Addendum To Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the

SYNTHETIC RESINS

Segment of the

PLASTICS AND SYNTHETIC MATERIALS MANUFACTURING

Point Source Category



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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ADDENDUM

to the

DEVELOPMENT DOCUMENT

for

PROPOSED EFFLUENT LIMITATION GUIDELINES

and

NEW SOURCE PERFORMANCE STANDARDS

for the

SYNTHETIC RESINS SEGMENT
of the
PLASTICS AND SYNTHETICS MANUFACTURING
PCINT SOURCE CATEGORY

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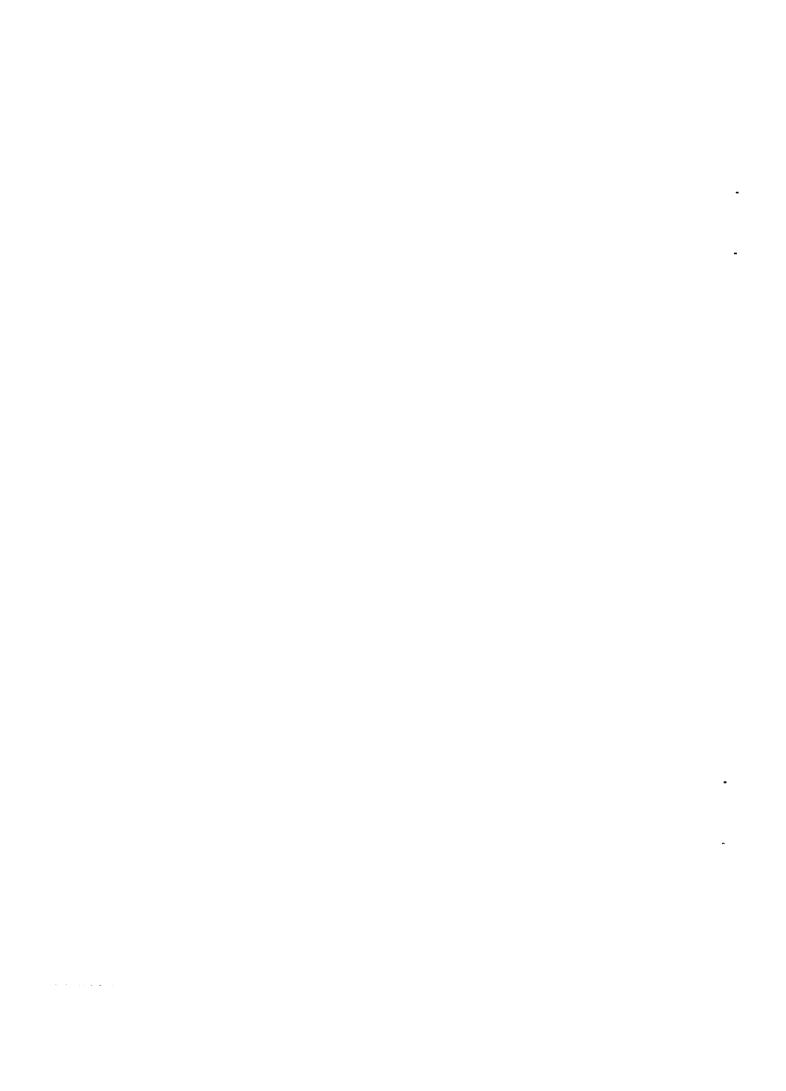


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ABSTRACT

This document is an addendum to the Development Document for Effluent Limitations Guidelines and Standards of Performance for the Resins Segment of the Plastics and Synthetics Industry which was prepared for the purpose of developing effluent limitations guidelines for the industry to implement Sections 304, 306 and 307 of the Federal Water Pollution Control Act of 1972 (PL 92-500). This addendum is a result of a substantial amount of additional information made available by industrial sources following publication of the original document. The guidelines and standards developed herein are for the following products:

Epoxy Resins, Melamine Resins, Phenolic Resins, Urea Resins

The effluent limitations guidelines in this report set forth the degree of reduction of pollutants in effluents that is attainable through the application of best practicable control technology currently available (BPCTCA) and the degree of reduction attainable through the application of best available technology economically achievable (BATEA) by existing point sources for July 1, 1977, and July 1, 1983, respectively. Standards of performance for new sources are based on the application of best available demonstrated technology (BADT).

Annual costs for this segment of the plastics and synthetics industry for achieving BPCTCA control by 1977 are estimated at \$2.0 million, and costs for attaining BATEA control by 1983 are estimated at \$6.4 million. The annual costs of BADT for new sources in 1977 is estimated at \$1.9 million.

Supporting data and rationale for the development of proposed effluent limitations guidelines and standards of performance are contained in this development document.

