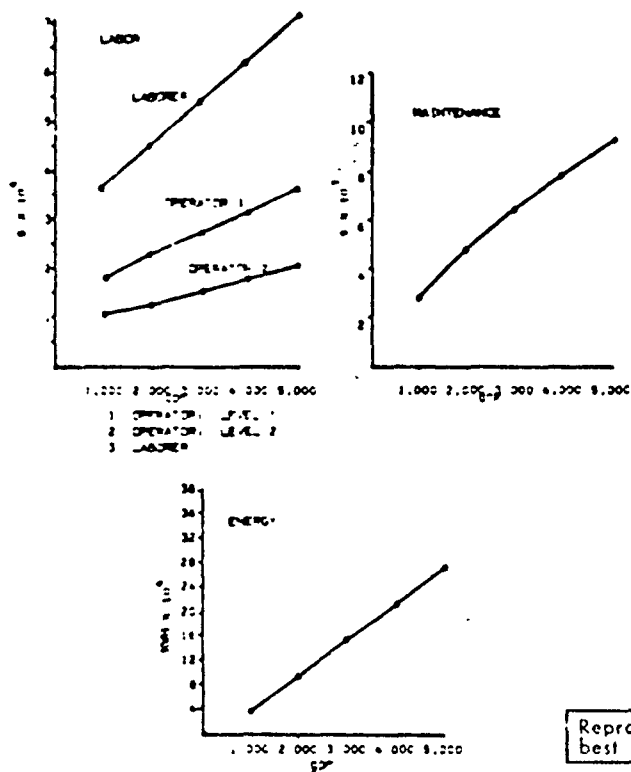


Figure 77. Evaporation: changes in operating requirements with scale [143].

It is roughly estimated that there were 80 to 100 contract solvent recovery operations in 1975 distributed throughout the United States. They are spread throughout the country's most populated areas, which also have large numbers of metal finishing operations. The greatest number of solvent reclaimers are in EPA Region V, which encompasses Ohio, Indiana, Illinois, Wisconsin, Michigan, and Minnesota. Many contractors normally take feedstock from out-of-state. In these plants, quantities handled can vary from 100,000 liters per year to 9,000,000 liters per year.

There are two basic modes of contract operation:

1. The contractor recovers the solvent, returns the material to its source, and is paid either by the quantity of dirty solvent originally taken or by the quantity of clean solvent returned.
2. The contractor buys the spent solvent (or in some cases is paid to haul it away), recovers the solvent, and sells it on the open market.

One of these systems is usually the primary mode with the alternative method accounting for a small portion of a contractor's business. The one favored depends on the system he finds most profitable. Most operations are owned by small individual companies, and only a few companies own more than one plant. Most solvent reclaimers have no substantial financial backing and are therefore limited in production facilities and expansion potential.

The feedstock is usually transported from its source to the recovery plant by the recovery contractor in his own trucks. More than 50 percent is transported in 55-gallon drums, and the remainder is transported in bulk tankers.

U.S. Department of Transportation regulations (CFR 8173.26) require "red label" liquids -- those with a flash point below 38°C (100°F) -- to be shipped in new drums or reconditioned ones displaying the reconditioner identification number and the pressure test date. This regulation applies whether the shipment is made by common carrier or in a private vehicle and affects large quantities of spent and reclaimed solvents.

#### 6.5.2.2 Waste Characterization--

6.5.2.2.1 Contents of Wastes--There is only one basic waste stream from solvent recovery operations; i.e., the still bottoms or sludges. Occasionally, this stream is incinerated on-site and the remaining ash residue becomes the waste stream. Analytical characteristics of still bottom samples collected from solvent reclaiming operations are shown in Table 76. These data are obtained from various sources (as indicated in the footnotes). However, the concentrations, and even presence of various hazardous materials fluctuates. This is due to differences in the



TABLE 76. CHARACTERISTICS OF STILL BOTTOM SAMPLES COLLECTED  
FROM SOLVENT RECLAIMING OPERATIONS

Sample designation	Percent volatile carried off at 103 - 105°C	Percent solids	Cd mg/L	Cr mg/L	Cu mg/L	Ni mg/L	Pb mg/L	Zn mg/L	Percent major components	Flash point °C °F	pH	Percent ash
1	77			280			1,700	190		48 118		
2	79			60			500	130		44 111		
3	89			60			400	130		51 124		
4	89								6% trichloroethylene	75 167		
5	99			10			100	10		40 104		
6	41									46 115		
7	14								3% trichloroethylene	no flash		
8	14									58 136		
9	61									53 127		
10	28									90 194		
11	97								45% trichloroethylene	84 183		
12	97								50% trichloroethylene	86 187		
13	59			160			1,200	100		68 154		
14	58			110			1,200	990		82 180		
15	83			10			100	10		74 165		
16	61			730			3,700	410		79 174		
17			0.48	2.0	0.54	60	0.23	25			4.7	

(continued)

TABLE 76 (continued)

Sample designation	Percent volatile carried off at 103 - 105°C	Percent solids	Cd mg/L	Cr mg/L	Cu mg/L	Ni mg/L	Pb mg/L	Zn mg/L	Percent major components	Flash point °C	Flash point °F	pH	Percent ash
18	25		39	139	346	192	1,898	3,467	25% toluene, mineral spirits, xylene, trace amounts of perchloroethylene, methanol, trichloroethylene				10.51
19		30							Acetone Xylene 30 ± 10 Toluene 15 ± 10 Naphthalene 30 ± 10 Paint pigments 20 ± 10 Oil 1.5 ± 0.5 Phenol <100 ppm	5	41	7.0	
20		30							Miscellaneous organic solvents, 50-70% Pigments, resin, etc., 30-50%	5	40		2 - 4
21		15		<100	<100	<100	1,140	1,700	Toluene 0.1% Ethyl benzene 0.4% Xylene 2.9% Trimethyl benzene 4.4% C <sub>8</sub> - C <sub>13</sub> aliphatics 92.2% Benzene <0.1%	0	32		7.03
22									1,1,1-trichloroethane 80-90% Paint pigments 10-20%				
23									Acetone 77% Methanol 12% Water 11% 50% thinner				

\*Designation No. 1 to 16 are from Reference 161. Designation No. 17-22 are from generator waste analysis form to landfilling obtained from state EPA offices. Designation No. 23-24 are from Reference 162.

characteristics and origins of the various batches of feedstock received during any given time period. The findings may be summarized as follows:

1. The majority of samples have a high volatile fraction indicating a large proportion of solvent and other volatile organics.
2. Waste streams from the recovery of chlorinated hydrocarbons contain considerable quantities of chlorinated solvents and therefore must be considered a potentially hazardous waste stream.
3. Waste streams from the recovery of solvents contain considerable quantities of metallic or other constituents which are potentially toxic, flammable, or both and must be considered a potentially hazardous waste stream.

6.5.2.2.2 Ultimate Disposal of Sludges [46]--The disposal method used for most sludges generated is incineration, either on-site or by an off-site contractor. Only 14 percent of the waste goes directly to a landfill, and other methods account for only a fraction of the total waste disposal. Two plants were using still bottoms as asphalt extender and concrete block fillers, but this type of use represents less than 0.1 percent of the total waste disposal on a national basis. The chlorinated solvent waste still bottoms sometimes are transported to an off-site contractor for deep well injection disposal. The ashes from incineration are landfilled.

#### 6.5.3 Economic Evaluation [46]

The principal factor affecting the economics of a solvent recovery operation is the size of the system used. Modern equipment varies in capacity from 2.8 - 6,100 liters (1/2 - 1,600 gallons) per hour and the economics improve considerably with size. This is because of the relative capital cost per unit of capacity is less as is overhead and maintenance, and operating labor costs are similar for all sizes of evaporators. Thus, they are considerably less per unit for a larger system. However, the economics of a large unit are seriously reduced if it cannot be efficiently utilized due to lack of raw material.

In general, on-site reclamation utilizes small-capacity systems, in the range of 75-380 liters (20-100 gallon) per hour due to the scale of their operation while private contractors will employ larger capacity units up to 1,500 liters (400 gallons) per hour, especially when located in a highly industrialized area. Contractors are usually prepared to transport their raw material from considerable distances since increased quantities of feedstock improve the overall operating efficiency of their plant.

It appears that in many areas DOT regulations are not enforced and that old drums are being used to ship solvents to and from reclaimers. Strict enforcement of these regulations could add up to 13¢/liter (50¢/gallon) to the total cost of hauling solvent to and from reclaimers in drums [46].

The actual value of recovered solvent varies considerably with the type of solvent, the size and type of reclaiming process used, the degree of purity of the product, and the general economic climate of the time and place in which it is being sold. Generally, the value of reclaimed solvent is closely tied to the value of the virgin material and will sell for from 50 percent to 90 percent of the value of virgin solvent. Actual prices range from 5¢/liter (20¢/gallon) for simple distillation of cheap solvent up to perhaps \$3/liter (\$10/gallon) for careful refining of a valuable solvent in special equipment.

The total recovery costs shown would at least double if the same reclaiming systems were installed on a contractor's site due to the costs of land, buildings, waste disposal, overhead, labor, and auxiliary equipment. However, several private contractors have reduced their costs substantially by purchasing used equipment. In many cases, costs of transporting feedstock will far exceed actual recovery costs.

#### 6.5.4 Future Trends and Developments

With the rapid increase in the cost of virgin solvents in recent years, the economics of solvent recovery have improved and the growth rate of this industry is increasing. No reversal of this trend is likely to occur in the near future in face of continuing price rises, particularly of petroleum derivatives. In addition, there is a considerably larger market to be tapped since the metal cleaning operation alone utilizes more than 58 million gallons per year of various solvents and at least 76 percent of the spent solvents are not reclaimed [46].

The technology for solvent recovery is relatively simple and well proven so no new developments are likely for reclaiming solvents, the bulk of materials handled. It appears, however, that greater use will be made of fractionation towers in the future so that a purer product of greater value can be obtained for more sensitive uses.

Also, reprocessing will move into new fields to recover more complex solvents and other basic materials included with present industrial wastes. Much of the technology for these processes is presently available or under development and only requires an attractive market to stimulate its use.

#### 6.5.5 Alternative Disposal Technology

Besides reclamation methods mentioned in the previous sections, solvents can be disposed of by several other routes: landfill, deep well injection, incineration and waterways [39,81]. Solvents can also be collected and disposed by off-site disposal service. Table 77 indicates the percent of plants and the quantity of solvent using various disposal routes [39]. It is shown in the table that the largest quantity of solvents goes to the reclaimer. However, Table 77 only represents 35 percent of the solvents used in the metal finishing industry. The major amount of solvents used seem to be either lost in the process or just illegally dumped [39].

TABLE 77. QUANTITY OF SOLVENT BY DISPOSAL ROUTES [39]

Disposal route	Percent of plants	Solvent disposed		
		Gallon/month (x 10 <sup>3</sup> )	Gallon/year (x 10 <sup>3</sup> )	Average gallon/year per plant
Incineration	2	8	96	251
Waterways	13	112	1,344	504
Landfill	18	135	1,620	441
Disposal service	39	547	6,564	822
Reclaimer	21	904	10,848	2,509

##### 6.5.5.1 Landfill--

The hazardous waste landfill may be used for ultimate disposal of any hazardous solvent wastes emanating from operation and treatment facilities. A more detailed description for landfill operations is provided in Section 6.1.5.

Major emissions from landfill operations are sometimes comprised of fugitive hydrocarbons resulting from vaporization and evaporation of solvent wastes. Solvents buried in drums will have a much slower evaporation rate. However, it is believed this method is rarely used due to the economics.

Methods have been developed to modify landfills to make them acceptable for receipt of chemical wastes. These operations provide for protection of the surface and subsurface waters by location to avoid these waters. Barriers and collection devices may be employed if there is potential for leaching or percolation to groundwaters. Liners are sometimes used to keep leachate from entering groundwaters. Landfills should be sited to take advantage of geological factors. Cover material can also be utilized to eliminate evaporation and infiltration of water.

According to EPA regulations, liquid waste cannot be landfilled unless it is "solidified." Solidification of a 55-gallon drum of 100 percent liquid solvent waste by some absorbent results in about two drums of material. Commercially, the landfill disposal charge is in the range of \$190 to \$230 per drum of liquid waste.<sup>a</sup> Due to higher cost, most strict regulations and major environmental threats of leaching/run-off and odor, landfill of most hazardous organic wastes will not be technically attractive. The method will normally be selected only if other methods are not suitable.

#### 6.5.5.2 Incineration--

Incineration is the control technology most universally applicable to sources of volatile organics. Because of its need for supplemental fuel [133], incineration is most useful when the heat developed during combustion can be recovered and used to offset other plant energy needs. A description, together with regulations and costs for incineration are provided in Section 6.2.3. Although incineration can be extremely effective in destroying certain types of wastes, it is important to recognize that the cost of incineration for wastes can vary widely. The cost primarily depends on the type and concentration of organics and the type of facility required to handle the waste. Table 78 gives disposal charges for some organic wastes by incineration. Transportation costs are not included in the table.

Obviously, the disposal charge for halogenated compounds is much higher than that for other compounds. Also, wastes which are hard to handle or have low heat contents would increase the charge.

Generally speaking, incineration of organic solvents is technically viable and environmentally desirable, but the high unit costs will cause industry to prefer to utilize other less costly alternatives if they are acceptable to regulatory agencies.

#### 6.5.5.3 Deep-Well Injection--

Deep-well disposal is a method for disposing of solvent wastes by injection into the earth. The prime consideration is the geology and hydrology of the area where the deep-well injection plant is located. Injection can pollute groundwaters unless site selection, construction, and operation are controlled. If the area is uncovered, evaporation occurs and hydrocarbon emission results.

Emissions from deep wells probably occur through the well casing, through the injection tubing, and out the wellhead facilities. Corrosion of the casing can cause leaks through the system where gases can emanate through the porous strata. Earthquakes or lateral strata movement to abandoned oil/water drill areas can also release emissions. However, emissions from deep-well disposal units are considered negligible when the proper type of well is utilized.

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<sup>a</sup>Personal communication with Robert Ross & Sons, Inc.

TABLE 78. DISPOSAL CHARGES OF ORGANIC WASTE BY INCINERATION<sup>a</sup>

Designation number	Wastes	Percent of contents	Disposal charge, \$55-gallon drum	
			Regular	Side-door <sup>b</sup>
7188	Apricot pit oil	90 - 100	25.75	52.45
7189	Phenol	100		63.95
7187	p-cresol acetate	100	19.10	32.45/15 gal drum
8065	Thionyl chloride	100		276.55
5620	Motor oil	40	28.75	51.75
	Acetone	40		
	Methanol	11		
	Toluene	4		
5624	1,2-Dichlorobenzene	65	111.50	138.20
5626	Ethylene dichloride	80	111.50	138.20
2638	Ethyl benzene	95 - 100	23.00	46.00
2641	Hexane	75 - 90	23.00	46.00
2642	Toluene	90 - 100	17.25	40.25
2644	Toluene	95 - 100		58.10
	Thionyl chloride	0 - 5		
4893	Methylene chloride	90	129.95	152.95
	Still bottoms (residual dimethyl chloride)	10		
4894	Methylene chloride	98	135.05	158.05
	Still bottoms (residual dimethyl chloride)	2		
4998	Methanol	85	23.60	46.00
	Chlorobenzene	15		
5000	Ethylene acetate	93	17.25	40.25

a

<sup>b</sup>"Side-Door" Method of Incineration will be used when the viscosity of the waste is such that it will not pour from the drum or when hazard warrants. Because "Side-Door" Incineration requires a much longer processing time, drums of waste that require "Side-Door" Incineration will be scheduled for delivery/pick-up on a limited quantity basis.

The disposal charge of deep well injection for waste solvent is in the range of \$15 to \$40 per metric ton (6-15¢/gal) assuming it is comparable to the disposal charge for oil wastewater [85].

#### 6.5.4 Waterways [151,152]

Dilute wastewaters are sometimes discharged in a receiving lake, river, estuary or ocean after appropriate treatment. Surface discharge via a pipe or ditch leading to the shoreline is the least expensive approach. Submerged discharge devices include: open-end pipes, nozzle-end pipes, diffuser systems consisting of a closed-end pipe with slots or holes along it, and split discharges through a branched-pipe system.

The location of the discharge point and type of dispersion mechanism are of importance in protecting water users and avoiding unsightly conditions. A properly designed subsurface dispersion system can allow the full assimilative capacity of the receiving body to be utilized. Treatment requirement can thus be lowered.

Discharge devices are installed to protect against shoreline contamination, oil slicks, and fog formation, and to protect plant intake water. The design of a dispersion system is dependent upon the uses of the receiving water body, location of nearby intakes, flow and turbulent nature of waterways, and physical/chemical effluent and stream characteristics. Although the least expensive disposal method, waterway disposal is not widely practiced because of its potential for violating the Clean Water Act and other regulations.

### 6.6 DISPOSAL AND RECLAMATION OF PAINTS

#### 6.6.1 Disposal Methods

The paint application method with the biggest impact on the amount of paint wastes generated by metal coating processes is spray coating. Spray coating, as discussed in Section 5, is used by 60 percent of the industry and accounts for 90 percent of the waste paint generated. This is estimated to be between 103,500 and 194,400 metric ton/year (112,500 and 216,000 ton/year). This waste is not listed specifically as a hazardous waste according to the Resource Conservation and Recovery Act (RCRA) but it should be tested for hazard potential according to the RCRA procedures before disposal. As discussed in Section 5, the variety of materials used in paints make some paint wastes potentially hazardous while others may not be hazardous.

The information available indicates that landfilling is the principal paint waste disposal method. One survey [46] indicates that 13 plants contacted landfilled their paint wastes. The hazardous

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[151] Ross, R. D. Industrial waste disposal. New York, Reinhold Book Corporation, 1968. 340 p.

[152] Diffusion of effluents into receiving waters. Manual on disposal of refinery wastes, Volume 1. New York, American Petroleum Institute, 1963.



or nonhazardous nature of the waste (based on RCRA tests) decides whether the waste can be disposed of in a sanitary landfill or a secured landfill, respectively.

It is possible for this waste to be incinerated. This is not commonly done, however. This is mostly due to the increased cost of incineration plus landfilling versus landfilling alone. One source [18] provided estimates of typical costs. A cost of \$10/metric ton (wet) is given [\$13/metric ton (dry)] for sanitary landfilling. For incineration plus sanitary landfilling of the ash, the cost increased to \$51/metric ton (wet) [\$67/metric ton (dry)]. The next best step, which would be incineration plus disposal of the ash in a secure landfill, increases the cost slightly to \$54/metric ton (wet) [\$71/metric ton (dry)]. Since incineration reduces the waste to an innocuous ash, this third alternative is not practiced, according to the literature. The second method is not commonly practiced, either. The survey that indicated that all of the 13 plants landfilled their wastes also indicated that 2 of those plants sent some (no amount given) of their coating wastes to an incinerator first.

#### 6.6.2 Reclamation

Reclamation of paint waste is not commonly practiced. There is, however, an existing process for converting waste paint to original quality product [153]. Based on the knowledge of this company, it is the only one in existence today. It handles wastes from two automotive assembly plants. The process has a capacity of 1,000 gal/day (20, 55-gal drums/day). This process is specifically designed to handle overspray paint waste from spray coating operations. Because overspray is essentially still the virgin paint, it is more amenable to reclaiming (or more correctly recycling). This process does not handle scrapings or other dried waste paint. It is also sensitive to contamination. Care must be taken to ensure that the paint is not contaminated by oils, greases, soaps, silicones, asphaltic sealers, vinyl compounds, latexes or paint strippers. For example, excessive quantities of highly alkaline wash water compounds may dechromatize sensitive colors such as iron blues, chrome greens, moly-oranges, and some organic reds. Acid conditions must also be avoided. A compound (such as clay) should be used to keep the solution as close to neutral as possible.

The overspray is collected by a vertical wash water curtain. The wash water is chemically treated prior to spraying by adding a flocculating agent. The flocculants are of three general classes. They are sodium or potassium hydroxides or alkaline salts, suitable polyelectrolytes (such as polyacrylamides, some proteins and

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[153] Telephone communications with Robert A. Thomas, President, Clyde Paint and Supply Company, Inc., Clyde, Ohio.

polysaccharides) and various kaolinities and bentonites. The overspray is flocculated as it hits the wash water and is collected in a tank under the spray booth. The paint forms a layer on top of the water. This layer is skimmed off either manually or mechanically and put into 55-gallon drums. The drums are sent to the reclaimer [154].

The sludge has a very thick, dough-like consistency. A preliminary mixing step using dough-type mixers is performed to make the sludge easier to work with. Large particulates are removed through a rough straining operation. The particulates are removed because they will not accept solvent. The amount of particulates depends on the waste. Solvent is then mixed into the sludge to bring it to a paint viscosity. The solvent blend used depends on what the original product specifications were. The solvent/sludge mixture is then dehydrated by vacuum distillation. The solvent-to-water lost ratio is about 7 gallons solvent/1 gallon water. The solvent is refluxed back into the kettle. After dehydration, the mixture is allowed to cool. The desired viscosity is achieved by adding the correct solvents and additives. These are determined by the original paint composition. The mixture is then filtered and centrifuged to remove any particulate contaminants. The final product should meet the physical standards of the original paint. The product is filled into drums for shipping or storage.

The most recent (1971) cost figures indicate a cost savings of \$0.50 to \$1.50 per gallon delivered to the customer.

### 6.6.3 Conclusions and Recommendations

The biggest contributor of waste paint is the spray coating operation. Almost all of this waste is disposed of directly into landfills. Very little is incinerated prior to landfilling. This waste paint can be reclaimed and a process for this exists. However, there is apparently little interest at this time in reclaiming the waste. This is due to the apparent ease with which the waste can be landfilled and the fact that only one small reclaiming operation exists.

It is quite possible that this is not a significant problem. Since RCRA has mechanisms to determine the hazardous nature of wastes, this will help to ensure that wastes get proper disposal. Further study could be done on determining how much of the paint waste is actually hazardous.

Since a reclamation process exists, this may deserve further investigation. A study of the economic advantages of reclaiming may also be of interest.

[154] Lapointe, A. J. Quality coatings derived from overspray solid wastes. First international antipollution coating seminar; 1971 December 14; Chicago. Chemical Coaters Association.

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APPENDIX A  
OIL COMPOSITION DATA

Composition data for new (raw material) and waste straight oils, emulsified oils, and synthetic fluids are listed in this appendix. Raw material data are listed first (Table A-1) followed by waste data (Table A-2). Data are presented in sequence of straight oils, emulsified oils, and synthetic fluids for both the raw materials and wastes. Also, raw materials applications and their physical properties, and the type of metal working operation generating the waste are identified wherever they are known.

Data were scrutinized and assigned a data quality rating based on an A-B-C quality system. Data with an "A" quality are those found to have been sampled and analyzed with some QA/QC protocol attached; e.g., demonstrated comparison with analytical standards, use of splits, blanks, etc. "B" quality is assigned to data with documented sampling and analysis procedures but no evidence of QA/QC. "C" quality data are those values for which no documentation has been provided and/or the accuracy is undeterminable.



TABLE A-1. METAL WORKING OIL COMPOSITION DATA

Process or material description	Material Composition		Physical characteristics	Data quality
	Component	Weight percent		
Cutting oil, petroleum base	Petroleum hydrocarbons	97	Specific gravity: 0.912	C
Cutting oil, petroleum base, fatty oil	Mineral oils	84	Specific gravity: 0.898	B
	Ethylene-propylene copolymer	2	Insoluble in water	
	Lard oil	8	Flash point: 182°C (360°F)	
	Di-tertiary-nonyl-polysulfide	4		
	Chlorinated paraffin			
Cutting oil, sulfurized mineral-lard oil	Odorant (16 ppm)			C
	Mineral oil base		Flash point: 177°C (350°F)	
	Fatty oil	6		
Cutting oil, sulfurized mineral-lard oil	Sulfur	1.96	Pour point: -23°C (-10°F)	C
	Mineral oil base		Flash point: 171°C (340°F)	
	Fatty oil	6		
Soluble metal working oil, petroleum based	Sulfur	1.99	Pour point: -34°C (-30°F)	C
	Petroleum oil		Specific gravity: 0.99	
	Chlorinated wax		Water-soluble	
Soluble oil, petroleum based; for machining and grinding	Emulsifiers			C
	Odorants			
	Dye			
Rust protective, oil-based	Petroleum base oil	50	Specific gravity: 0.9340 to 0.9537	C
	Chlorinated paraffin	7-10		
	Kerosene	10	Volatiles, volume percent: 10-15	
Rust protective, asphalt-based	Petroleum hydrocarbons		NA	C
	Petroleum sulfonates			
	Petroleum oxides			
Rust protective, asphalt-based	Limestone	65	Flammable liquid	B
	Asphalt	18	Boiling point: 123°C (253°F)	
	Naphtha	15	Vapor pressure @ 868 mm Hg: 2.0	
	Asbestos	2	Vapor density (Air = 1): 3.1	
Rust-proofing compound, oil-based			Percent volatile by volume, %: 25	C
			Solubility in water: 0	
	Petroleum naphtha	>10		
Synthetic metal working fluid, heavy duty for stainless steels and hardened tool steels, grinding, belt grinding and machining	Mineral spirits	>10		C
	Methylene chloride	>10		
Synthetic metal working fluid, heavy duty for stainless steels and hardened tool steels, grinding, belt grinding and machining	Synthetic base fluids		pH (5% emulsion): 9.0	C
	Proprietary grinding aids	20	Weight, lb/gal: 8.4	
	Chlorine	8	Water-soluble	
	Sulfur	2	Recommended dilution: 20:1 to 100:1	

(continued)

TABLE A-1 (continued)

Process or material description	Material Composition		Physical characteristics	Data quality
	Component	Weight percent		
Synthetic metal working fluid, moderate duty machining and grinding fluid for cast iron, steel, copper, and aluminum alloys	Synthetic base fluids		pH, concentrate: 9.9	C
	Chlorine/chloride	<0.01	pH, 1:40 dilution: 8.9	
	Sulfur	0.32	Weight, lb/gal: 8.35	
			Water-soluble Recommended dilution: 20:1 to 50:1	
Coolant, synthetic lubricant for machining or grinding	Synthetic fluid		Water-soluble	C
	Alkaline liquid		pH: 10.5-10.9	
	Water base		Biodegradable	
	Bactericide		Recommended dilution: 6:1 to 25:1	
Coolant, synthetic lubricant for machining, grinding and drilling	Synthetic base fluid		Water-soluble	C
	Tertiary amine		Biodegradable	
	Fatty acid		Recommended dilution: 10:1 to 40:1	
	Chelating agent			
	Bactericide			
	Oxidizing salt			
Cutting fluid, synthetic for grinding, machining, and drilling	Synthetic base fluid, proprietary-formulation		Water-soluble	C
			pH: 8.9-9.1	
			Biodegradable	
			Recommended dilution: 20:1 to 50:1	
			Specific gravity: 1.0428	
Forming lubricant for steel, tin-plate, and non-ferrous metal cans			Weight, lb/gal: 8.69	C
	Mineral oil		Appearance: clear, dark oil	
	Polyglycol		Boiling point: 600°-680°F	
	Chlorinated esters		Flash point: 310°F (C.O.C.)	
	Petroleum sulfonate		Fire point: 340°F (C.O.C.)	
	Amine soaps		Specific gravity: 0.960 ± 0.005	
			pH of 5-10% dilution: 8.8 ± 0.5	
			Vapor pressure @ >60 mm Hg: 0.005	
			Viscosity at 100°F: 750 sec (S.U.V.)	
			Pour point: less than 0°F	
			Pounds/gallon at 60°F: 8.25 ± 0.05	
			Solubility in water	
			Recommended dilution: 1:10 to 1:20	
Quench oil	Emulsified oil		Specific gravity: 1.07	C
	Morpholine	1	Soluble in water	
	Sodium nitrite	2	Recommended dilution: 1:3 to 1:20	
			Appearance: cloudy yellow fluid	

TABLE A-2. WASTE OIL COMPOSITION DATA

Process and/or waste description		Waste composition <sup>a</sup>	Data quality
One month old cutting oil	A.P.I. gravity	22.0	B
	Ash content, %	0.16	
	Carbon residue, %	2.2	
	Pour point, °F	-25	
	Flash point, °F	380	
	Fire point, °F	405	
	Heat of combustion, Btu/lb	17,800	
	Viscosity, SUS @ 100°F	196.3	
	Viscosity, SUS @ 210°F	31.8	
	Sulfur, %	0.3	
	Silver, mg/L	0.0	
	Sodium, mg/L	180	
	Zinc, mg/L	12	
	Copper, mg/L	150	
	Aluminum, mg/L	33	
	Barium, mg/L	120	
	Nickel, mg/L	5	
	Chromium, mg/L	28	
	Calcium, mg/L	1,900	
	Iron, mg/L	520	
	Silicon, mg/L	90	
	Tin, mg/L	21	
	Lead, mg/L	15	
	Phosphorus, mg/L	150	
	Boron, mg/L	120	
	Magnesium, mg/L	42	
	Vanadium, mg/L	8	
	Molybdenum, mg/L	7	
	Manganese, mg/L	17	
	Cadmium, mg/L	3	
	Titanium, mg/L	0	

(continued)

TABLE A-2 (continued)

Process and/or waste description		Waste composition <sup>a</sup>	Data quality
Machine tool cutting lubricants and cooling oil from lathes, drill presses, milling machines, grinders, and screw machines	Petroleum oil, %	80	B
	Water, %	20	
	Volatile materials at 100°C, %	33	
	Non-volatile materials, %	67	
	Non-combustible materials at 650°C, %	0.1	
	Lead, mg/L	21.3	
	Zinc, mg/L	13.6	
	Nickel, mg/L	<0.01	
	Copper, mg/L	12.7	
	Cadmium, mg/L	<0.01	
	Chromium, mg/L	<0.01	
	Perchloroethylene, mg/L	50-100	
274 Waste machine oil and cleaner	Machine oil, %	70	
	Trichloroethylene, %	30	
Waste cutting oil	Ash content, %	0.05	B
	Carbon residue, %	0.1	
	Pour point, °F	+5	
	Flash point, °F	270	
	Fire point, °F	200	
	Heat of combustion, Btu/lb	20,000	
	Viscosity, SUS @ 100°F	27.4	
	Viscosity, SUS @ 210°F	10.3	
	Acid, mg KOH/g	0.3	
	Sulfur, %	0.3	
	Silver, mg/L	0.0	
	Sodium, mg/L	1	
	Zinc, mg/L	190	
	Copper, mg/L	12	

(continued)

TABLE A-2 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Waste cutting oil (continued)	Aluminum, mg/L	3
	Barium, mg/L	7
	Nickel, mg/L	0
	Chromium, mg/L	1
	Calcium, mg/L	82
	Iron, mg/L	18
	Silicon, mg/L	2
	Tin, mg/L	8
	Lead, mg/L	8
	Phosphorus, mg/L	15
	Boron, mg/L	0
	Magnesium, mg/L	1
	Vanadium, mg/L	0
	Molybdenum, mg/L	1
	Manganese, mg/L	6
	Cadmium, mg/L	5
	Titanium, mg/L	0
Waste cutting oil and coolant	Bilayered liquid	B
	Total solids, %	5
	Dissolved solids, %	<1
	pH	7.6
	Flash point (organic phase), °F	102
	Closed cup (aqueous phase), °F	162
	Btu per lb, organic phase	16,550
	Btu per lb, aqueous phase	20
	Ash, %	3
	Kerosene, %	0.4
	Light lube oils, %	5
	Heavy lube oils, %	30
	Trichloroethylene, %	10

(continued)

TABLE A-2 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Waste cutting oil and coolant (continued)	Silver, mg/L	30
	Arsenic, mg/L	<0.01
	Cadmium, mg/L	4.2
	Chromium, mg/L	520
	Copper, mg/L	96
	Nickel, mg/L	300
	Lead, mg/L	3,500
	Zinc, mg/L	43
	Antimony, mg/L	<0.01
	Total cyanide, %	0.02
	Free cyanide, %	<0.02
	Sulfide, %	3.2
	Bisulfite, %	<4.0
	Sulfite, %	4.0
Waste oil from machine lubrication in the manufacturing of cold formed parts	pH	6.8
	Oil, %	99
	Lead, mg/L	114
	Zinc, mg/L	324
	Nickel, mg/L	4.0
	Copper, mg/L	41.8
	Beryllium, mg/L	6.5
	Cadmium, mg/L	0.17
	Chromium, mg/L	2.5
	Mercury, mg/L	<0.1
	Arsenic, mg/L	<0.1
	Phosphorus, mg/L	190
	Sulfur, mg/L	875
	Cyanide, mg/L	0.5
	Phenols, mg/L	0.96
	PCB, mg/L	<0.5
	Noncombustible ash, %	0.88

(continued)

TABLE A-2 (continued)

Process and/or waste description	Waste composition <sup>a</sup>			Data quality
		High	Low	Average
Waste cutting oil from roll presses, punch presses, etc.	Water, %	59	28.7	33.6
	Oil, %	66.4	41	66.4
	Copper, mg/L	3.5	2.4	2.9
	Zinc, mg/L	5.2	10.6	6.4
	Nickel, mg/L	0.3	1.5	0.8
	Chrome, mg/L	4.3	10.6	6.6
Waste lubricating and cutting oils from machining operations	Oil, %		70-100	
	Water, %		0-30	
	Solids, %		0-5	
	Zinc, mg/L (maximum)		75	
	Phosphorus, mg/L (maximum)		2,187	
	Phenolic antioxidant, mg/L (maximum)		10,000	
	Phosphate ester additive, mg/L (maximum)		2,600	
	Sulfur, mg/L (maximum)		6,000	
	Chlorine, mg/L (maximum)		21,000	
	Tricresyl phosphate, mg/L (maximum) (2,6-di-tert-butylphenol)		26,000	
	4,4'-methylenebis, mg/L (maximum)		10,000	
Machining fluid waste	Oils, %		97.4	
	Solids, %		1.6	
	Solvent (aliphatic), %		1.0	
	Lead, mg/L		0.01	
	Zinc, mg/L		1.2	
	Nickel, mg/L		0.12	
	Copper, mg/L		0.08	

(continued)

TABLE A-2 (continued)