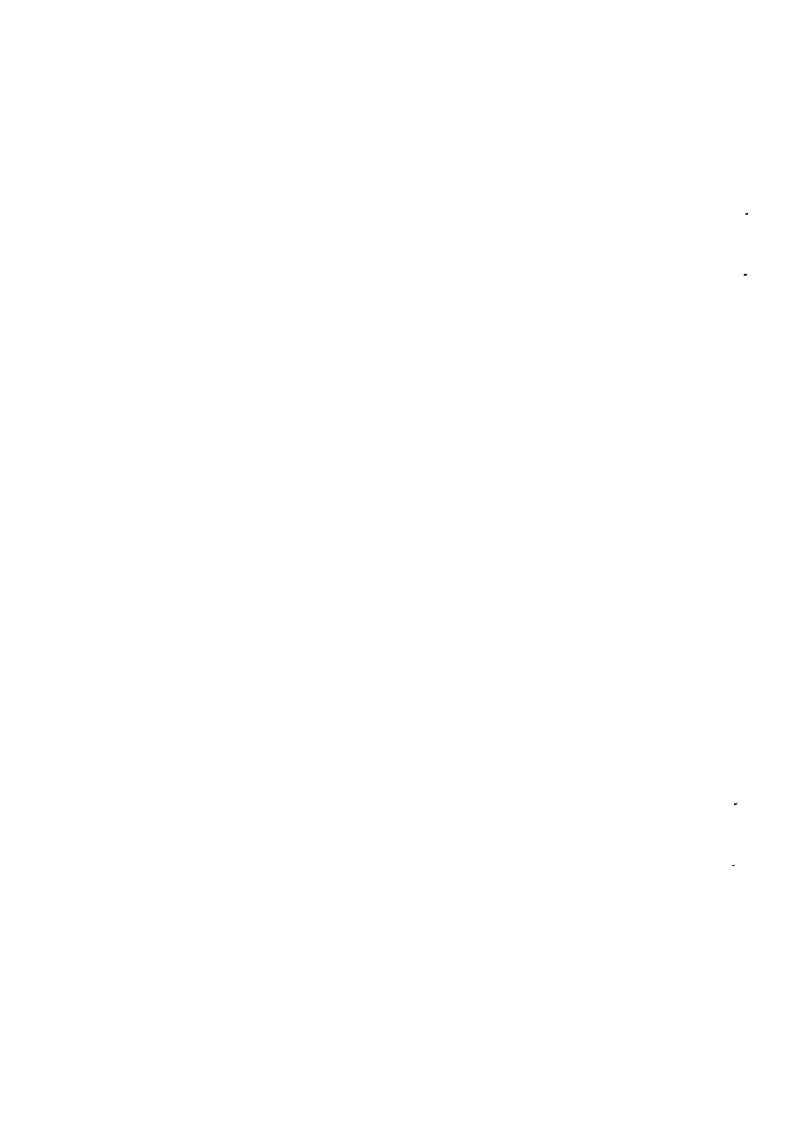


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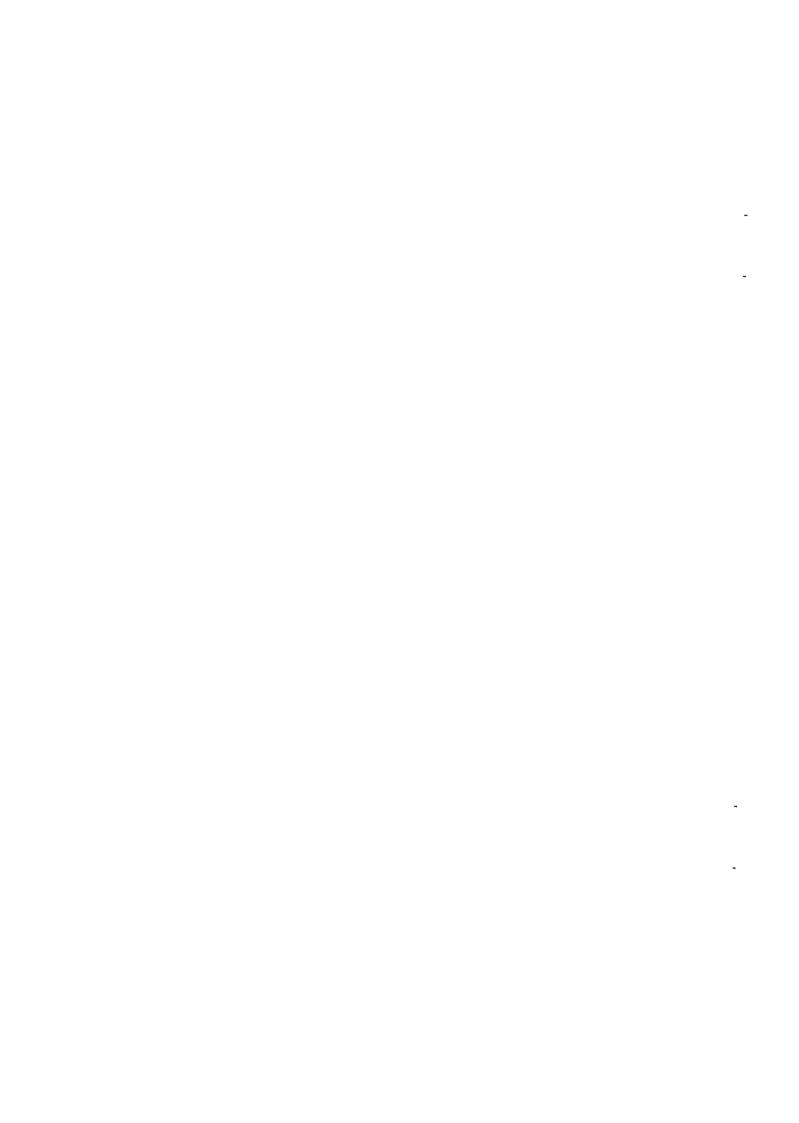
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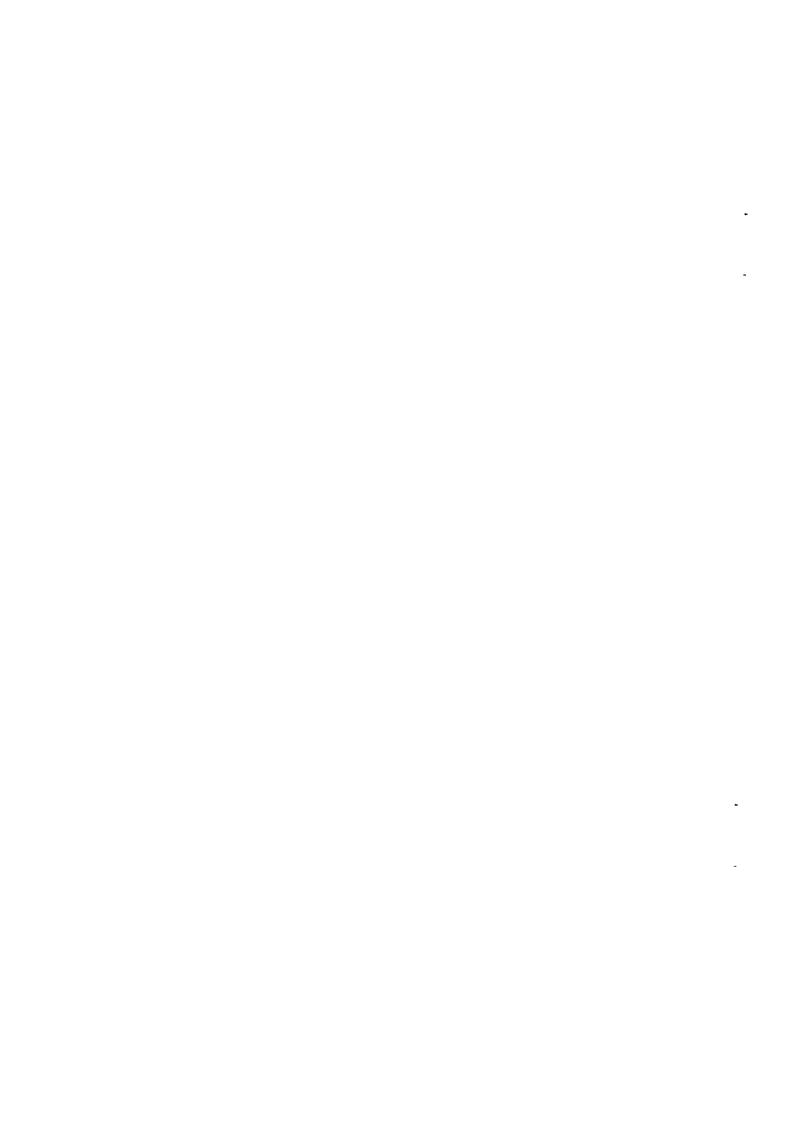
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SECTION I

CONCLUSIONS

In this reassessment of a part of the plastics and synthetics industry, approximately 100 company operations are involved in the production of the four products: epoxies, melamines, ureas, and phenolics. The 1972 production for these four products was estimated to be 1.0 million kkg (2.3 billion pounds) per year. This is about 9 percent of the total (26 billion) pounds per year production of eighteen larger-volume synthetic resins which were studied earlier (including these four products).