Process and/or waste description		Waste composition <sup>a</sup>	Data quality
Machining fluid waste (continued)	Beryllium, mg/L	0.002	
	Cadmium, mg/L	0.22	
	Chromium, mg/L	0.24	
	Mercury, mg/L	0.001	
	Chlorine, mg/L	800	
	Bromine, mg/L	8	
	Phosphorus, mg/L	41.6	
	Sulfur, mg/L	3,800	
	PCB, mg/L	6.9	
	Phenols, µg/L	4.5	
Oil and chlorinated solvent waste and waste from metal stamping operation	Cutting oil, %	25-65	C
	Petroleum oil, %	10-15	
	Perchloroethylene, %	15-25	
	Forsnic acid, %	5	
Waste drawing oil from punch press	A.P.I. gravity	25.8	B
	Pour point, °F	+20	
	Heat of combustion, Btu/lb	19,500	
	Viscosity, SUS @ 100°F	1546.1	
	Viscosity, SUS @ 210°F	126.4	
	Acid, mg KOH/g	0.4	
	Sulfur, %	0.5	
	Silver, mg/L	0.0	
	Sodium, mg/L	12	
	Zinc, mg/L	200	
	Copper, mg/L	3	
	Aluminum, mg/L	3	
	Barium, mg/L	220	
	Nickel, mg/L	0	

(continued)



TABLE A-2 (continued)

Process and/or waste description		Waste composition <sup>a</sup>	Data quality
279	Waste drawing oil from punch press (continued)	Chromium, mg/L	5
		Calcium, mg/L	38
		Iron, mg/L	6
		Silicon, mg/L	2
		Tin, mg/L	7
		Lead, mg/L	4
		Phosphorus, mg/L	58
		Boron, mg/L	0
		Magnesium, mg/L	1
		Vanadium, mg/L	6
		Molybdenum, mg/L	1
		Manganese, mg/L	3
		Cadmium, mg/L	4
		Titanium, mg/L	0
	Spent drawing solution from aluminum wire operation	Mineral oil, %	68
		Tallow oil, %	17
		Aluminum fines, %	15
	Quench oil	Naphthalene based oil, %	10-90
		Water, %	10-90
		Organic solids, %	10-30
	Sludge from quench oil tank	Paraffinic oil, %	30-50
		Water, %	10-20
		Carbon scale, rust, dirt, %	40-60
	Waste emulsified oil	A.P.I. gravity	2.1
		Viscosity, SUS @ 100°F	229.0
		Viscosity, SUS @ 210°F	83.9

(continued)

TABLE A-2 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Waste emulsified oil (continued)	Sulfur, %	0.1
	Silver, mg/L	0.0
	Sodium, mg/L	400
	Zinc, mg/L	160
	Copper, mg/L	15
	Aluminum, mg/L	39
	Nickel, mg/L	4
	Chromium, mg/L	7
	Calcium, mg/L	0
	Iron, mg/L	18
	Silicon, mg/L	22
	Tin, mg/L	140
	Lead, mg/L	50
	Phosphorus, mg/L	270
	Boron, mg/L	2
	Magnesium, mg/L	11
	Vanadium, mg/L	7
	Molybdenum, mg/L	16
	Manganese, mg/L	20
	Cadmium, mg/L	21
	Titanium, mg/L	21
Emulsified oil from a steel mill	Oil, %	0.51
	Water, %	99.49
	Oil phase analysis	
	Hydrocarbon oil, %	79.56
	Polar additives, %	20.44
	Polar additives consist of a mixture containing petroleum oxides (i.e., oxidized petroleum fraction) and petroleum sulfonates (i.e., alkyl acrylsulfonate salts)	

(continued)

TABLE A-2 (continued)

Process and/or waste description		Waste composition <sup>a</sup>	Data quality
Machine coolant	Oil, %	20	C
	Water, %	80	
Emulsified oil used as a metal working fluid in aluminum can manufacturing plant	Metals		B
	Cu, ppm	39	
	Co, ppm	11	
	Ni, ppm	100	
	Pb	Not detectable	
	Sb	Not detectable	
	Hg	Not detectable	
	As	Not detectable	
	Cd	Not detectable	
	Cr	Not detectable	
	Solids, %	57	
	Volatile organics	Less than 100 ppb	
	Pesticides and PCB's	Less than 100 ppb	
	Base/Neutrals	Less than 100 ppb	
	Acid extractables	Less than 100 ppb	
Emulsified oil from machining and grinding	Oil, %	2	B
	Water, %	98	
	Oil phase composition		
	Chlorinated paraffin, %	7-10	
	Kerosene, %	10	
	Oil, %	50	

(continued)

TABLE A-2 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Emulsified oil from aluminum can manufacturing plant	Food based oil, %	8
	Water, %	91
	Aluminum fines, %	1
Spent emulsified oil from cold rolling of strip and sheet steel from a specialty steel plant	pH	6.7
	BOD <sub>5</sub> , mg/L	3,250
	COD, mg/L	18,000
	Oil and grease, mg/L	7,200
	TOC, mg/L	5,200
	Dissolved solids, mg/L	1,600
	Suspended solids, mg/L	590
	Volatile solids, mg/L	1,800
	Total solids, mg/L	2,190
	Methylene blue activated substances, mg/L	180
Wastewater soluble grinding coolant and oil based rust proofing materials	Water, %	88.5
	Cimcool Five Star 40, %	2.7
	No. 2 fuel oil, %	2.2
	Oakite 117, %	3.3
	Oakite special protective oil, %	3.3
	Cimcool Five Star 40 components	
	Cadmium, %	<0.0001
	Chromium, %	<0.0005
	Lead, %	<0.0005
	Nickel, %	<0.0005
	Zinc, %	<0.0001

(continued)

TABLE A-2 (continued)

Process and/or waste description	Waste composition <sup>a</sup>		Data quality
Wastewater soluble grinding coolant and oil-based, rust-proofing materials (continued)	Oakite 117 components		
	Mineral spirits, %	>10	
	Petroleum naphtha, %	>10	
	Methylene chloride, %	>10	
	Oakite special protective oil components		
	Petroleum hydrocarbons, %	>10	
	Petroleum sulfonates, %	<10	
Wastewater soluble oil	Petroleum oxidates, %	<10	
	pH	8.1	B
	Water, %	78	
	Petroleum oil, %	16	
	Soap, %	4	
	Biocide, %	1	
	Lead, mg/L	73.9	
	Zinc, mg/L	1,110	
	Nickel, mg/L	7.5	
	Copper, mg/L	44	
	Mercury, mg/L	<0.1	
	Beryllium, mg/L	7.5	
	Cadmium, mg/L	<0.1	
	Trivalent chromium, mg/L	14	
	Arsenic, mg/L	<0.1	
	Phosphorous, mg/L	25	
	Sulfur, mg/L	83	
	Cyanide, mg/L	1.05	
	Phenols, mg/L	5.7	
	PCB, mg/L	0.64	
	Noncombustible ash, %	0.835	

(continued)

TABLE A-2 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Machining fluid waste (emulsified oil)	Water, % 64	B
	Solids, % 15	
	Oil, % 21	
	Noncombustible ash, % 6.8	
	Lead, mg/L 0.02	
	Zinc, mg/L 8.7	
	Nickel, mg/L 2.1	
	Copper, mg/L 0.9	
	Beryllium, mg/L 0.008	
	Cadmium, mg/L 0.12	
	Chromium, mg/L 0.10	
	Chlorine, mg/L 1,100	
	Bromine, mg/L 12	
	Phosphorus, mg/L 50.8	
	Sulfur, mg/L 2,100	
	PCB, mg/L 24.3	
	Phenols, µg/L 2.8	
	Aromatic solvent, mg/L 21.2	
	Aliphatic solvent, mg/L 59.0	
Oily waste generated from the machining of metal parts	Ammonia, % 0.0040	B
	n-Butyl acetate, % <0.0013	
	Copper, % 0.00075	
	Formaldehyde, % <0.01	
	Formic acid, % <0.01	
	Hydrochloric acid, % 0.02	
	Methylene chloride, % <0.0044	
	Nickel, % 0.00014	
	Oil and grease, % 31.4	
	Perchloroethylene, % 0.0447	

(continued)

TABLE A-2 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Oily waste generated from the machining of metal parts (continued)	Polychlorinated biphenyls, %	<0.005
	Sodium hydroxide, %	0.043
	Sodium metasilicate (as total silica), %	<0.001
	Sulfuric acid, %	0.73
	Toluene, %	<0.0013
	Trichloroethylene, %	<0.0052
	Xylene (total), %	<0.0028
Emulsified oil coolant from machine shop	pH	7.9
	Oil, %	2
	Water, %	98
	Lead, mg/L	2.0
	Zinc, mg/L	7.13
	Nickel, mg/L	<0.03
	Copper, mg/L	0.25
	Cadmium, mg/L	<0.03
	Chromium, mg/L	0.95
	Phosphorus, mg/L	590
Spent water soluble oil from tapping, roll mill, etc., operations	Water soluble mineral oil, %	5-100
	Water, %	0-95
	Iron and aluminum fines, %	0-2
Spent can forming lubricant	Quakerol #539, %	5
	Water, %	95
Quakerol #539 is composed of amine soap, polyglycol, mineral oil, and petroleum sulfonate chlorinated ester		C

(continued)

TABLE A-2 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Oily waste generated from the machining of metal parts	Ammonia, mg/L	12
	n-Butyl acetate, mg/L	0.42
	Copper, mg/L	2.7
	Formaldehyde, mg/L	100
	Formic acid, mg/L	100
	Free isocyanate, mg/L	
	Hydrochloric acid, mg/L	1,800
	Methylene chloride, mg/L	1.4
	Naphtha, mg/L	
	Nickel, mg/L	0.5
	Oil and grease, %	3.62
	Perchloroethylene, mg/L	1.9
	Polychlorinated biphenyls, mg/L	1
	Sodium hydroxide, mg/L	5,200
	Sodium metasilicate (as total silica), mg/L	10
	Sulfuric acid, mg/L	5,100
	Toluene, mg/L	0.42
	Trichloroethylene, mg/L	1.6
	Xylene (total), mg/L	0.84
Waste lubricant from a cold forming operation	Mineral oil and fatty oil, %	10-95
	Lead oleate, %	3-10
	Lead, %	2-8
	Water	Balance
Machine coolant	Water, %	70-90
	Paraffinic oil, %	5-10

(continued)



TABLE A-2 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Emulsified oil from metal grinding operation	Oil and grease (up to), %	5
	Water (up to), %	97
	Total solids, %	1.53
	Chlorine, mg/L	570
	Phosphorus, mg/L	8.1
	Sulfur, mg/L	130
	1,1,1-Trichloroethane, mg/L	28
Waste coolant and lubricant from grinding and machining operation	Flammable liquid	
	Flash point, °F	>200
	Solids, %	1
	Water, %	80
	Trim sol, %	2
	DuBois C-1575A, %	2
	Trim 7030, %	2
	Hydraulic oil, %	10
	Mineral spirits, %	1
	Trim Sol Components	
	Petroleum oil, chlorinated wax, emulsifiers, odorants, and dye	
	Trim 7030 Components	
	Mixture of amine and potassium oleates, borates, and nitrites	
	DuBois C-1575A Components	
	Cyclohexanol, %	3
	Aromatic petroleum solvent, %	40

(continued)

TABLE A-2 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Waste oil and coolant from machining operations	pH	8.7
	Solids, %	10
	Oil, %	0-30
	Coolant, %	0-10
	Water, %	80
	Lead, mg/L	0-250
	Zinc, mg/L	0-1,500
	Nickel, mg/L	0-40
	Copper, mg/L	0-50
	Mercury, mg/L	<0.0002
	Beryllium, mg/L	0-0.02
	Cadmium, mg/L	0-4.0
	Total chrome, mg/L	0-500
	Arsenic, mg/L	0-0.05
	Sulfur, mg/L	0-300
	Cyanide, mg/L	0-1.0
Water soluble die spray hydraulic oil	pH	5.1
	Oil, %	76
	Water, %	24
	Ash, mg/L	538
	Cadmium, mg/L	2.5
	Chromium, mg/L	0.08
	Copper, mg/L	9.3
	Lead, mg/L	0.55
	Nickel, mg/L	0.39
	Zinc, mg/L	0.83
	Chloroform, mg/L	22
Spent oil from die casting machines	Mineral oil, %	65-69
	Water, %	31-35
	Iron, %	0-2

(continued)

TABLE A-2 (continued)

Process and/or waste description		Waste composition <sup>a</sup>	Data quality
Oil, grease, and water from die casting process	Oil and grease, %	30-40	C
	Water, %	60-70	
Emulsifier	Completely water-soluble		B
	pH	6.83	
	BOD <sub>5</sub> , mg/L	32,955	
	COD, mg/L	>900,000	
	Iron, mg/L	6.88	
	Nickel, mg/L	1.2	
	Potassium, mg/L	8.3	
	Chromium, mg/L	<0.01	
	Cobalt, mg/L	<0.01	
	Ash, %	0.01	
Rustproofing oil	Oil, %	20	C
	Water, %	80	
	Oil phase composition		
	Paraffinic oil, %	55-65	
	Sulfonated petroleum hydrocarbons, %	5-15	
	Butyl cellosolve, %	5-10	
	Oxidized hydrocarbons, %	20-30	
Machine cutting fluid	Petrochem 130, %	5	B
	Water, %	95	
Petrochem 13, composition: soft water, sodium nitrite, triethanolamine, diethylene glycol, butyl carbitol, Petronate L, Acintol D20LR			

(continued)

TABLE A-2 (continued)

Process and/or waste description		Waste composition <sup>a</sup>	Data quality
Chemical coolant	pH	9.0	C
	Amine borates, %	>10	
	Sodium nitrite, %	>10	
	Glycol, %	1-10	
	Water, %	>10	
	Non-ionic surfactants, %	1-10	
Waste machining oil	Mineral oil, %	45	
	Ethylene glycol, %	45	
	Sulfonate, %	5	
	Acrylate copolymer, %	4	
	Lead, mg/L	51	
	Zinc, mg/L	150	
	Nickel, mg/L	1.2	
	Copper, mg/L	5.9	
	Cadmium, mg/L	0.72	
	Chromium, mg/L	1.2	
	Mercury, mg/L	0.32	
	Chlorine, mg/L	220	
Heat treating quench solution	Water, %	90	B
	Polyacrylate, %	10	
	(Aque-Quench 120 from E. F. Houghton and Company)		

<sup>a</sup>Data are reported as found in State files. Percentages given are by volume or weight are not known.

## APPENDIX B

### SOLVENT DESCRIPTION AND COMPOSITION DATA

Composition data for new (raw material) and waste degreasing solvents are listed in this appendix. Brief descriptions of degreasing solvents and composition data for solvents and hydrocarbon stabilizers are listed first (Tables B-1 through B-3) followed by waste composition data (Table B-4). Also, raw material applications and the type of operation generating the waste are identified wherever they are known.

Data were scrutinized and assigned a data quality rating based on an A-B-C quality system. Data with an "A" quality are those found to have been sampled and analyzed with some QA/QC protocol attached; e.g., demonstrated comparison with analytical standards, use of splits, blanks, etc. "B" quality is assigned to data with documented sampling and analysis procedures but no evidence of QA/QC. "C" quality data are those values for which no documentation has been provided and/or the accuracy is undeterminable.

TABLE B-1. DEGREASING SOLVENTS

Compound	Characterization and applications <sup>a</sup>
<u>Halogenated Solvents</u>	
Trichloroethylene	<p>Trichloroethylene (<math>\text{ClCH}=\text{CCl}_2</math>) is a stable, colorless liquid with a chloroform-like odor. It has been used because of its high solvency power and its low cost. For 1976, trichloroethylene sold for \$0.435/kg.</p> <p>Trichloroethylene can be vaporized with low-pressure (135.7 kPa to 204.6 kPa) steam because of its low boiling point (87.2°C). Stabilized trichloroethylene is used for degreasing applications.</p>
Fluorocarbons	<p>In addition to trichlorotrifluoroethane, trichlorofluoromethane and tetrachlorodifluoroethane are also used in solvent cleaning processes on a small, specialized scale. All three have high density (1.5 times that of water), low boiling point (0°C to 50°C), low viscosity, low surface tension, and acceptable stability. Fluorocarbons are principally used as aerosols. Trichlorotrifluoroethane is also used as a solvent in dry-cleaning operations.</p>
Methylene chloride	<p>Methylene chloride (<math>\text{CH}_2\text{Cl}_2</math>) is a colorless, volatile liquid. It is a low-volume degreasing solvent with an estimated annual consumption of <math>5.6 \times 10^4</math> metric tons. Methylene chloride is the most active of the degreasing solvents (high solvency power). The low boiling point requires refrigerated water (12.7°C to 15.5°C)</p>

(continued)

TABLE B-1 (continued)

Compound	Characterization and applications <sup>a</sup>
Methylene chloride (continued)	on the degreaser condensing coils, and the high latent heat of vaporization requires removal of more heat than other solvents. Methylene chloride is stable under degreasing conditions. In 1976, the cost was estimated to be \$0.435/kg. Methylene chloride consumption in metal vapor degreasing has more than doubled since 1972, indicating a switch from other solvents such as trichloroethylene.
1,1,1-Trichloroethane	1,1,1-Trichloroethane (methyl chloroform ( $\text{CH}_3\text{CCl}_3$ )) is a colorless liquid. It is the largest volume vapor degreasing solvent, with $1.68 \times 10^5$ metric tons/yr being consumed. 1,1,1-Trichloroethane is the degreasing solvent most like trichloroethylene in its degreasing properties. It must be stabilized for degreasing applications because it decomposes in the presence of water to form hydrochloric and acetic acids. Improperly stabilized, 1,1,1-trichloroethane can also decompose in the presence of aluminum or magnesium. Stabilizers for 1,1,1-trichloroethane (0.05 g/100 g @ 25°C) require a special separator and dessicant to remove water from the system. The estimated 1976 cost was \$0.467/kg.
Perchloroethylene	Perchloroethylene ( $\text{Cl}_2\text{C}=\text{CCl}_2$ ) is a colorless liquid with a chloroform-like odor. It is the third largest volume vapor degreasing solvent, with $1.1 \times 10^5$ metric tons consumed each year.

(continued)

TABLE B-1 (continued)

Compound	Characterization and applications <sup>a</sup>
Perchloroethylene (continued)	The boiling point (121.1°C) of perchloroethylene is beneficial for two reasons: (1) it aids in the removal of high melting waxes and greases and (2) it allows the solvent to condense on the work for a longer period of time, thereby giving a longer cleaning cycle. Perchloroethylene is also stabilized for degreasing use. In 1976, the cost was estimated to be \$0.377/kg.
Carbon tetrachloride	Carbon tetrachloride (CCl <sub>4</sub> ) is a heavy, colorless liquid with an ethereal odor. It is used occasionally as a solvent and diluent, dry cleaning agent, or degreaser. It is miscible in all proportions with alcohol, benzene, chloroform, ether, and petroleum ether. If ingested or inhaled, it will cause injury depending on the dose. Death can result from prolonged exposure to high concentrations. The cost in 1976 was estimated to be \$0.372/kg.
<u>Nonhalogenated Solvents</u>	
Acetone	Acetone (CH <sub>3</sub> COCH <sub>3</sub> ) is a colorless liquid giving off a fragrant, mintlike odor. Acetone generally is rated moderately toxic. It is widely used in industry as a solvent for fats, oils, waxes, nitrocellulose, and other cellulose derivations. The cost in 1976 was estimated to be \$0.110/kg.

(continued)



TABLE B-1 (continued)

Compound	Characterization and applications <sup>a</sup>
Butanol	Butyl alcohol ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ) is a colorless liquid emitting a choking odor resembling that of isoamyl alcohol. It is used as a solvent in the manufacture and preparation of various materials such as airplane dopes, lacquers, and plastics. In industry, it is used primarily because of its ability as an extender (making substances soluble in each other). For example, a mixture of acetone, butyl alcohol, methyl or ethyl alcohol, and methyl ethyl ketone in methylene chloride is used as a paint stripper. The 1976 cost of butanol was estimated to be \$0.485/kg.
Methyl ethyl ketone (2-butanone)	Methyl ethyl ketone ( $\text{CH}_3\text{COCH}_2\text{CH}_3$ ) is a colorless liquid discharging an odor resembling acetone. Methyl ethyl ketone has a slight to moderate toxicity rating. Maximum allowable concentration is 250 ppm in air or 735 mg/m <sup>3</sup> . The estimated 1976 cost was \$0.440/kg.
Naphthas (petroleum distillates, Stoddard solvents)	Petroleum naphthas are composed of approximately 65% hydrocarbons in the five to eight carbon range, while 35% have nine or more carbon atoms. They contain approximately 2% toluene and a maximum of 0.5% benzene. Naphthas consist of approximately 10% aromatics, from 20% to 60% naphthenes, and from 70% to 30% paraffins, depending on whether the naphtha is low naphthenic or high naphthenic.

(continued)

TABLE B-1 (continued)

Compound	Characterization and applications <sup>a</sup>
Toluene	Toluene ( $C_6H_5CH_3$ ) (methylbenzene or toluol) is a colorless liquid exuding a benzene-like odor. Its boiling point is $110.4^\circ C$ and its flash point is $4.4^\circ C$ . It is moderately toxic; the maximum allowable concentration is 200 ppm in air. Toluene is derived from coal tar, and commercial grades usually contain small amounts of benzene as an impurity. Its cost in 1976 was estimated to be \$0.187/kg. It is used as a solvent for the extraction of various materials, as a diluent in cellulose ether lacquers, and in the manufacture of benzoic acid, benzaldehyde, explosives, dyes, and other organic compounds.
Hexane	Hexane [ $CH_3(CH_2)_4CH_3$ ] is a colorless liquid having a low toxic hazard rating. Maximum acceptable concentration is 100 ppm in air and 360 mg/m <sup>3</sup> of air. Its cost in 1976 was estimated to be \$0.167/kg.
Mineral spirits	Mineral spirit is also called turpentine substitute, white spirit, or petroluem spirit. It is a clear, water-white refined hydrocarbon solvent with a minimum flash point of $21^\circ C$ . Its toxic hazard rating is considered to be slight to moderate.
Xylene	The xylenes [ $C_6H_4(CH_3)_2$ ] are colorless liquids with toxicity comparable to toluene. The maximum allowable concentration of xylene is 200 ppm in air. It is used as a solvent for gums and oils

(continued)

TABLE B-1 (continued)

Compound	Characterization and applications <sup>a</sup>
Xylene (continued)	and in the manufacture of dyes and other organic substances. The cost of xylene in 1976 was estimated at \$0.182/kg. It is slightly soluble in water and is miscible with absolute alcohol and other common organic solvents.
Cyclohexane	Cyclohexane (C <sub>6</sub> H <sub>12</sub> ), also known as hexahydrobenzene or hexamethylene, is a colorless mobile liquid giving off a pungent odor and is moderately toxic. In high concentrations, it may act as a narcotic and/or skin irritant. Maximum allowable concentration is 400 mg/m <sup>3</sup> of air. Cyclohexane is a solvent for resins and rubber. It is also used as a degreasing agent and a paint thinner. It is insoluble in water but is completely miscible with alcohol, ethers, hydrocarbons, chlorinated hydrocarbons, and most other organic solvents. Its cost was estimated to be \$0.288/kg in 1976.

<sup>a</sup>Chemical Marketing Reporter. 209(12):46-56, 1976 September 20.

TABLE B-2. SOLVENT COMPOSITION

Process and/or material description	Material composition		Physical characteristics			
	Ingredient	Weight percent	Volatile volume percent	Weight, lb/gal	Flammable liquid	Data quality
Solvent	Mineral spirits	>10				C
	Petroleum naphtha	>10				
	Methylene chloride	>10				
Solvent	Xylene	31.34	100	7.40	yes	
	Toluene	20.54				
	Ethylene glycol					
	Ethyl ether acetate	29.55				
	Isopropyl alcohol	13.27				
	Ethyl cellosolve Acetate ester	5.30				

TABLE B-3. STABILIZERS USED IN HALOGENATED HYDROCARBONS

Stabilizing compound	Solvent <sup>a</sup>	Typical solute concentration, wt. %	Range of concentration, wt. %	TIV, g/m <sup>3</sup>	U.S. Patent number	Patent issued to
Organic mercaptans and disulfides (Aonyl mercaptan, 2-mercaptoethyl methyl ether, bis(di-alkoxyphosphinothionyl) disulfide, bis(1-piperazinylthiocarbonyl) disulfide, cyclohexyl mercaptan, 2-mercaptoethanol, 2,3-dimercapto-1-propanol, dimethyl disulfide, di-tert-butyl disulfide, 4,4'-dithiodimorpholine, 2,2'-dithiobis(benzothiazole), dibenzyl disulfide, decamethylene dithiol, furfuryl Mercaptan) With butylene oxide	MC	0.1			3,641,169	DOW
		0.3			3,641,169	DOW
Diakyl sulfoxides (Glycidol (2,3-epoxy-1-propanol), dimethyl Sulfoxide, 3-(methylamino)propionitrile, 3-(dimethylamino)propionitrile, methylethanolamine, morpholine, acetonitrile, butylene oxide)	MC		0.05 to 6		3,535,392	PPG
1,3,5-Cycloheptatriene	PERC, TCENE	0.05			3,642,645	WCGG
1,3,5-Cycloheptatriene	PERC, TCENE	0.1			3,642,645	WCGG
With 1-(dimethylamino)propene-2		0.05			3,642,645	WCGG
Dipentene (terpene)	AER	0.5			3,352,789	ALL
Indene	AER	0.30		0.450	3,352,789	ALL
p-Mentha-1,5-diene	AER	0.30			3,352,789	ALL
α-Methylstyrene	AER	0.30			3,352,789	ALL
Trimethyl orthoformate (TMOF)	MC	0.75		0.250	3,564,061	PCPSG
With nitromethane		0.75			3,564,061	PCPSG
TMOF	MC	0.5			3,564,061	PCPSG
With acetonitrile		0.5		0.070	3,564,061	PCPSG
TMOF	MC	1.0			3,564,061	PCPSG
With trioxane		1.0			3,564,061	PCPSG
TMOF	MC	0.75			3,564,061	PCPSG
With 1,4-dioxane		0.75		0.180 <sup>c</sup>	3,564,061	PCPSG
TMOF	MC	0.50			3,564,061	PCPSG
With acetonitrile		0.25		0.070	3,564,061	PCPSG
And tert-butyl alcohol		0.25		0.300	3,564,061	PCPSG

See footnotes at end of table

(continued)

TABLE B-3 (continued)

Stabilizing compound <sup>1</sup>	Solvent <sup>a</sup>	Typical solute concentration, wt %	Range of concentration, wt %	TLV, g/m <sup>3</sup>	U.S. Patent number	Patent <sup>b</sup> issued to
TMOF	MC	2.10			3,564,061	PCPSG
With methanol		0.60		0.260	3,564,061	PCPSG
And methylformate		0.30		0.250	3,564,061	PCPSG
Benzotriazole	PFRC	0.5	0.1 to 2.5		3,337,471	DOW
Oxazole	MC	2	1 to 4		3,676,355	UKF
Polyamines (ethylenediamine, triethylenediamine, 4,4'-ethylenedimorpholine, pyrrole, 1,1'-ethylenedipiperidine, diisopropylamine, diethylenetriamine, tetraethylenepentamine, n-methylpyrrole)	PLRC, TCENE, CH	0.004	0.001 to 0.02		3,424,805	WCCG
N,N-Dimethyl-p-phenylenediamine	MC	0.13			3,546,125	DOW
N,N,N',N'-Tetramethyl-o-phenylenediamine	MC	1.1			3,546,125	DOW
N,N,N',N-Tetramethylbenzidine	MC	0.22			3,546,125	DOW
Quaternary ammonium compounds	MC, TCENE, CH		0.005 to 0.2		3,314,892	CI
With volatile epoxy compounds			0.01 to 1.0		3,314,892	CI
And organic amines (pyridine, picoline, triethylamine, aniline, dimethylaniline, nalkylmorpholines, diisopropylamine, N-methylpyrrole)			0.005 to 0.2		3,314,892	CI
2-Methyl-2-oxazoline	MC	0.44			3,494,968	DOW
2-Phenyl-2-oxazoline	MC	0.65			3,494,968	DOW
2-(1-Aziridinyl)-2-oxazoline	MC	0.25			3,494,968	DOW
Diaziridine compounds and N-ethylpyrrole (1,2-diethyldiaziridine, N-methylpyrrole)	TCENE, CH	6.8			3,551,505	SCB
$\alpha$ -Methyl-1-aziridineethanol	MC		1.0 to 4.0		3,328,474	DOW
2-(1-Aziridinyl)ethyl acetate						
Lactams (Caprolactam)	MC, CH	0.5	0.05 to 5		3,496,241	FMC
With glycidol(2,3-epoxy-1-propanol)		0.25			3,496,241	FMC
(2,3, and 4)-Pyridinecarboxaldehyde	MC	0.25			3,444,248	DOW
(2,3, and 4)-Acetylpyridine	MC	0.50	0.36 to 0.54		3,444,248	DOW
(2,3, and 4)-Cyanopyridine	MC	0.35	0.31 to 0.39		3,452,108	DOW
p-Nitrobenzonitrile	MC	0.33			3,454,659	DOW
o-Nitrobenzonitrile (2-nitro-p-tolunitrile, 4-nitro-m-tolunitrile, 2,3-dimethyl-4-nitrobenzonitrile)	MC	0.77			3,454,659	DOW

See footnotes at end of table

(continued)

TABLE B-3 (continued)

Stabilizing compound	Solvent <sup>a</sup>	Typical solute concentration, wt %	Range of concentration, wt %	TLV, g/m <sup>3</sup>	U.S. Patent number	Patent <sup>b</sup> issued to
(3 and 8)-Aminoquinoline	MC	0.12			3,471,903	DOW
Acetaldehyde dimethylhydrazone	TCENE, CH	0.025			3,417,152	MIS
With butylene oxide		0.2			3,417,152	MIS
With butylene oxide		0.1			3,417,152	MIS
And propylene oxide		0.1		0.240	3,417,152	MES
And thymol		0.05			3,417,152	MES
(or formaldehyde dimethylhydrazone)						
Crotonaldehyde dimethylhydrazone	TCENE	0.025			3,403,190	MES
With butylene oxide		0.2			3,403,190	MES
And nitromethane		0.05		0.240	3,403,190	MES
With <i>p</i> -tert-pentylphenol		0.002			3,403,190	MES
<i>p</i> -(Dimethylamino)benzaldehyde	MC		0.11 to 11.1		3,444,247	DOW
Methoxyacetonitrile	MC	2.9			3,565,811	DOW
And butylene oxide		0.32			3,565,811	DOW
And nitromethane		0.44			3,565,811	DOW
Or propargyl alcohol		0.35		0.0-2 <sup>C</sup>	3,565,811	DOW
Acetonitrile	MC	1.0		0.07 <sup>C</sup>	3,590,088	DNAG
And tert-butyl alcohol		5.0		0.300	3,445,532	DNAG
And 1,4-dioxane		0.7		0.180 <sup>C</sup>	3,445,532	DNAG
Acetonitrile	MC	3.0		0.070	3,445,532	DNAG
And nitromethane		1.0		0.250	3,445,532	DNAG
And 1,4-dioxane		0.8		0.180 <sup>C</sup>	3,445,532	DNAG
Acetonitrile	MC	0.5		0.070	3,445,532	DNAG
And tert-butyl alcohol		3.0		0.300	3,445,532	DNAG
And nitromethane		0.7		0.250	3,445,532	DNAG
Nitromethane	MC	3.0		0.250	3,549,715	PPG
With butylene oxide		1.0			3,549,715	PPG
With 2-propanol		3.0		0.980	3,549,715	PPG
3-Methoxy-1,2-epoxypropane	MC	0.5			3,536,766	DOW
With 1,4-dioxane		2.5		0.130 <sup>C</sup>	3,536,766	DOW
And nitromethane		0.5		0.250	3,536,766	DOW
And methyl glycidyl ether		0.5			3,536,766	DOW
Propylene oxide	CFA	0.5	0.5 to 3.0		3,445,527	DAKK
With nitromethane		0.05		0.250	3,445,527	DAKK
3-Methoxyoxetane	MC	3.0			3,532,761	PPG
1,2-Dimethoxyethylene	MC	2.0	1 to 5		3,549,547	DOW

See footnotes at end of table

(continued)

TABLE B-3 (continued)

Stabilizing compound	Solvent <sup>a</sup>	Typical solute concentration, wt %	Range of concentration, wt %	TLV, g/m <sup>3</sup>	U.S. Patent number	Patent <sup>b</sup> issued to
2-Methoxy-2,3-dihydropyran	MC	1.4			3,661,788	ICI
Or 2-ethoxy-2,3-dihydropyran		0.5	0.5 to 2		3,661,788	ICI
And isopropyl nitrate		2			3,661,788	ICI
4,7-Dihydro-1,3-dioxepin	MC	4	2 to 10		3,518,202	DOW
And nitromethane		1	0.25 to 2	0.250	3,518,202	DOW
Or propargyl alcohol		0.5	0.25 to 0.5	0.002 <sup>C</sup>	3,518,202	DOW
And butylene oxide		0.5	0.25 to 1.0		3,518,202	DOW
Or epichlorhydrin		0.5	0.25 to 1.0	0.019 <sup>C</sup>	3,518,202	DOW
Furfuryl alcohol	MC	0.066		0.020	3,475,503	DOW
Furfuryl mercaptan	MC	0.11			3,475,503	DOW
5-Formylfurfuryl alcohol	MC	0.19			3,475,503	DOW
2-Thiophenmethanol	MC	0.47			3,475,503	DOW
2,5-Tetrahydrofuran dimethanol	MC	0.29			3,475,503	DOW
2-(2 and 3)-Pyridyl ethanol	MC	0.32	0.28 to 0.35		3,475,503	DOW
<i>o</i> -Aminobenzyl alcohol	MC	0.37			3,475,503	DOW
<i>p</i> -Methoxybenzyl alcohol	MC	0.21			3,475,503	DOW
3-Methyl-2-thiophenemethanol	MC	0.33			3,475,503	DOW
1,3-Dioxolane	MC		1 to 3		Reissue	AR
With phenolic antioxidants ( <i>p</i> - <i>tert</i> -butylphenol, 2,6-di- <i>tert</i> -butyl- <i>p</i> -cresol, nonylphenol, 4,4'-thiobis(6- <i>tert</i> -butyl) <i>m</i> -cresol)			0.01 to 0.1		26,025	
1,4-Dioxane	MC	2.84		0.180 <sup>C</sup>	3,629,128	ETH
With nitromethane		0.3921		0.250	3,629,128	ETH
With butylene oxide		0.2601			3,629,128	ETH
With <i>N</i> -methylpyrrole		0.005			3,629,128	ETH
With diisopropylamine		0.003			3,629,128	ETH
3-Methylpropionaldehyde	MC	2			3,505,415	DNAG
4-Methyl-2-butanone	MC	2			3,505,415	DNAG
Isobutyric acid, methyl ester	MC	1			3,505,415	DNAG
And nitromethane		1		0.250	3,505,415	DNAG
4-Methyl-4-methoxy-2-pentanone	MC	1			3,505,415	DNAG
With acetonitrile		0.5		0.070	3,505,415	DNAG
And <i>tert</i> -butyl alcohol		0.5		0.300	3,505,415	DNAG
With <i>tert</i> -butyl alcohol		1		0.300	3,505,415	DNAG
And methyl ethyl ketone		1		0.590	3,505,415	DNAG