The 1972 water usage was estimated to be 20 thousand cubic meters per day (5.3 MGD). Water usage (at current hydraulic loads) was projected to increase at 7.2 percent per year through 1977, while production was projected to increase at 8 percent per year in the same period.

For the purpose of setting effluent limitations guidelines and standards of performance, the industry parameters giving the most effective categorization were found to be those waste water characteristics established earlier, (16) i.e.,

Raw waste load, with a BOD5 value of more than or less than 10 kg/kkg of product separating high and low waste load subcategories and attainable BOD5 concentrations as demonstrated by plastics and synthetics plants using technologies which are defined herein as the basis for BPCTCA. Three groupings were defined with average effluent concentrations under 20 mg/liter (low attainable BCD5 concentration), from 30 to 75 mg/liter (medium attainable BOD5 concentration), and over 75 mg/liter (high attainable BOD5 concentration).

Based on these two dimensions of categorization, the four products were placed in Major Subcategories III and IV as given below.

- Major Subcategory I low waste load, low attainable BOD5 concentration (0 products).
- Major Subcategory II high waste load, low attainable BOD5 concentration (0 products).
- Major Subcategory III high waste load, medium attainable BOD5 concentration treatability (1 product: epoxy resins).
- Major Subcategory IV high waste load, low treatability (3 products: phenolics, urea and melamines).

Additional subcategorization within the above four major subcategories was necessary to account for the waste water

generation which is specific to the individual products and their various processing methods. The separation of each individual product into separate subcategories simplifies the application of the effluent limitations guidelines and standards of performance by providing clear and unambiguous direction for the proper standard applicable to that product. The substantial advantage of clarity appears to outweigh any technical advantages of product grouping. Hence, for these reasons the individual product subcategories are used for the application of effluent limitations guidelines and standards of performance in this category.

Further subdivisions was found desirable for these four resins. For epoxy resins these were (1) batch and continuous manufacture of liquid resins and the manufacture of solids and solution resins and (2) manufacture by batch fusion. Phenolics were treated as a single category, based on data from a plant that produces a maximum of waste loading for this category. As more information is developed, further subcategorization may be desirable. Melamines and urea were combined into one category since they are often produced in the same location, and are processed in a similar fashion. Guidelines were developed for all subdivisions except solids or solution manufacture of melamines, phenolics and urea.

Annual costs of treatment in 1977 under BPCTCA guidelines for these four products were estimated at \$2.0 million out of a total of \$62.5 million for the eighteen synthetic resins. By 1983, under BATEA guidelines, existing plants would be expected to have annual costs of \$6.4 million (4 products) out of a total of \$177.1 million (18 synthetic resins). By 1977, under BADT-NSPS, the annual costs for new plants are estimated at \$1.9 million (4 products) out of a total of \$34.9 million (18 products). The estimated average costs over the four products for BPCTCA, BATEA, and BADT-NSPS technologies respectively were: \$0.34 (\$1.29), \$1.06 (\$4.00), and \$0.75 (\$2.85) per cubic meter (per thousand gallons).

The average range of water pollution control costs under BPCTCA for the four products was estimated at 0.4 to 1.0 percent of current sales price. On average, the range of costs for applying EATEA to existing plants was 1.4 to 3.5 percent of sales price. The average cost of BADT-NSPS was estimated at 1.4 percent of sales price.

SECTION II

RECOMMENDATIONS

BOD5, COD and suspended solids are the critical constituents requiring guidelines and standards. Other constituents are even more specific to the product subcategory and are summarized below for this addendum group:

Subcategory Other Element or Compound

Epoxy Resins Phenolic Compounds
Phenolic Resins Phenolic Compounds
Urea Resins Organic Nitrogen
Melamine Organic Nitrogen

Effluent limitations guidelines and standards of performance are proposed for phenolic compounds for the specified product. The additional pollutant parameter, organic nitrogen, was selected because nitrogen chemicals are used in the processes and appear in the waste waters of specific product subcategories. However, insufficient data was available on raw waste loads or treated waste waters to permit proposing guidelines and standards at this time. Receiving water quality standards should determine if limitations are necessary for organic nitrogen.

Best practicable control technology currently available (BPCTCA) for existing point sources is based on the use of municipal sewage treatment systems or the application of end-of-pipe technology such as biological treatment for BOD5 reduction as typified by activated sludge, aerated lagoons, trickling filters, aerobic-anaerobic lagoons, etc., with appropriate preliminary treatment typified by equalization to dampen shock loadings, settling, clarification, and chemical treatment for removal of suspended solids, oils, other elements, and pH control, subsequent treatment typified by clarification and polishing processes for additional BOD and suspended solids removal and dephenolizing units for phenolic compound removal when needed. Application of in-plant technology and changes which may be helpful in meeting EPCTCA include segregation of contact process waste from noncontact waste waters, elimination of once-through barometric condensers, control of leaks, and good housekeeping practices.

Best available technology economically achievable (BATEA) for existing point sources is based on the best in-plant practices of the industry which minimize the volume of waste-generating water as typified by segregation of contact process waters from noncontact waste water, maximum waste water recycle and reuse, elimination of once-through barcmetric condensers, control of leaks, good housekeeping practices, and end-of-pipe technology, for the further removal of suspended solids and other elements typified by media filtration, chemical treatment, etc., and further COD removal as typified by the application of adsorption

processes such as activated carbon and adsorptive flocs, and incineration for the treatment of highly concentrated small volume wastes and additional biological treatment for further BOD5 removal when needed.

Best available demonstrated technology (BADT) for new source performance standards (NSPS) are based on BPCTCA and the maximum possible reduction of process waste water generation as defined in BATEA, the application of media filtration and chemical treatment for additional suspended solids and other element removal, and additional biological treatment for further BOD5 removal as needed.

The levels of technology defined above as BPCTCA, BATEA, and BADT-NSPS are correlated to effluent limitations guidelines and standards of performance in the tollowing tables. The tables are based on attainable effluent concentration by the application of EPCTCA, BATEA and BACT as defined above, demonstrated process waste water flow rates, and consideration for the normal variations which occur in properly designed and operated treatment facilities.

TABLE II-1 BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE EFFLUENT LIMITATIONS GUIDELINES (kg/kkg (1b/1000 1b) of Production)

		во р 5		COD		SS	
	Subcategory	Maximum average of daily values for any period of thirty consecutive days	Maximum for any one day	Maximum average of daily values for any period of thirty consecutive days	any one day	Maximum average of daily values for any period of thirty consecutive days	Maximum for any one day
	Epoxy Resins						
(Ji	Batch & Continuous (liquid, solid & solution)	2.i	3.9	32	58	1.4	2.6
	Batch, Fusion (solid & solution)	0,25	0.45	3.9	6.7	0.17	0.30
	Phenolic Resins	3.7	6.7	19	34	1.5	2.7
	Urea & Melanine Resins						
	Batch (liquid)	0.20	0.38	3.2	5.5	0.13	0.25

TABLE II-2

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE EFFLUENT LIMITATIONS GUIDELINES (PHENOLIC COMPOUNDS)

		kg/kkg (1b/1000 1b)	of production
Product	Parameter	Maximum average of daily values for any period of thirty consecutive days	Maximum for any one day
o			
Epoxy Resins			
Batch & Continuous (liquid, solid & solution)	Phenolic Cmpds	0.011	0.022
Batch Fusion (solid & solution)	Phenolic Cmpds	0.0013	0.0025
Phenolic Resins	Phenolic Cmpds	0.011	0.023

TABLE II-3

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE EFFLUENT LIMITATIONS GUIDELINES

kg/kkg (1b/1000 lb of production)

		во:	D _c	COL)	SS	
	Subcategory	Maximum average of daily values for any period of thirty consecutive days	Maximum for any one day	Maximum average of daily values for any period of thirty consecutive days	Maximum for any one day	9	aximum for ny one day
	Epoxy Resins						
7	Batch & Continuous (liquid, solid & solution)	0.95	1.3	4.8	6.5	0.28	0.33
	Batch, Fusion (solid & solution)	0.12	0.17	0.65	0.88	0.04	0.65
	Phenolic Resins	0.96	1.3	5	6.8	0.30	0.35
		• .					
	Urea & Melamine Resins						
	Batch (liquid)	0.06	0.08	0.09	0.13	0.017	0.021

TABLE 11-4

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE EFFLUENT LIMITATIONS GUIDELINES

(PHENOLIC COMPOUNDS)

			kg/kkg (1b/1000 1b)	of production
	Product	Parameter	Maximum average of daily values for any period of thirty consecutive days	Maximum for any one day
ထ	Epoxy Resins			
	Batch & Continuous (liquid, solid & solution)	Phenolic Cmpds	0.0017	0.0033
	Batch, Fusion (solid & solution)	Phenolic Cmpds	0.00022	0.00044
	Phenolic Resins	Phenolic Cmpds	C.0035	0.0035