See footnotes at end of table

(continued)



TABLE B-3 (continued)

Stabilizing compound	Solvent <sup>a</sup>	Typical solute concentration, wt %	Range of concentration, wt %	TLV, g/m <sup>3</sup>	U.S. Patent number	Patent <sup>b</sup> issued to
1,4-Cyclohexanedione	MC	0.25			3,546,305	DOW
1,2-Cyclohexanedione	MC	0.33			3,546,305	DOW
2,5-Butanedione	MC	0.17			3,546,305	DOW
2,5-Butanedione	MC	0.28			3,546,305	DOW
<i>p</i> -Benzoquinone	MC	0.24		0.0004	3,546,305	DOW
2,3-Dihydro-1,4-dithiin (also 5-methyl-2,3-dihydro-1,4-dithiin)	MC, TCENE		0.2 to 4.5		3,439,051	ICI
Polysulfones	PERC	0.092			3,396,115	DOW
Trimethylene sulfide	MC	0.17			3,467,722	DOW
3-Hydroxytrimethylene sulfide	MC	0.20			3,467,722	DOW
Isopropyl nitrate	MC	2	2 to 4		3,609,091	ICI
With acetonitrile		2			3,609,091	ICI
And nitromethane		1	0.75 to 1		3,609,091	ICI
And butylene oxide		0.25	0.1 to 1		3,609,091	ICI
With acrylonitrile		2	0.5 to 4		3,609,091	ICI
Any butylene oxide		0.25	0.1 to 1	0.045 <sup>c</sup>	3,609,091	ICI
Iron benzoate	TCENE, PERC	12	10.2 to 14.3		3,527,703	DOW
Sodium benzoate	TCENE, PERC	0.025	0.020 to 0.027		3,527,703	DOW
Zinc benzoate	TCENE, PERC	10	0.41 to 38.3		3,527,703	DOW
Sodium didecyl phosphate (or sodium dioctyl phosphate)	PERC	1.5			3,441,620	STA
Benzyl fluoride	MC	0.14	0.82 to 8.1		3,681,469	DOW
Benzotrifluoride	MC	4.9			3,681,469	DOW
Ethyl propargyl ether	PERC	0.25			British 773,447	DIA
Propargyl benzoate	PERC	0.25			773,447	DIA
2-Butyne-1,4-diol-dibenzoate	PERC	0.25			773,447	DIA
With isoeugenol		0.01			773,447	DIA
Propargyl alcohol	AERO	0.01		0.002 <sup>c</sup>	2,872,725	
Nitromethane	AER	2	0.1 to 5		3,085,116	DUP
Nitroethane	AER	1	0.1 to 5		3,085,116	DUP
2-Nitropropane	AER	2	0.1 to 5		3,085,116	DUP
Propargyl alcohol	TCENE	0.1	0.05 to 0.5	0.002 <sup>c</sup>	2,803,676	DOW
With pyrrole		0.05	0.01 to 0.05		2,803,676	DOW
And diisopropylamine		0.001	0.0005 to 0.01		2,803,676	DOW

See footnotes at end of table

(continued)

TABLE B-3 (continued)

Stabilizing compound	Solvent <sup>a</sup>	Typical solute concentration, wt %	Range of concentration, wt %	TLV <sup>c</sup> g/m <sup>3</sup>	U.S. Patent number	Patent <sup>b</sup> issued to
Methylbutynol (and 2 prior)	TCENE	0.1	0.05 to 0.5		2,803,676	DOW
1,4-Dioxane	CH	1			2,923,747	DOW
Nitromethane		1			2,923,747	DOW
Vinylidene chloride		0.5			2,923,747	DOW
2-Butyn-1,4-diol	AERO, CH	0.5			2,892,725	CEL
3-Methyl-1-butyn-3-ol	CH		0.1 to 0.5		2,542,551	RH
3-Methyl-1-butyn-3-ol (with thymol, di-tert-butyl-p-cresol, epichlorohydrin, butylene oxide, amines, dioxane)	CH		0.005 to 0.3		2,911,449	AIR

Note.—Blanks indicate no data.

<sup>a</sup> MC -- Methyl chloroform; 1,1,1-trichloroethane  
 PERC -- Perchloroethylene  
 TCENE -- Trichloroethylene  
 AER -- Aerosols; trichlorofluoromethane and ethanol

CFA -- Chloro-fluoro alkanes  
 CH -- Chlorinated hydrocarbons  
 AERO -- Methylene chloride and methanol (aerosols)

<sup>b</sup> DOW -- Dow Chemical Corporation  
 PPG -- PPG Industries, Inc.  
 WCGG -- Wacker-Chemie GmbH, Germany  
 ALL -- Allied Chemical Corporation  
 PCPSG -- Produits Chimiques Peciney-Saint-Gobain, France  
 UKF -- Uguine Kuhlmann, France  
 CI -- Canadian Industries, Limited, Canada  
 SCP -- Solvay ANC Cie, Belgium  
 FMC -- FMC Corporation  
 MES -- Montecatini Edison Spa, Italy  
 DNAG -- Dynamit Nobel AG, Germany  
 DKKK -- Daikin Kogyo K. K., Japan  
 ICI -- Imperial Chemical Industries, Limited, Great Britain  
 AR -- Argus Chemical Corporation  
 ETH -- Ethyl Corporation  
 STA -- Stauffer Chemical Corporation  
 DIA -- Diamond Alkali Company  
 DUP -- E. I. Du Pont de Nemours and Company  
 CEL -- Celanese Corporation  
 RH -- Rohm & Haas Co.  
 AIR -- Air Reduction Corporation

<sup>c</sup> TLV for skin contact.

TABLE B-4. WASTE COMPOSITION DATA

Process and/or waste name		Waste composition <sup>a</sup>	Data quality
Degreasing solvent	Liquid oil, %	10	C
	Grease, %	60	
	Perchloroethylene, %	5-10	
	Hy-Flo (diatomaceous earth), %		
	Soap, %	20-25	
	Dirt, %		
Parts degreasing operation	Alcohol, %	77	B
	Perchloroethylene, %	12	
	Wax and grease, %	11	
	Lead, mg/kg	70	
	Cadmium, mg/kg	0.8	
	Nickel, mg/kg	4.9	
	Antimony, mg/kg	6.9	
	Cobalt, mg/kg	0.4	
	Mercury, mg/kg	7.4	
	Chromium, mg/kg	5.4	
	Copper, mg/kg	30.6	
	Zinc, mg/kg	83	
	Lithium, mg/kg	0.2	
	Silver, mg/kg	2.4	
	Flash point, °F	95	
	Noncombustible material (600°C), mg/kg	750	
Degreasing operation	Trichloroethylene, %	90	C
	Oil, %	10	
Vapor degreasing operation	Trichloroethylene, %	80-90	C
	Polymerized vinyl plastisol fragments, %	5-10	
	Oil and grease, %	2-5	

(continued)

TABLE B-4 (continued)

Process and/or waste name		Waste composition <sup>a</sup>	Data quality
Vapor degreasing operation	Freon, %	25 ± 5	C
	Trichloroethylene, %	40 ± 20	
	Oil, %	27 ± 13	
	Solids, %	7 ± 3	
Degreasing	1,1,1-Trichloroethane, %	60	B
	Oil, %	40	
Degreasing	1,1,1-Trichloroethane, %	50-65	B
	Oil and grease, %	35-45	
	Water, %	<2	
	Residue, %	2.5	
Degreasing	Trichloroethylene, %	37	B
	Water, %	35	
	Oil and grease, %	24	
	Noncombustible ash, mg/kg	28,000	
	Lead, mg/kg	435	
	Cadmium, mg/kg	0.8	
	Nickel, mg/kg	185	
	Chromium, mg/kg	4.5	
	Copper, mg/kg	18	
	Zinc, mg/kg	1,116	
	Chlorine, mg/kg	296,000	
Degreasing	Trichloroethylene, %	10	B
	Water, %	82	
	Oil and grease, %	5	

(continued)

TABLE 3-4 (continued)

Process and/or waste name	Waste composition <sup>1</sup>		Data quality
Degreasing (continued)	Noncombustible ash, mg/kg	7,700	
	Lead, mg/kg	54	
	Cadmium, mg/kg	0.4	
	Nickel, mg/kg	3.0	
	Chromium, mg/kg	1.3	
	Copper, mg/kg	0.9	
	Zinc, mg/kg	430	
	Chlorine, mg/kg	80,000	
Degreaser	High flash naphtha, %	60	B
	Ethylene chloride, %	16	
	Oil, %	6.17	
	Zinc, mg/kg	179	
	Nickel, mg/kg	53,053	
	Copper, mg/kg	4,980	
	Chromium, mg/kg	25,444	
Aircraft equipment cleaning	Trichloroethylene, %	30	C
	Other solvents, %	40	
	Oil, %	30	
Aircraft parts cleaning	Chlorinated hydrocarbons		C
	Phenolic compounds		
	Oil		
	Water		
	pH	10.0	
Degreasing	Water, %	80	B
	Toluene and xylene, %	17	
	Grease, %	3	

(continued)

TABLE B-4 (continued)

Process and/or waste name	Waste composition <sup>a</sup>	Data quality
Degreasing	Acetone Alcohol Water Grease Oil	C
Degreasing	Freon, % Oil and grease, %	90-95 5-10 B
Parts cleaning	Acetone, % 1,1,1-Trichloroethane, % Isopropanol, % Methanol, % Trichloroethylene, % Freon, % Transene 100, % Toluene, % MEK, % Bromides and solvent, % Paint solvent, % Xylene, % Dimethyl formamide, % De SOLV 8090, % Oil, water, impurities, %	24.2 13.5 10.5 6.5 2.4 7.9 0.7 9.1 0.5 18.2 0.4 0.3 0.1 0.6 5.1 B
Degreasing	Oil, % Tetrachlorethene, % 1,1,1-Trichloroethene, % MEK, %	5-10 60-65 10-20 2-5 C

(continued)

TABLE B-4 (continued)

Process and/or waste name	Waste composition <sup>a</sup>	Data quality
Parts cleaning	1,1,1-Trichloroethane, %	3-5
	Alcohol, %	10-15
	Oil, %	75-80
Degreasing	1,1,1-Trichloroethane, %	80
	Oil and grease, %	20
Degreasing	Oil, %	39
	Mineral thinners, %	10
	Freon, %	24
	Chloroethane VG, %	27
Degreasing	Trichloroethylene, %	90-95
	Oil and grease, %	5-10
Degreasing	1,1,1-Trichloroethane, %	10-40
	Grease and solids, %	50-70

<sup>a</sup>Data are reported as found in State files. Whether percentages given are by volume or weight is not known.

## APPENDIX C

### COMPOSITION DATA FOR NEW AND WASTE SURFACE COATINGS

Composition data for new (raw material) and waste surface coatings are listed in this appendix; raw material data (Tables C-1 and C-2) are followed by waste data (Table C-3). The type of operations generating the waste are identified wherever known.

Data were scrutinized and assigned a data quality rating based on an A-B-C quality system. Data with an "A" quality are those found to have been sampled and analyzed with some QA/QC protocol attached; e.g., demonstrated comparison with analytical standards, use of splits, blanks, etc. "B" quality is assigned to data with documented sampling and analysis procedures but no evidence of QA/QC. "C" quality data are those values for which no documentation has been provided and/or the accuracy is undetermined.



TABLE C-1. PRODUCT SURFACE COATING COMPOSITION DATA

Coating description	Material composition		Physical characteristics			
	Ingredient	Weight percent	Volatile by volume percent	Weight, lb/gal or (specific gravity)	Flammable liquid	Data quality
Lacquer, yellow tracer	Pigments					
	Chrome yellow	11.25	89.00	(0.9459)	Yes	B
	Titanium dioxide	1.25				
	Vehicle					
	Vinyl resin	8.00				
	Plasticizers	3.50				
	Ketones	39.00				
	Aromatic hydrocarbon solvents	25.75				
	Other					
	Aliphatic hydrocarbon solvent	8.25				
	Alcohols	2.25				
	Additives	0.75				
Lacquer, white tracer	Pigments					
	Titanium dioxide	10.00	83.20	(0.9627)	Yes	B
	Vehicle					
	Vinyl resin	10.50				
	Plasticizer	7.50				
	Ketones	43.00				
	Other					
	Aromatic hydrocarbon solvents	28.50				
	Additives	0.50				

(continued)

TABLE C-1 (continued)

Coating description	Material composition		Physical characteristics			
			Volatile by volume percent	Weight, lb/gal or (specific gravity)	Flammable liquid	Data quality
Lacquer, orange tracer	Pigments					
	Molybdate orange	4.50	88.00	(0.9447)	Yes	B
	Chrome yellow	3.50				
	Vehicle					
	Vinyl resin	9.00				
	Plasticizer	4.75				
	Ketones	45.00				
	Other					
	Aromatic hydrocarbon solvents	32.50				
	Additives	0.75				
Lacquer, green tracer	Pigments					
	Chrome yellow	5.00	88.00	(0.9243)	Yes	B
	Phthalocyanine blue	0.25				
	Titanium dioxide	0.50				
	Extender pigments	0.60				
	Vehicle					
	Vinyl resin	9.00				
	Plasticizer	5.00				
	Ketones	45.00				
	Other					
	Aromatic hydrocarbon solvents	34.00				
	Additives	0.65				

(continued)

TABLE C-1 (continued)

Coating description	Material composition		Physical characteristics			
	Ingredient	Weight percent	Volatile by volume percent	Weight, lb/gal or (specific gravity)	Flammable liquid	Data quality
Lacquer, black tracer	Pigments					
	Channel black	1.15	91.50	(0.8764)	Yes	B
	Vehicle					
	Vinyl chloride/vinyl acetate copolymer	10.60				
	Aromatic hydrocarbon	37.75				
	Other					
	Ketone	49.00				
Lacquer, red tracer	Plasticizers	1.50				
	Pigments					
	Molybdate orange	7.50	83.50	(0.9723)	Yes	B
	B.O.N. red	3.50				
	Vehicle					
	Vinyl resin	9.50				
	Plasticizer	7.00				
	Aromatic hydrocarbon solvents	32.50				
	Other					
	Ketones	39.50				
	Additives	0.50				

(continued)

TABLE C-1 (continued)

Coating description	Material composition		Physical characteristics			
			Volatile by volume percent	Weight, lb/gal or (specific gravity)	Flammable liquid	Data quality
Lacquer, pink tracer	Pigments					
	Titanium dioxide	3.75	84.40	(0.9303)	Yes	B
	Lithol red	1.25				
	B.O.N. red	0.25				
	Vehicle					
	Vinyl resin	10.00				
	Plasticizers	7.50				
	Ketones	42.00				
	Other					
	Aromatic hydrocarbon solvents	35.00				
	Additives	0.25				
Ink, blue tracer	Pigments					
	Titanium dioxide	4.50	87.20	(0.9267)	Yes	B
	Phthalocyanine blue	1.10				
	Vehicle					
	Vinyl resin	9.00				
	Plasticizers	5.00				
	Ketones	46.50				
	Other					
	Aromatic hydrocarbon solvents	33.00				
	Additives	0.90				

(continued)

TABLE C-1 (continued)

Coating description	Material composition		Physical characteristics			
	Ingredient	Weight percent	Volatile by volume percent	Weight, lb/gal or (specific gravity)	Flammable liquid	Data quality
Ink, tan tracer	Pigments					
	Red and brown iron oxides	5.00	82.40	(0.9807)	Yes	B
	Titanium dioxide	3.00				
	Vehicle					
	Vinyl resins	16.50				
	Plasticizer	4.50				
	Cresols	6.00				
	Other					
	Ketones	41.50				
	Aromatic hydrocarbon solvents	23.25				
	Nitroparaffin	0.25				
Alkyd enamel, black gloss	Mineral spirits	55	63.9	7.45	Yes	B
	Aromatic naphtha	<5				
	Xylene	<5				
Alkyd enamel, black semi-gloss	Mineral spirits	45	60.4	8.29	Yes	B
	Xylene	<5				
Tank coating	Xylene	25	64	9.84	Yes	B
	Petroleum distillate	15				
	Petroleum distillate	5				
	Zinc chromate pigment	5				

(continued)

TABLE C-1 (continued)

Coating description	Material composition		Physical characteristics			
			Volatile by volume percent	Weight, lb/gal or (specific gravity)	Flammable liquid	Data quality
316 Primer, rust protective	Alkyd resin		-a			C
	Linseed oil					
	Pigments		-b			
	Zinc/chromate					
	Red iron oxide					
Tank coating	Inert additives					
	Solvent: aliphatic hydrocarbon					
	Epoxy resin and amine		-c			C
	Pigments - unspecified chemical resistant					
	Solvents		-d			
Paint, gray primer	Ketones					
	Aromatic hydrocarbons					
	Glycol ether					
	Paint composition, % of volatile volume					
	Xylene	66.6	39.32	10.35	Yes	B
	Aromatic naphtha	27.8				
	Ethylbenzene	4.3				
	Mineral spirits	1.3				
	TOTAL	100.0				

(continued)

TABLE C-1 (continued)

Coating description	Material composition		Physical characteristics			
			Volatile by volume percent	Weight, lb/gal or (specific gravity)	Flammable liquid	Data quality
Paint, gray primer (continued)	Aromatic hydrocarbon with 8 or more carbon atoms except ethyl benzene, 94.47% of volatiles					
	Ethylbenzene and/or toluene and/or trichloroethylene, 4.31% of volatiles					
Acrylic enamel	Paint composition, % of volatile volume					
	Xylene	73.1	43.35	9.05	Yes	B
	n-Butyl alcohol	7.1				
	2-Ethoxyethyl acetate	5.2				
	Ethylbenzene	4.0				
	Toluene	4.0				
	2-Butoxyethyl acetate	3.9				
	Mineral spirits	2.2				
	Diethylaminoethanol	0.5				
	TOTAL	100.0				
	Aromatic hydrocarbon with 8 or more carbon atoms except ethyl benzene, 75.56% of volatiles					
	Ethylbenzene and/or toluene and/or trichloroethylene 8.05% of volatiles					

(continued)

TABLE C-1 (continued)

Coating description	Material composition		Physical characteristics			
	Ingredient	Weight percent	Volatile by volume percent	Weight, lb/gal or (specific gravity)	Flammable liquid	Data quality
Acrylic enamel, tan	Diethylene glycol mono-butyl ether	<5	58.0	10.2	Yes	B
	Ethylene glycol	<5				
	N,N-Dimethylethanolamine	<0.5				
	Lead as % nonvolatile	<0.06				
Acrylic enamel, white	Diethylene glycol mono-butyl ether	<5	55.9	10.7	Yes	B
	Ethylene glycol	<5				
	N,N-Dimethylethanolamine	<0.5				
	Lead as % nonvolatile	<0.06				
Modified acrylic primer	Strontium chromate pigment	5	54	9.7	No	B
	Emulsion					
Enamel, modified alkyd green machinery coating	Pigments					
	Phthalocyanine blue	0.25			Yes	B
	Yellow iron oxide	2.50				
	Extender pigment	18.25				
	Titanium dioxide	6.25				
	Other		64.00	-		
	Alkyd resin	26.00				
	Aromatic hydrocarbon solvents	15.00				
	Aliphatic hydrocarbon solvents	27.50				
	Tinting, driers and additives	4.25				

(continued)



TABLE C-1 (continued)

Coating description	Material composition		Physical characteristics			
	Ingredient	Weight percent	Volatile by volume percent	Weight, lb/gal or (specific gravity)	Flammable liquid	Data quality
Paint, black water reducible baking epoxy	Water	49	70	9.45-9.65	No	B
	Solids	39				
	Pigments					
	Carbon black	2.4				
	Lead silicochromate	4.0				
	Urea formaldehyde	4.0				
	Methylated melamine	3.9				
	Vehicle					
	Epoxy ester	12.7				
	Solvents					
	See below					
	Additives					
	Ammonium compounds (as NH, OH)	1.5				
	Others					
Epoxy primer	Talc	7.9				
	Butyl cellosolve	4.8				
	n-Butanol	0.5				
	Methyl cellosolve	3.7				
	Xylol	30	70.72	9.57	Yes	B
	Toluol	10				
	Methyl ethyl ketone	5				
	Methyl isobutyl ketone	Less than 5				
	Butanol	Less than 5				
	Butyl cellosolve	Less than 5				

(continued)

TABLE C-1 (continued)

Coating description	Material composition		Physical characteristics			
	Ingredient	Weight percent	Volatile by volume percent	Weight, lb/gal or (specific gravity)	Flammable liquid	Data quality
Epoxy primer, zinc rich	Xylol	20	59.1	20.5	Yes	B
	Mineral spirits	Less than 5				
	Zinc (metal)	35				
Epoxy primer	Xylol	60	76.89	9.06	Yes	B
	Cobaltous napthenate	0.010				
Paint, guide coat	Ethylene glycol ethyl ether acetate	19.60	81.76	8.75	Yes	B
	Xylene	6.70				
	Methyl ethyl ketone	27.17				
	Diethylene glycol butyl ether	4.01				
	Toluene	10.45				
Paint, gray primer	Xylene	15.07	67.21	9.97	Yes	B
	Toluene	10.61				
	Lactol spirits	3.23				
	Long range VM&P naphtha	10.99				
	Isopropanol	5.25				
	n-Butanol	0.64				
	Mineral spirits	0.09				

(continued)

TABLE C-1 (continued)

Coating description	Material composition		Physical characteristics			
	Ingredient	Weight percent	Volatile by volume percent	Weight, lb/gal or (specific gravity)	Flammable liquid	Data quality
Paint, black primer	Xylene	47.24	77.78	8.62	Yes	B
	Diacetone alcohol	5.44				
	Isopropanol	5.13				
	Toluene	11.33				
	Aromatic hydrocarbon 150	0.31				

<sup>a</sup> Solids, volume percent: 63.

<sup>b</sup> Flash point, minimum: (83°F).

<sup>c</sup> Solids, volume percent: 50.

<sup>d</sup> Flash point, minimum: (60°F).



TABLE C-2. CLASSIFICATION AND COMPOSITION OF PAINTS [ ]

PAINT CLASS	PAINT DESCRIPTION (FORMULATION)	COMPOSITION OF BINDER	SUGGESTED USE	NV kg/lit (lb/gal)	kg OV/lit NV (lb OV/gal NV)	
					buy	use
1Aa - SPRAY, Air drying, solvent borne	1. Medium Oil Alkyd White Enamel (Ashland P-31)	52% Soybean Oil, 34% Phth. Anh. in Aliphatics (Aroplaz 1082460)	TTR266d - Type IV, low vis., color fast	1.50 (12.5)	2.09 (17.4)	2.09 (17.4)
	2. Modified Alkyd Red Primer (Ashland Q-405a)	32% Linseed/Tung Oil, 39% Phth. Anh. in Xylene - Modifier: Phenolic resin (Aroplaz X663X50)	TTF515 & TTP664c fast dry, lift resist.	1.90 (15.3)	1.09 (9.10)	1.39 (11.6)
	3. Modified Alkyd Brown Primer (Ashland Q-315a)	32% Linseed/Tung Oil, 39% Phth. Anh. in Xylene - Modifier: Phenolic resin (Aroplaz X663X50)	Rust inhibiting, lacq. resisting	2.21 (18.4)	1.39 (11.6)	1.39 (11.6)
	4. Modified Alkyd Green Primer (Ashland P-111)	29% Linseed Oil, 30% Phth. Anh. in VM & P - Modifier: Resin (Aroplaz 1385V10)	Fast drying, lt. color, Drums, machinery, etc.	1.70 (14.2)	1.69 (14.1)	1.69 (14.1)
	5. Urethane Lacquer Blue (Ashland B-501)	25% Urethane in Xylene/MIBK/but. 20/50/30 (Arothane M529)	For flexing parts like bumpers, etc.	1.69 (14.0)	3.37 (28.1)	4.45 (37.1)
	6. Short Oil Alkyd White Enamel (Ashland P-49)	30% Tall Oil, 40% Phth. Anh. in Xylene (Aroplaz A065X50)	Fast drying, economical, industrial finish	1.73 (14.4)	1.50 (12.5)	2.12 (17.7)
	7. Medium Oil Alkyd White Gloss Enamel (Ashland I-46)	51% Soybean Oil, 30% Phth. Anh. in mineral spirits	High viscosity, general purpose, flexible, hard	1.61 (13.4)	1.24 (10.3)	1.78 (14.8)
	8. Zinc Rich Primer (Mirasol 601)	Epoxyester Xylene, naphtha/acetate	Industrial weld-through primer	3.82 (31.8)	1.10 (9.20)	Unk Unk
1Aw - SPRAY, Air drying, water borne	1. Short Oil Alkyd White Enamel (Ashland P-216)	Soybean Oil resin in Butoxy ethanol/water solution (Aroclon 363)	Industrial coatings	1.75 (14.6)	0.51 (4.26)	0.51 (4.26)
1Ba - SPRAY, Bake cured, solvent borne	1. Thermoset Acrylic White Enamel (Ashland P-36)	Selfcrosslink acrylic in ethoxy ethanol/xylene (Aronet 701X43-50)	Quality coat, good adhesion	1.64 (13.7)	1.63 (13.6)	1.94 (16.2)
	2. Thermoset Acrylic Black Enamel (Ashland P-188)	Acrylic resin in Xylene cross-link/melamine (Aroset 4110X60)	High gloss automotive, industrial coatings	1.15 (9.60)	1.03 (8.60)	1.28 (10.7)
	3. Thermoset Acrylic White Enamel (Ashland P-232)	Acrylic resin in Xylene cross-link/melamine (Aroset 4110X60)	High gloss automotive, industrial coatings	1.58 (13.2)	1.06 (8.80)	1.06 (8.80)
	4. Short Oil Alkyd White Primer (Ashland P-63)	32% Tall Oil, 40% Phth. Anh. in Xylene (Aroplaz 1453X50)	Light color industrial finishes	1.67 (13.9)	1.22 (10.2)	1.51 (12.6)
	5. Non-oxidizing Alkyd White Enamel (Ashland P-122a)	35% Coconut Oil, 41% Phth. Anh. in Xylene (Aroplaz 2580X60)	Ultradurable exterior & automotive	1.66 (13.8)	0.90 (7.50)	1.03 (8.60)

(continued)

TABLE C-2 (continued)

PAINT CLASS	PAINT DESCRIPTION (FORMULATION)	COMPOSITION OF BINDER	SUGGESTED USE	Wt kg/lit (lb/gal)	kg OV/111 SV (lb OV/gal SV) buy use	kg OV/111 SV (lb OV/gal SV) buy use
1Bx - (continued)	6. Non-oxidizing Alkyd Yellow, Gray, Green (Ashland R-172)	67 Caster Oil, 17 Phth. Anh. in xylene (Aroplaz 7407X50)	Semi-dry Alkyd Enamel & baked enamel	2.35 (19.6)	2.65 (22.1)	7.27 (60.6)
1Bw - SPRAY, Bake cured, water borne	1. Safflower & Linseed Gray Surfacer (Ashland Q-509)	Linseed/Caster Oil in Butyl Ethanol water solution (Aroclon 12)	Sealable primer	2.08 (17.1)	0.67 (5.60)	0.67 (5.60)
	2. Medium Short Alkyd Orange Enamel (Ashland P-225)	Safflower Oil Alkyd in water/t. but./butoxyl ethanol water solution (Aroclon 126)	Exterior, durable, bake or air dry	1.92 (16.0)	0.84 (7.00)	0.84 (7.00)
	3. Medium Short Alkyd Red Primer (Ashland Q-514)	Safflower Oil Alkyd in water/t. but./butoxyl ethanol water solution (Aroclon 126)	Exterior, durable, bake or air dry	2.15 (19.6)	0.76 (6.30)	0.76 (6.30)
	4. Medium Short Alkyd Green Enamel (Ashland P-223c)	Safflower Oil Alkyd in water/t. but./butoxyl ethanol water	Exterior, durable, bake or air dry	1.54 (12.8)	0.84 (7.00)	0.84 (7.00)
2Ax - DIP, FLOW, CURTAIN, Air drying, solvent borne	1. Medium & Short Alkyd/Modified Rosin Gray Enamel (Ashland P-134)	51% Soybean, 30 Phth. Anh. (Aroplaz 7407X50) 35% Soybean, 172 Phth. Anh. (Aroplaz 7424X50) Phenol-Rosin (Arochem 115)	Fast drying, general use, flexible, hard, tough	1.51 (12.6)	1.36 (11.3)	1.96 (16.3)
	2. Medium & Short Modified Rosin Black Enamel (Ashland P-135)	51% Soybean, 101 Phth. Anh. (Aroplaz 7407X50) 35% Soybean, 172 Phth. Anh. (Aroplaz 7424X50) Phenol-Rosin (Arochem 115)	Fast drying, general use, flexible, hard, tough	1.10 (9.20)	1.45 (12.1)	2.09 (17.4)
2Aw - DIP, FLOW, CURTAIN, Air drying, water borne	1. Short, Modified Alkyd Orange Enamel (Ashland P-235a)	Safflower Oil Rosin - water dispersion type (Aroclon 585)	Fast drying, good adhesion & toughness	1.49 (12.4)	0.11 (0.90)	0.11 (0.90)
	2. Short, Modified Alkyd White Enamel (Ashland P-238)	Safflower Oil Rosin - water dispersion type (Aroclon 585)	Fast drying, good adhesion & toughness	1.69 (14.1)	0.12 (1.00)	0.12 (1.00)
2Bx - DIP, FLOW, CURTAIN, Bake cured, solvent borne	1. Short Alkyd Yellow Enamel (Ashland P-140)	357 Tall Oil, 182 Phth. in Xylene/Aliphatic (Aroplaz 7415XN50)	Toys, etc. Excellent for electrostatic spray	1.27 (10.6)	1.73 (14.4)	2.09 (17.4)

(continued)



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TABLE C-2 (continued)

PAINT CLASS	PAINT DESCRIPTION (FORMULATION)	COMPOSITION OF BINDER	SUGGESTED USE	NV kg/lit (lb/gal)	kg OV/lit NV (lb OV/gal NV)	
					buy	use
2Ba - (continued)	2. Oil Free Alkyd	Polyester in aromatic solvents (Aroplaz 6025R70)	Industrial high flexi- bility	1.29 (10.0)	1.16 (9.70)	1.16 (9.70)
2Bw - DIP, FLOW, CURTAIN, Bake cured, water borne	1. Short Oil Alkyd Red Enamel (Ashland P-243)	Safflower Oil Resin in water dispersion (Aroclon 585)	High gloss, high solids, Industrial use	1.32 (11.0)	0.48 (4.00)	0.48 (4.00)
	2. Short Oil Alkyd White Enamel (Ashland P-233)	Safflower Oil Resin in water dispersion (Aroclon 585)	High gloss, high solids, Industrial use	2.04 (17.0)	0.28 (2.30)	0.28 (2.30)
	3. Short Oil Alkyd Black Enamel (Ashland P227)	Safflower Oil Resin in water dispersion (Aroclon 585)	High gloss, high solids, Industrial use	1.46 (12.2)	0.29 (2.40)	0.29 (2.40)
	4. Modified Oil Maleinized Black Primer (Ashland Q-510)	Linseed/Castor Oil Resin in eth- oxy ethanol glycol butyl (Aroclon 125)	Rust inhibitive	2.17 (18.1)	0.64 (5.30)	0.64 (5.30)
	5. Medium Short Alkyd Orange Primer (Ashland P-234)	Safflower Oil Resin in Butoxy ethanol/t. butanol water solu- tion (Aroclon 377)	High gloss, hard flexible mar-resistant	1.52 (12.7)	1.01 (8.40)	1.01 (8.40)
	6. Modified Alkyd Gray Primer (Ashland 8635P1154)	Maleinized Oil Resin in Butoxy ethanol/mineral spirits water solution (Aroclon 507)	Tough resin, outstanding pigment suspension for automotive use	1.92 (16.0)	0.60 (5.00)	0.60 (5.00)
	7. Maleinized Oil Resin Black Primer (Ashland Q-519)	Linseed Oil Resin in water solu- tion (Aroclon 525)	Corrosion resistant, economical	1.34 (11.2)	0.95 (7.90)	0.95 (7.90)
	8. Maleinized Oil Resin Black Primer (Ashland Q-515)	Linseed Oil Resin in water solu- tion (Aroclon 525)	Automotive use	1.46 (12.2)	0.76 (6.30)	0.76 (6.30)
3Aa - COIL & ROLL, Air or mild heat drying, solvent borne	1. Medium Oil Alkyd Red Shop Coat (Ashland Q-14)	52% High Soya, 147 Phth. Anh. in Min. Spirits (Aroplaz 1082H50)	Low viscosity TIR266d-IV, high color retention	1.60 (13.3)	1.10 (9.20)	1.10 (9.20)
	2. Medium Oil Alkyd Flat White Enamel (Ashland H-105a)	52% High Soya, 142 Phth. Anh. in Min. Spirits (Aroplaz 1082H50)	Low viscosity TIR266d-IV, high color retention	2.06 (17.2)	1.16 (9.70)	1.69 (14.1)
	3. Short Oil Alkyd White Enamel (Ashland B-15)	18% Soyabean Oil, 43% Phth. Anh. in Xylene/Min. Spirits (Aroplaz 7310X50)	Very flexible, high weather durability	2.24 (18.7)	1.27 (10.6)	1.57 (13.1)
3Ba - COIL & ROLL, Bake cured, solvent borne	1. Oil Free Polyester White (Ashland P-87)	Non-oxidizing Alkyd in Arom./ methyl-heptyl ketone (Aroplaz 6022R65)	Exterior coil coat	1.79 (14.9)	0.79 (6.60)	0.79 (6.60)

(continued)

TABLE C-2 (continued)