TABLE II-5

BEST AVAILABLE DEMONSTRATED TECHNOLOGY FOR NEW SOURCE PERFORMANCE STANDARDS

kg/kkg (1b/1000 lb of production)
COD

		ВО	BOD ₅ COD			S	ss		
	Subcategory	Maximum average of daily values for any period of thirty consecutive days	Maximum for any one day	Maximum average of daily values for any period of thirty consecutive days	Maximum for any one day	Maximum average of daily values • for any period of thirty consecutive days	Maximum for any one day		
	Epoxy Resins								
	Batch & Continuous (liquid, solid & solution)	0.67	1.2	9.2	12.9	0.20	0.30		
9	Batch Fusion (solid & solution)	0.11	0.19	1.5	2.1	0.03	0.05		
	Phenolic Resins Batch (liquid)	0.69	1.3	19	34	0.21	0.31		
			4						
	Urea & Melamine Resins								
	Batch (liquid)	0.06	0.11	0.10	0.18	0.02	0.04		

TABLE 11-6

BEST AVAILABLE DEMONSTRATED TECHNOLOGY FOR NEW SOURCE PERFORMANCE STANDARDS (PHENOLIC COMPOUNDS)

kg/kkg (1b/1000 lb of production)

Maximum for

Maximum average

		·	of daily values for any period of thirty consecutive days	any one day
	Epoxy Resins			
10	Batch & Continuous (liquid, solid & solution)	Phenolic Cmpds	0.0012	0.0024
	Batch, Fusion (solid & solution)	Phenolic Cmpds	0.00019	0.00038
	Phenolic Resins	Phenolic Cmpds	0.0013	0.0025

Parameter

SECTION III

INTRODUCTION

Purpose and Authority

Section 301 (b) of the Act requires the achievement by not later than July 1, 1977, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best practicable control technology currently available as defined by the Administrator pursuant to Section 304 (b) of the Act. Section 301 (b) also requires the achievement by not later than July 1, 1983, of effluent limitations for point sources, other than publicly owned treatment works, which are technology based on the application of the best available economically achievable and which will result in further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to Section 305 (b) of the Act. Section 306 of the Act requires achievement by sources of a Federal standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants.

Section 304 (b) of the Act requires the Administrator to publish, within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best control measures and procedure innovations, operation methods and other alternatives. The regulations proposed herein set forth effluent limitations guidelines pursuant to Section 304 (b) of the Act for the epoxy, melamine, phenolic, and urea resins of the plastic and synthetic materials manufacturing source category.

Section 306 of the Act requires the Administrator, within one year after a category of sources is included in a list published pursuant to Section 306 (b) (1) (A) of the Act, to propose regulations establishing Federal standards of performances for new sources within such categories. The Administrator published in the Federal Register of January 16, 1973 (38 F.R. 1624), a list of 27 source categories. Publication of the list constituted announcement of the Administrator's intention of establishing, under Section 306, standards of performance applicable to new sources within the plastic and synthetic materials manufacturing source category, which was included within the list published January 16, 1973.

Methodology

The effluent limitations guidelines and standards of performance proposed in EPA 440/1-73/010, "Development for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Synthetic Resins Segment of the Plastics and Synthetic Materials Manufacturing Point Source Category," were developed in the following manner. The plastics and synthetics industry was first categorized for the purpose of determining whether separate limitations and standards are appropriate for its different segments. Considerations in the industry subcategorization process included raw materials, products, manufacturing processes, raw waste characteristics and raw waste treatability and attainable effluent concentrations.

The raw waste characteristics for each subcategory were identified through analyses of (1) the sources and volumes of water and waste waters and (2) the constituents (including thermal) of all waste waters including toxic or hazardous constituents and other constituents which result in taste, odor, color, or are toxic to aquatic organisms. The constituents of waste waters which should be subject to effluent limitations quidelines and standards of performance were identified.

The full range of control and treatment technologies existing within the industry was identified. This included an identification of each distinct control and treatment technology, including both in-plant and end-of-process technologies, which are existent or capable of being designed for each subcategory. It also included an identification, in terms of the amount of constituents (including thermal) and the chemical, physical, and biological characteristics of pollutants, of the effluent level resulting from the application of each of the treatment and control technologies. The problems, limitations, and reliability of each treatment and control technology and the required implementation time were also identified. In addition, the nonwater quality environmental impact, such as the effects of the application of such technologies upon other pollution problems, including air, solid waste, noise, and radiation, were identified. The energy requirements of each of the control and treatment technologies were identified as well as the cost of the application of such technologies.

The information, as outlined above, was then evaluated in order to determine what levels of technology constituted the "best practicable control technology currently available," "best available technology economically achievable," and the "best available demonstrated control technology, processes, operating methods, or other alternatives." In identifying such technologies, various factors were considered. These included the total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application, the age of equipment and facilities involved, the process employed, the engineering aspects of the application of various types of control techniques process changes, nonwater quality

environmental impact (including energy requirements), the treatability of the wastes, water use practices, and other factors.

The data for identification and analyses were derived from a number of sources. These sources included EPA research informapermit applications, records of selected state tion, EPA agencies, published literature, previous EPA technical guidance for plastics and synthetics manufacture, a survey of waste water treatment practice by the Manufacturing Chemists Association, consultation, and on-site visits and qualified technical interviews at plastics and synthetics manufacturing facilities practicing exemplary waste water treatment in plants within the United States. Samples for analyses were obtained from selected plants in order to establish the reliability of the data obtained. All references used in developing the guidelines for effluent limitations and standards of performance for new sources reported in EPA 440/1-73/010 are listed in Section XIII of that document.

For these resins, the effluent limitations guidelines recommended in the development document for Synthetic Resins (EPA 440/1-73/010) were based on engineering judgment since no plant with an exemplary waste water treatment facility was found. Subsequent to publication of those guidelines, various manufacturers of these resins preferred data and opinions on raw waste loads and treatability to assist in the development of guidelines on a more realistic basis. These data are the bases for the guidelines developed in this document. Because these resins are usually produced in multi-product manufacturing plants, the data have been in the form of raw waste loads, hydraulic flows and the performance characteristics of waste water treatment facilities receiving effluents from more than one manufacturing process.

General Description of the Industry

The plastics and synthetics industry in general is described in EPA 440/1-73/010. Items relating directly to the resins covered in this addendum, along with additional specific information, are discussed in the following paragraph.

Epoxy resins are more frequently produced at different locations than the phenolics, urea, and melamine resins. The latter three are usually produced at the same location and often in the same basic equipment. Therefore, the waste water from their manufacture will often be combined.

Much of the liquid resin production of phenolics, ureas and melamines are located near their principal end users, such as the forest products industry where large quantities are used in manufacturing chip board and exterior plywood.

Except for the continuous processes for producing liquid epoxies, these resins are made in batch kettles and reactors: the larger

producers obtain their high rates by multiple vessels. Table III-1 shows an estimate of the 1972 consumption of these resins.

The principal producers of epoxy resins are Celanese, Ciba, Dow Chemical, Reichhold, Resyn, Shell and Union Carbide. There are, however, many other companies that buy resin from the major producers for modification into special formulations.

Some of the larger producers of phenolic resins are Ashland, Borden, Celanese, Ciba, Dow Chemical, General Electric, Georgia Pacific, Hooker, Monsanto, OCF, PPG Industries, Pioneer, Rohm & Haas, Schenectady Chemical and Union Carbide.

The major manufacturers of urea and melamine resins are Allied Chemical, American Cyanamid, Ashland Chemical, Borden, Cargil, Monsanto, Reichhold, Rohm & Haas and Scott Paper.

Plant sizes vary considerably within the subcategories discussed in this addendum. There are many small plants making special formulations from purchased resins; however, some also begin with the monomers. Many of these are individual plants which may vary production between several or all of the resin product subcategories described. The larger plants are often part of a petrochemical complex, often including production of one or more of the monomers. Representative plant production capacities for these subcategories are shown in Table III-2.

Because of their dependence on petroleum and gas feedstocks, many of the large resin manufacturing plants are located on the Gulf Coast. The Gulf Coast is a fortuitous location since a large market exists in the lumber industry of the Southeast. However, a significant number of resin manufacturing plants are located in the Northwest and Central United States as well as a few in the Northeast because the limited shelf life of the formulations makes it more desirable to ship the raw materials over great distances than the final product. Thus, a manufacturer of phenol formaldehyde resin for grinding wheels may locate a plant in upper New York State and buy his raw materials from petrochemical plants located elsewhere in the country. Such products are produced in relatively small quantities and often discharge their waste water to municipal systems.

TABLE III-1

1972 CONSUMPTION OF PLASTICS AND SYNTHETICS

Products	Consumption 1000 kkg	Number of Companies	
Urea and Melamine Resins	411	11	
Phenolic Resins	652	81	
Epoxy Resins	95	>29*	

^{*}Includes both unmodified and modified resins.

TABLE III-2
REPRESENTATIVE PLANT PRODUCTION CAPACITIES

		Plant Capacities			
	Product	Smal1		Large	
		Mil lbs/yr	1000 kkg/yr	Mil lbs/yr	1000 kkg/yr
	Epoxy Resins				
	Batch & continuous (liquid, solid & solution)	11.3	25	45.4	100
	Batch, fusion (solid & solution)	11.3	25	45.4	100
16	Phenolic Resins				
	Batch (liquid)	11.3	25	45.4	100
	Urea & Melamine Resins				
	Batch (liquid)	6.8	15	27.2	60

t i

Product and Process Technology

Brief descriptions of the chemical nature of the products and the manufacturing process technology are presented in this section with special emphasis on indicating those process operations which generate waste waters.