PAINT CLASS	PAINT DESCRIPTION (FORMULATION)	COMPOSITION OF BINDER	SUGGESTED USE	NV lb/gal (lb/gal)	OV/lit NV (lb OV/gal NV)	
					buy	use
3Bs - (continued)	2. Silicone modifier Polyester White Enamel (Ashland P-77)	70% Oil Free Alkyd, 30% Silicone in Aromatic/polyester/butanol (Aroplaz 1711A960)	Good durability, economical	1.82 (15.2)	0.70 (5.80)	0.70 (5.80)
	3. Oil Free Polyester White Gloss Enamel (Ashland P-84)	85% Oil Free Alkyd, 15% Silicone in Arom./but. ac. (Aroplaz 6025R70)	Good exterior durability, economical	1.84 (15.3)	0.66 (5.50)	0.66 (5.50)
	4. Oil Free Polyester White Gloss Enamel (Ashland P-88)	Oil Free Alkyd in Aromatics (Aroplaz 602JR 0)	Low temperature curing, interior & exterior	2.04 (17.0)	0.73 (6.10)	0.73 (6.10)
	5. Oil Free Polyester White Gloss Enamel (Ashland P-89)	Oil Free Alkyd in Aromatics (Aroplaz 6029S60)	Low temperature curing, interior & exterior	1.81 (15.1)	0.85 (7.10)	0.85 (7.10)
	6. Oil Free Polyester White Gloss Enamel (Ashland P-81)	Oil Free Alkyd in Aromatics (Aroplaz 6025R70)	High flexibility, color retention, adhesion	2.82 (23.5)	0.66 (5.50)	0.66 (5.50)
3Bw - COIL & ROLL, Bake cured, water borne	1. Oil Free Polyester White Gloss Enamel (Ashland P-240)	Thermoset Alkyd in Butoxy ethanol water solution (Arolon 465)	Excellent color retention	1.74 (14.5)	0.32 (2.70)	0.32 (2.70)
	2. Medium Short Alkyd Red Primer (Ashland Q-514)	Safflower Oil in butanol/butoxy ethanol water solution (Arolon 376)	High gloss, adhesion, corrosion resistant, flexible	2.35 (19.6)	0.76 (6.30)	0.76 (6.30)
	3. Medium Short Alkyd Green Enamel (Ashland P-223c)	Safflower Oil in butanol/butoxy ethanol water solution (Arolon 376)	High gloss, adhesion, corrosion resistant, flexible	1.55 (12.9)	0.84 (7.00)	0.84 (7.00)
4Bw - ELECTROCOATS, Bake cured, water borne	1. Short Oil Alkyd Red Primer (Ashland Q-602)	Soy Oil Resin in n-butanol water solution (Arolon 369)	Automotive & other high quality uses	1.44 (12.0)	0.31 (2.60)	0.31 (2.60)
	2. Short Oil Alkyd Flat Black (Ashland P-702)	Soy Oil Resin in n-butanol water solution (Arolon 369)	Automotive & other high quality uses	1.50 (12.5)	0.30 (2.80)	0.30 (2.80)
	3. Short Oil Alkyd Gloss Black (Ashland P-704)	Soy Oil Resin in n-butanol water solution (Arolon 369)	Automotive & other high quality uses	1.14 (9.50)	0.47 (3.90)	0.47 (3.90)
	4. Short Oil Alkyd Gray Primer (Ashland Q-601)	Soy Oil Resin in n-butanol water solution (Arolon 369)	Automotive & other high quality uses	1.43 (11.9)	0.31 (2.60)	0.31 (2.60)
	5. Short Oil Alkyd White Enamel (Ashland P-701)	Soy Oil Resin in n-butanol water solution (Arolon 369)	Automotive & other high quality uses	1.33 (11.1)	0.34 (2.80)	0.34 (2.80)

(continued)

TABLE C-2 (continued)

PAINT CLASS	PAINT DESCRIPTION (FORMULATION)	COMPOSITION OF BINDER	SUGGESTED USE	NV kg/lit (lb/gal)	kg OV/lit NV (lb OV/gal NV)	
					buy	use
SB - POWDERS, Bake cured	1. Epoxy, Conventional		Indoor or primer <sup>1</sup>	1.20-	0.012-	0.012-
				1.30	0.018 <sup>2</sup>	0.018 <sup>2</sup>
				(10.0-	(0.120-	(0.120-
				15.0)	0.150) <sup>2</sup>	0.150) <sup>2</sup>
				1.16-	0.007-	0.007-
				1.79	0.010 <sup>3</sup>	0.010 <sup>3</sup>
	2. Epoxy, low Temperature		Outdoor metal <sup>1</sup>	(9.60-	(0.040-	(0.040-
				14.9)	0.080) <sup>3</sup>	0.080) <sup>3</sup>
				1.16-	0.042-	0.042-
				1.79	0.078 <sup>2</sup>	0.078 <sup>2</sup>
				(9.60-	(0.350-	(0.350-
				14.9)	0.640) <sup>2</sup>	0.640) <sup>2</sup>
	3. Thermoset Polyester, Melamine cured		Outdoor metal <sup>1</sup>		0.030-	0.030-
					0.048 <sup>4</sup>	0.048 <sup>4</sup>
					(0.250-	(0.250-
					0.400) <sup>4</sup>	0.400) <sup>4</sup>
				1.16-	0.048-	0.048-
				1.79 <sup>3</sup>	0.060	0.060 <sup>3</sup>
	4. Thermoset Polyester, Isocyanate cured		Furniture, fencing <sup>6</sup>	(9.60-	(0.400-	(0.400-
				14.9)	0.500) <sup>3</sup>	0.500) <sup>3</sup>
					0.054-	0.054-
					0.070 <sup>5</sup>	0.070 <sup>5</sup>
					(0.450-	(0.450-
					0.580) <sup>5</sup>	0.580) <sup>5</sup>
5. Thermoplastic Polyester	Outdoor metal & equipment <sup>1</sup>	1.15-	0.001-	0.001-		
		1.31	0.004 <sup>6</sup>	0.004 <sup>6</sup>		
		(9.60-	(0.010-	(0.010-		
		10.9)	0.030) <sup>6</sup>	0.030) <sup>6</sup>		
		1.20-	0.030-	0.030-		
		1.52	0.042 <sup>2</sup>	0.042 <sup>2</sup>		
6. Thermoset Acrylic		(10.0-	(0.250-	(0.250-		
		12.7)	0.350) <sup>2</sup>	0.350) <sup>2</sup>		
			0.098-	0.098-		
			0.124 <sup>2</sup>	0.124 <sup>2</sup>		
			(0.820-	(0.820-		
			1.030) <sup>2</sup>	1.030) <sup>2</sup>		

(continued)



TABLE C-2 (continued)

PAINT CLASS	PAINT DESCRIPTION (FORMULATION)	COMPOSITION OF BINDER	SUGGESTED USE	NV lb/lit (lb/gal)	lb OV/lit NV (lb OV/gal NV)	
					buy	use
5B - (continued)	7. Vinyl		Outdoor furniture, bicycles <sup>1</sup>	1.20- 1.68	0.005- 0.026 <sup>7</sup>	0.005- 0.026 <sup>7</sup>
	8. Cellulose Acetate Butyrate		Fencing, wires, under- ground uses <sup>7</sup>	(10.0- 14.0)	(0.050- 0.220) <sup>7</sup>	(0.050- 0.220) <sup>7</sup>
			Furniture <sup>1</sup>	1.14- 1.32 (9.50- 11.0)	0.060- 0.096 <sup>4</sup> (0.500- 0.800) <sup>4</sup>	0.060- 0.096 <sup>4</sup> (0.500- 0.800) <sup>4</sup>
					0.030- 0.042 <sup>7</sup> (0.250- 0.350) <sup>6</sup>	0.030- 0.042 <sup>7</sup> (0.250- 0.350) <sup>6</sup>
6eh - RADIATION, Electron beam cured	1. Polyester, US Pat. 3,437,514 (Ford Motor Co.)	56% Styrene, 1% Maleic Anh.	Wood & metal	0.91† (7.60)†	0.048† (0.400)†	0.048† (0.400)†
	2. Clear Acrylic, US Pat. 3,437,514 (Ford Motor Co.)	97% Acrylates	Wood & metal	0.91† (7.60)†	0.048† (0.400)†	0.048† (0.400)†
	3. White Acrylic, US Pat. 3,437,513 (Ford Motor Co.)	90% Acrylates, 8% Styrene	Wood & metal	0.91† (7.60)†	0.048† (0.400)†	0.048† (0.400)†
	4. White Silicone Polyester, US Pat. 3,437,513 (Ford Motor Co.)	30% Polyester, 10% Styrene, 10% Acrylic Siloxane, 30% Methyl Methacrylate	Wood & metal	0.91† (7.60)†	0.048† (0.400)†	0.048† (0.400)†
6uv - RADIATION, Ultra violet ray cured	1. Polyester		Printed decorations	Unk (Unk)	0.024 <sup>8</sup> (0.200) <sup>8</sup>	0.060 <sup>8</sup> (0.500) <sup>8</sup>
	2. Acrylic		Clear overcoats	Unk (Unk)	0.024 <sup>8</sup> (0.200) <sup>8</sup>	0.060 <sup>8</sup> (0.500) <sup>8</sup>
	3. Poly-thioether (W.R. Grace & Co.)		Elevated temperature coats, magnetic wire	Unk (Unk)	Unk <sup>9</sup> (Unk) <sup>9</sup>	Unk <sup>9</sup> (Unk) <sup>9</sup>
7Aa - HIGH SOLIDS, Air drying, solvent borne	1. Acrylic White enamel (Rohm & Haas QR 368)	59% Acrylic oligomer, 41% Des- modur N in ethoxy ethanol acetate moistener	Large equipment, heat sensitive items, shop refinishing	1.58 (13.2)	0.68 (5.70)	0.68 (5.70)

(continued)


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TABLE C-2 (continued)

PAINT CLASS	PAINT DESCRIPTION (FORMULATION)	COMPOSITION OF BINDER	SUGGESTED USE	NV kg/lit (lb/gal)	kg OV/lit NV (lb OV/gal NV)	
					buy	use
73a - HIGH SOLIDS, Bake cured, solvent borne	1. Acryloid OL 42 White Enamel (Rohm & Haas)	Hydroxyl acrylic oligomer in ethoxy ethanol crosslink with melamine	Indoor & outdoor furni- ture, air conditioners, etc.	1.72 (14.3)	0.50 (4.20)	0.50 (4.20)
	2. Acrylic White Enamel (Rohm & Haas)	40% Carboxyl acrylic oligomer, 60% Epoxy in crosslink with Methyl-ethyl-ketone/toluene 75/25 wt%	Low energy porcelain replacements	1.69 (14.1)	0.59 (4.90)	0.59 (4.90)
89w - LOW SOLVENT, Bake cured, water borne	1. Acrylic White Enamel (Ashland EF-11)	Acrylic emulsion in water (Avalon X-801)	General industrial or outdoor over primer	1.19 (9.90)	0.18 (1.50)	0.18 (1.50)
99w - POWDER SLURRY, Bake cured, water borne	1. Acrylic White Enamel	Acrylic powder in water	General industrial	1.36 (11.3)	0.018# (0.150)#	0.018# (0.150)#

<sup>1</sup> G. E. Cole, Jr.; SME paper, FC 74-560, and direct communication.

<sup>2</sup> R. D. Hardy & T. W. Selts; SME paper, FC 74-589.

<sup>3</sup> O. J. S. van, Sherwin-Williams Co.; Newer Formulations, and direct communication.

<sup>4</sup> T. W. Selts, Sherwin-Williams Co.; direct communication.

<sup>5</sup> P. B. Gribble, SFM-Glidden-Jurkee; direct communication.

<sup>6</sup> R. A. Johnston, Eastman Chemical Products, Inc.; Newer Formulations, and direct communication.

<sup>7</sup> J. W. Hagen, Union Carbide Corporation; direct communication.

<sup>8</sup> S. F. Schroeter, General Electric Company; "The Ultraviolet Cure of Solventless Resins", Non-polluting Coatings & Coating Processes; Gordon & Prane, Editors, Plenum Press, New York, N. Y. 1973.

<sup>9</sup> A. D. Katley, W. R. Grace & Company; SME paper, FC 75-331.

# Data given for Paint Class 5B only include liberated organic coreactants.

† Data given are estimates.

‡ Data given include liberated organic coreactants.

TABLE C-3. WASTE COATING COMPOSITION DATA

Process and/or waste description		Waste composition <sup>a</sup>	Data quality
Paint sludge from spray painting at truck assembly plant	Pigments, %	20	C
	Resin, %	60	
	Moisture, %	20	
Paint sludges from auto assembly plant	Toluene, %	5-33	C
	Ethyl alcohol, %	2-11	
	Diacetone alcohol, %	1-4	
	Isopropyl alcohol, %	1-15	
	N-Butyl alcohol, %	1-16	
	Cellosolve acetate, %	1-6	
	Xylene, %	3-100	
	MEK, %	1-16	
	Ethylene glycol monoethyl ether, %	1-4	
	V.M. & P. naphtha, %	1-2	
	Aromatic naphtha, %	9-30	
	N-Butanol, %	1-2	
	Iso-butanol, %	1-2	
	Ketones, %	1-20	
	Esters, %	10-20	
	Crotonaldehyde, %	0-25	
	Diethylbenzene, %	0-25	
	Turpentine, %	0-11	
	Pigments, %	1-60	
	Barium sulfate		
	Aluminum silicate		
	Titanium dioxide		
	Montmorillonite clay		
	Magnesium silicate		
	Carbon black		

(continued)

TABLE -3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Paint sludges from auto assembly plant (continued)	Pigments, % Copper Lead Nickel Chrome	
Paint sludge from tractor manufacturing operations	Nonvolatiles, % 70.18 Volatiles, % 29.82 Water, % >25 Organic solvents Xylene, % <4 Naphtha, %  Composition of nonvolatile portion Alkyd type grey bake enamel, % 14 Alkyd type blue bake enamel, % 34 Alkyd type yellow bake enamel, % 37 Alkyd type black air-dry enamel, % 4 Alkyd type primer, % 11	B
Paint sludge from a tank plant	Total chromium, mg/L 600-2,000 Lead, mg/L 1-3 Zinc, mg/L 400-600 <sub>b</sub> Mercury ND <sub>b</sub> Arsenic ND <sub>b</sub> Copper, mg/L 60-100 pH 6.35 Solid paint, heterogeneous mixture	B

(continued)

TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Paint primer sludge	Alkyd resin Xylene Toluene Naphtha Zinc Iron	C
Finish paint sludge	Alkyd resin Xylene Toluene Naphtha Mineral spirits Titanium Iron Carbon	C
Paint sludge	Silicone resins Cellosolve acetate (acetate esters of ethylene glycol monoethyl ether) Isobutyl acetate Xylene Toluene Aluminum	C
Acrylic based paint residue (solids)	Resin, % 40-60 Moisture, % 25-30 Pigments (primarily carbon black), % 15-20 Solvent (trace of toluene), % 0.5-2	C

(continued)

TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Solvent based paint sludge	Flammable, volatile	C
	Alkyds, %	15
	Nitro cellulose, %	10
	Organic solvent, %	13
	Organic resin, %	4
	Organic and inorganic pigment, %	25
	Toluol, %	24
	Xylol, %	3
	Butyl acetate, %	2
	MIBK, %	1
	Isopropanol, %	3
	Lead, %	<0.5
	Chromium, %	<0.5
Acrylic copolymer based dewatered paint residue	Odorless waxy solid	B
	Softening point, °F	>160
	Flash point, °F	>250
	Moisture, %	<0.5
	Resin, %	60-62
	Free oil, %	3-4
	Pigments, %	34-37 <sup>b</sup>
	Solvent	ND <sup>b</sup>
	Pigments consist of titanium dioxide and some carbon black. No acrylic monomer present.	
Electrolytic paint sludge	Deionized water, %	85.5
	Alcohols, %	4.5
	Pigments, %	10.0
	pH	6.6-7.6

(continued)

TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Solvent based scrap automotive paint	The minimum and maximum are ranges one would expect to find from one drum (55 gallon) to another. The average represents what one would expect by mixing one truck load (approx. 4,000 gallons) of scrap paint.	C
	<u>Min/Avg/Max</u>	
General analysis		
Resin, %	10/25/40	
Solvent, %	10/50/95	
Water	--	
Pigment, %	5/25/30	
pH, %	6.5/7/8.5	
Detailed analysis		
Resin		
Acrylic copolymers, %	20/30/40	
Melamine, %	0/5/10	
Melamine copolymers, %	0/5/10	
Epoxy ester resin, %	0/3/12	
Solvents		
Acetone, %	5/10/15	
Xylene, %	0/10/20	
Toluene, %	0/10/15	
Acetate esters of ethylene glycol mono ethyl ether, %	0/10/15	
Misc. hydrocarbons, %	0/8/12	
Water	--	

(continued)

TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Solvent based scrap automotive paint (continued)	<div>Heavy metals in pigments</div> <div> Lead, mg/L 50/150/300  Mercury, mg/L 1/1/5  Nickel, mg/L 2/10/15  Arsenic, mg/L 1/1/10  Chromium, mg/L 50/400/2,000  Silica, mg/L 50/50/200  Copper, mg/L 50/100/3,000  Zinc, mg/L 50/3,000/6,000  Bromine, mg/L 10/16/3,000  Chlorine, mg/L 10/80/3,000 </div> <div>Total solids (pigments and resins left after heating at 250°F), % 5/12/45</div>	
Paint and water from paint spray booth-auto assembly plant	<div>pH 8.1</div> <div>Paint, % 61.5</div> <div>Water, % 38.5</div> <div>Lead, mg/kg &lt;10,000</div> <div>Zinc, mg/kg &lt;1,000</div> <div>Nickel, mg/kg &lt;100</div> <div>Copper, mg/kg &lt;1,000</div> <div>Chromium, mg/kg &lt;1,000</div> <div>Phenolics compound (by leach test), mg/kg 4.7</div>	B

(continued)



TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality	
Gray epoxy low bake primer sludge	Pigments, %	37	C
	Barium sulfate		
	Titanium dioxide		
	Silica		
	Carbon black		
	Vehicle solids, %	16	
	Epoxy ester resin, %	93	
	Nitrogen resin, %	7	
	Solvents, %	47	
	Aromatic hydrocarbons		
	Aliphatic hydrocarbons		
Liquid water base aluminum paint sludge	Ethylene glycol monobutyl ether		
	Butyl alcohol		
	Metallic aluminum pigment, %	6.2	B
	Alkyd resin, %	19.4	
	Driers and stabilizers, %	0.4	
Cosolvents, %	12.6		
Water, %	61.4		
Solid water base aluminum paint sludge	Metallic aluminum pigment, %	23.8	B
	Alkyd resins, %	74.6	
	Driers and stabilizers, %	1.6	
Liquid solvent base aluminum paint sludge	Metallic aluminum, %	12.7	B
	Suspending and tinting pigment, %	0.5	
	Phenolated alkyd resin, %	25.2	
	Aromatic and aliphatic hydrocarbon blend, %	61.6	

(continued)

TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Solid solvent base aluminum paint sludge	Metallic aluminum, %	33.1
	Suspending and tinting pigment, %	1.3
	Aromatic and aliphatic hydrocarbon blend, %	65.6
Liquid zinc rich welding primer sludge	Metallic zinc, %	71.2
	Suspending agent, %	2.7
	Epoxy ester, %	4.6
	Rubber, %	1.1
	Aromatic and aliphatic hydrocarbon blend, %	20.4
Solid zinc rich welding primer sludge	Metallic zinc, %	89.4
	Suspending agent, %	3.4
	Epoxy ester, %	5.8
	Rubber, %	1.4
Dip paint sludge	pH	7.2
	2-Butoxyethanol, %	15
	N-Butoxypropanol, %	<5.0
	Triethylamine, %	<0.5
	Chromium pigment, %	0.29
	Water	Balance
Overspray and drippings from spray paint booth	Lead, %	5
	Chrome, %	3
	Anodized aluminium, %	3
	Carbon black, %	1
	Iron oxide, %	6
	Iron blue, %	2

(continued)

TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Overspray and drippings from spray paint booth (continued)	Solvents	
	Xylol, %	
	Toluol, %	
	Naphtha, %	
	MEK, %	10
	Vehicle (resin), %	70
Paint spray booth sludge	Flammable	B
	Flash point, °F	53
	Vinyl tolunated alkyd resin, %	33.5
	V. M. & P. naphtha, %	51.7
	Calcium carbonate, %	11.5
	Titanium dioxide, %	3.0
	Lead, mg/kg	<10
	Nickel, mg/kg	<10
	Cadmium, mg/kg	<10
	Chromium, mg/kg	<10
	Mercury, mg/kg	<10
	Arsenic, mg/kg	<10
	Amines, mg/kg	<10
	Nitro-phenols, mg/kg	100
	Quinones, mg/kg	100
Dip prime sludge	Pigments, %	15-20
	Xylol, MIBK, cellosolve acetate, %	80-85
	Zinc, mg/L	247
Paint sludge	pH	7.0
	Water, %	70-95
	Sodium silicate, %	5-10

(continued)

TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Paint sludge (continued)	Sodium phosphate, %	5-10
	Sodium hydroxide, %	1-5
	Paint resin, %	5-10
	Pigments, %	1-5
Paint residue from productive painting operations	Ketones and alcohols, %	10-20
	Toluene, %	70-80
	Pigments, %	5-10
	Xylene, %	<1
Solvent based paint sludge	Flammable	
	Flash point, °F	200
	pH	8.0-9.0
	Noncombustible ash, %	6
	Aliphatic alcohols, %	9-13
	Toluene, %	1
	Aliphatic petroleum distillate, %	34-42
	Triethylamine, %	0.4
	Xylene, %	<1
	Manganese, %	<1
	Nickel, %	0.03
	Chromate, %	0.06
	Copper, %	<2
	Lead, %	0.25
Paint sludge from spray booth	Noncombustible ash, %	6.1
	Resins, fillers, pigments, %	87.7
	Lead, %	2.7

(continued)

TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Paint sludge from spray booth (continued)	Zinc, mg/L	260
	Nickel, mg/L	2
	Copper, mg/L	220
	Mercury, mg/L	16
	Beryllium, mg/L	2
	Cadmium, mg/L	1
	Hexavalent chromium, mg/L	9,100
	Arsenic, mg/L	8
	Phosphorus, mg/L	4,760
Paint sludge from painting automobile accessories	Flammable	B
	Flash point, °F	
	<32	
	Oil and grease, %	
	3.6	
	Pigments, %	
	30.4	
	Solvents, %	
	66.0	
	Aromatic hydrocarbons, %	
	17.9	
	Alcohol, %	
	13.5	
	Water, %	
	11.4	
	Naphtha, %	
	9.8	
	Ketones, %	
	9.2	
	Glycol, %	
	1.7	
	Esters, %	
	0.8	
	Phosphorus, mg/L	
	37	
	Phenol, mg/L	
	4.4	
	PCB	
	Aroclor 1242, mg/L	
	<2	
	Aroclor 1260, mg/L	
	<2	
	Lead, mg/L	
	190	
	Zinc, mg/L	
	11	

(continued)

TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Paint sludge from painting automobile accessories (continued)	Nickel, mg/L	8.8
	Copper, mg/L	12
	Beryllium, mg/L	<0.2
	Cadmium, mg/L	<0.2
	Chromium, mg/L	<0.05
	Mercury, mg/L	<0.01
	Chlorine, mg/L	10,570
	Bromine, mg/L	74
	Arsenic, mg/L	0.31
	Sulfur, mg/L	710
	Cyanide, mg/L	0.8
Paint sludge from painting automobile accessories	Flash point, °F	>200
	pH	8.4
	Water, %	45
	Resins, %	40
	Metals and dirt, %	15
	Noncombustible ash, %	57.2
	Lead, mg/L	3,345
	Zinc, mg/L	2,651
	Nickel, mg/L	70
	Copper, mg/L	1,682
	Cadmium, mg/L	0.8
	Chromium, mg/L	120
Water base paint residue-water reducible baking epoxy paint	Toxic	
	pH	8.0
	Water, %	64 ± 10
	Carbon black, %	2.4
	Lead silicochromate, %	4.0

(continued)

TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Water base paint residue-water reducible baking epoxy paint (continued)	Urea formaldehyde, %	4.0
	Methylated melamine, %	3.9
	Epoxy ester, %	12.7
	Ammonium compounds, %	1.5
	Talc, %	7.9
	Butyl cellosolve, %	4.8
	n-Butanol, %	0.5
	Methyl cellosolve, %	3.7
	Noncombustible ash, %	12 ± 1
	Lead, mg/kg	1,640
	Trivalent chromium, mg/kg	15
Paint sludge	Flammable	B
	Flash point, °F	
	pH	
	Solids (paint), %	
	Noncombustible ash, %	
	Lead, mg/kg	
	Zinc, mg/kg	
	Nickel, mg/kg	
	Copper, mg/kg	
	Beryllium, mg/kg	
	Cadmium, mg/kg	
	Chromium (total), mg/kg	
	Chromium (hexavalent), mg/kg	
	Mercury, mg/kg	
	Arsenic, mg/kg	
	Kjeldahl nitrogen, mg/kg	
	Phenol, mg/kg	

(continued)

TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Paint sludge (continued)	Total halogens reported as Chlorine, mg/kg 62 Bromine, mg/kg 33 Organic halogens reported as Chlorine, mg/kg 59 Bromine, mg/kg 32 Sulfur, mg/kg 140 Phosphorus, mg/kg 2,100 Oil and grease, mg/kg 143,000 Cyanide, mg/kg 35 PCB reported as Aroclor 1242, mg/kg <1 Aroclor 1260, mg/kg 7 Solvents V.M.P. naphtha, mineral spirits, and alcohol.	
Waste enamel from wire coating process	Toxic Flammable Cresylic acid (cresols-xlenols), % 30-50 Aromatic hydrocarbons (xylene), % 20-40 Resins (polyamide-polyester urethanes-amide-imides), % 15-30 Zinc, mg/L 63.5 Copper, mg/L 3.17 Cadmium, mg/L 1.00 <sup>b</sup> Lead, nickel, beryllium, chromium ND	C
Primer paint sludge from paint spray booth	Pigments and resins 34.5 Water 65.5	C

(continued)



TABLE C-3 (continued)

Process and/or waste description		Waste composition <sup>a</sup>	Data quality
Primer paint sludge from paint spray booth (continued)	Lead, mg/kg	<1,000	
	Zinc, mg/kg	<1,000	
	Nickel, mg/kg	<100	
	Copper, mg/kg	<100	
	Chromium, mg/kg	<1,000	
	Phosphorus, mg/kg	1,000 to 10,000	
Scrap enamel and solvent from magnet wire coating process	Flammable		C
	Flash point, °F	81	
	Toxic, corrosive		
	pH	~4.0	
	Polyester amide (maximum), %	40	
	Xylene (maximum), %	40	
	Cresylic acid (maximum), %	40	
	Trivalent chromium (maximum), mg/L	200	
	2,3,5-Trimethyl phenol, mg/L	0.01	
Waste enamel and solvents from magnet wire coating process	Flammable		B
	Flash point, °F	84-110	
	Toxic, odorous, irritant		
	Enamel resins in solution, %	1-5	
	Xylene, %	40-60	
	Cresylic acid, %	8-15	
	Ethyl alcohol, %	5-15	
	Phenol, %	3-6	
	Hydraulic oil, %	1-5	
	Melamine, mg/kg	350	
	Trivalent chromium, mg/kg	10-12	

(continued)

TABLE C-3 (continued)

Process and/or waste description		Waste composition <sup>a</sup>	Data quality
Paint sludge	Pigments, %	35	B
	Solvents and resins, %	65	
	Lead, %	0.22	
	Chromium, %	0.06	
Waste solvents and resins from magnetic wire coating operation	Xylene, %	~40	
	Phenol, %	~35	
	Cresylic acid, %	~25	
Waste paint	Paint pigments, %	31	B
	Xylene, %	17	
	Toluene, %	17	
	High boiling naphtha (such as SP-100 or kerosene), %	35	
Aluminum can painting process- solvent oil and paint sludge	Methyl ethyl ketone, %	15	B
	Paint sludge, %	15	
	Oil, %	40	
	Water, %	30	
Paint sludge	Paint, %	45-50	C
	Solvents, %	10-15	
	Latex, %	2-5	
	Water	Balance	
	pH	7.0	
Waste dip coat	Solids, %	73	B
	Liquid, %	27	
	pH	9.6	

(continued)

TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality	
Waste dip coat (continued)	Silica (colloidal), %	26.2	
	Silica (SiO <sub>2</sub> ), %	12.4	
	Aluminum oxide, %	37.0	
	Isopropyl alcohol, %	62	
Off-spec paint thinners	Acetone (90%)/Toluol (10%), %	30-70	C
	Butyl cellosolve, %	20-30	
	Butyl carbitol, %	10-30	
Off-spec spray paint	Water, %	50-60	C
	Aliphatic hydrocarbons, %	25-30	
	Fatty acids, %	10-15	
	Aluminum oxides, %	3-4	
	Titanium oxide, %	2-3	
Off-spec water base paint	Water, %	55	B
	Resin and solvent, %	30	
	Talc, %	12	
	Carbon black, %	3	
Off-spec primer	Flammable		B
	Flash point, °F	<70	
	Aromatic hydrocarbons (toluene, xylene, MEK), %	63.7	
	Resin, %	36.7	
	Noncombustible material (600°C), %	24.9	
	Lead, mg/kg	18.0	
	Cadmium, mg/kg	2.6	
	Nickel, mg/kg	1.2	
	Lithium, mg/kg	2.0	

(continued)

TABLE C-3 (continued)

Process and/or waste description		Waste composition <sup>a</sup>	Data quality
Off-spec primer (continued)	Mercury, mg/kg	6.0	
	Chromium, mg/kg	1.1	
	Copper, mg/kg	2.9	
	Zinc, mg/kg	38.2	
	Silver, mg/kg	0.2	
Waste paint thinner	Flammable		B
	Flash point, °F	<65	
	Toxic, irritant		
	Pigments, %	2.1	
	Aromatic hydrocarbons, %	27.7	
	Alcohol, %	20.5	
	Water, %	17.2	
	Naphtha, %	14.9	
	Ketones, %	13.9	
	Glycol ethers, %	2.5	
	Esters, %	1.2	
	Noncombustible ash, %	0.5	
	Lead, mg/L	152	
	Zinc, mg/L	37	
	Nickel, mg/L	1.4	
	Copper, mg/L	13.3	
	Cadmium, mg/L	29	
	Chromium, mg/L	23	
	Antimony, mg/L	5.3	
	Cobalt, mg/L	44.0	
	Lithium, mg/L	1.4	
	Silver, mg/L	2.3	

(continued)

TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Waste lacquer thinner from paint shop	Flammable	C
	Flash point, °F	
	21	
	Methyl ethyl ketone, %	
	~5	
	Isopropyl acetate, %	
	~5	
	Toluene, %	
	~50	
	Acetone, %	
	~10	
	Methyl isobutyl ketone, %	
	~5	
	Isopropyl alcohol, %	
	~5	
Paint filters and paint dust from clean-up of paint booths	Isobutyl, %	C
	~15	
	Methanol, %	
	~5	
	Xylene, %	
	~5	
	Solvent, %	
Grease and paint scraped from paint booth walls	56	B
	Pigments and resins, %	
	44	
	Zinc, mg/L	
	1,005	
Paint filters and paint dust from clean-up of paint booths	Chromium, mg/L	C
	73	
	Pigments, %	
	44	
	Resin, %	
Grease and paint scraped from paint booth walls	51	B
	Filter and dust, %	
	5	
	Diethylamine, mg/kg	
	<10,000	
Grease and paint scraped from paint booth walls	Paint solids, %	B
	92.5	
	Grease, %	
	7.5	
	Cadmium, mg/L	
	0.15	
	Chromium, mg/L	
Paint filters and paint dust from clean-up of paint booths	449	C
	Copper, mg/L	
	5.7	
	Nickel, mg/L	
	0.5	
Grease and paint scraped from paint booth walls	Lead, mg/L	B
	1,940	
Paint filters and paint dust from clean-up of paint booths	Zinc, mg/L	10.9

(continued)

TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Waste paint thinners and paint solids from paint clean-up operations	Aromatic hydrocarbons, %	62.4
	Oxygenated hydrocarbons, %	30.1
	Butyl ester/glycol ether, %	3.1
	Paint solids, %	4.4
	Noncombustible material (600°C), mg/kg	2,520
	Lead, mg/kg	1,920
	Cadmium, mg/kg	0.3
	Nickel, mg/kg	5.9
	Cobalt, mg/kg	11.8
	Iron, mg/kg	32.1
	Chromium, mg/kg	160
	Copper, mg/kg	3.9
	Zinc, mg/kg	54
	Antimony, mg/kg	1.2
	Silver, mg/kg	0.8
Waste generated during cleaning of paint spraying equipment	Toluene, %	62
	Hexane, %	13
	Trichloroethylene, %	11
Waste from clean up of painting operation	Flammable	
	Flash point, °F	20-80
	Volatile	
	Aliphatic petroleum distillate, %	48
	Toluene, %	43
	Paint solids, %	9
	Noncombustible ash, %	0.35
	Lead, mg/L	1,225
	Zinc, mg/L	30.3
	Nickel, mg/L	49.3

(continued)

TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Waste from clean up of painting operation (continued)	Copper, mg/L Cadmium, mg/L Chromium, mg/L	27.5 <0.1 47.0
Waste solvent generated during cleaning paint brushes or guns	Flammable Flash point, °F Xylenol/toulene, % Dirt, paint, and other material from cleaning, %	81 85-95 0-15
Alcohol rinse for waste enamel for wire coating process	Flammable Denatured-ethyl alcohol, % Cresylic acid, % Water, % Lead, mg/L Zinc, mg/L Copper, mg/L Nickel, cadmium, chromium	70-95 5-25 1-10 0.8 1.6 19.0 <sub>b</sub> ND
Acid rinse for waste enamel from wire coating process	Flammable Irritant Solids, % Xylenols, % Cresols, % Mixed resins (polyamides, etc.), % Phenol, % Lead, mg/L Zinc, mg/L Copper, mg/L	5 40-50 30-40 2-15 0-3 0.8 2.8 29.0

(continued)

TABLE C-3 (continued)

Process and/or waste description	Waste composition <sup>a</sup>	Data quality
Acid rinse for waste enamel from wire coating process (continued)	Cadmium, mg/L	1.8 <sup>b</sup>
	Nickel	ND <sup>b</sup>
	Chromium	ND <sup>b</sup>
Paint sludge from water wash air pollution control device	Noncombustible material (600°C), %	32.7
	Paint resins and pigments, %	70-96
	Water, %	4-30
	pH	8.0
	Lead, mg/kg	7,695
	Cadmium, mg/kg	0.7
	Nickel, mg/kg	7.5
	Cobalt, mg/kg	2.4
	Chromium, mg/kg	238
	Copper, mg/kg	6.8
	Zinc, mg/kg	1,095
	Lithium, mg/kg	1.8
	Silver, mg/kg	0.5 <sup>b</sup>
	Chlorine	ND <sup>b</sup>
	Bromine	ND <sup>b</sup>
	Antimony	ND <sup>b</sup>

<sup>a</sup>Data are reported as found in State files. Whether percentages given are by volume or weight is not known.

<sup>b</sup>Not detected.