Epoxy Resins

Epoxy resins are characterized by the presence of the epoxy group within their structure. Rather than an end resin in itself, the epoxy family should be regarded as intermediates. They all require further reaction with a second component, or curing agent as the second material is often termed, in order to yield the final thermoset material.

Almost all of the commercially produced epoxy resins are made by the reaction between epichlorohydrin and bisphenol A. Small volumes, however, are produced from polyols other than bisphenol A, such as aliphatic glycols and novolak resins formed from phenol and formaldehyde. It is also possible to produce epoxy resins by introducing the epoxy group after the polymer has been formed. An example of this is the epoxidation of a polybutadiene material. The double bond present in these materials forms the site for the epoxy linkage. The following discussion, however, is limited to the materials produced from epichlorohydrin and bisphenol A.

Epichlorohydrin is a liquid with a boiling point of 117°C (242°F). Bisphenol A is a solid which melts at 152°C (305°F). Bisphenol A is insoluble in water, dissolving to the extent of 0.3 percent at 85°C (185°F) whereas epichlorohydrin is somewhat more soluble (approximately 5 percent). The reaction between the two raw materials takes place under alkaline conditions as shown by the equations in Figure III-1. The first step, shown by Equation 1, is the condensation of the epichlorohydrin with the bisphenol A to form the chlorohydrin compound. This compound is dehydrohalogenated with caustic soda to form epoxy linkages yielding diglycidyl ether of bisphenol A, as shown by Equation 2. Sodium chloride and water of reaction are also formed as byproducts with the ether. Further reaction between the ether and additional bisphenol A results in growth in the chain length, as shown by Equation 3.

Operating conditions and type of catalyst are selected to minimize the formation of side chains and to prevent phenolic termination of the principal chain. The final resin properties are enhanced when the chain is terminated with epoxy groups, as shown in Equation 3, and when the chain is linear with minimum branching. The possibility of branching exists since epichlorohydrin could react with the hydroxyl group to start a side chain.

The product epoxy resins fall into two broad categories, the low molecular weight liquids and the high molecular weight solids.

(1)
$$2 \text{ CH}_1\text{-CHCH}_2\text{CI}$$
 + $HO \longrightarrow CH_3$ Bisphenol A

Epichlorohydrin

$$CH_3 \subset CH_3 \longrightarrow CH_3 \subset CHCH_4$$

$$CH_3 \subset CH_3 \longrightarrow CH_3 \subset CHCH_4$$

$$CH_3 \subset CHCH_4 \supset CHCH_2 \supset CHCH_2 \longrightarrow CHCH_2 \supset CHCH_2 \supset CHCH_3 \supset CHCH_2 \supset CHCH_3 \supset CHCH_2 \supset CHCH_2 \supset CHCH_2 \supset CHCH_2 \supset CHCH_3 \supset CHCH_2 \supset CH$$

CH₃

FIGURE III-1 REACTIONS BETWEEN EPICHLOROHYDRIN AND BISPHENOL A

In the liquids, n, the number of repeating units in the final chain as designated in Equation 3, is low, ranging in commercial materials from 0.1 to 0.6 as the average value. For solid materials, n ranges from 1.8 to 16. Control over chain length is exercised primarily by the ratio of the two reactants charged to the system. To produce the low molecular weight liquids, a large excess of epichlorohydrin is used so that n is close to 0 in the final product. In order to produce the high molecular weight solid resins, the ratio of epichlorohydrin per mole of bisphenol A is usually less than 2.

There are two general approaches to carrying out the synthesis of epoxy resins. In the one-step process all of the reactions shown earlier proceed at the same time. These are usually carried out in the presence of sodium or potassium hydroxide. In the two-step process, reaction 1 is carried out by itself in the presence of a catalyst. Sodium or potassium hydroxide is then added to carry out the dehydrohalogenation and further condensation or polymerization as a second stage.

Regardless of which of these two approaches is used, the overall chemistry remains the same.

The product resins are utilized by the customer in conjunction with a curing agent to provide the crosslinking necessary to form a thermo-set material. The curing agents used cover a broad variety of materials such as amines, polyamides, acids, acid anhydrides, resins such as phenolic, urea or melamine formaldehyde combinations, any of which are capable of reacting with either the epoxy groups or the hydroxyl groups present in the resin. The specific material picked depends upon the properties desired in the end resin.

There is substantial production of the so-called modified epoxies. Most of these are manufactured by reacting some material such as a fatty acid, tall oil or the like to form an ester with some of the epoxy groups present in the resin. The degree of esterification carried out depends upon the properties desired in the final material. Most of these modified epoxies find their way into coatings markets.

Manufacture and Waste Water Generation

Continuous Process, Liquid Resins and Liquid Resin Solutions - The low molecular weight liquid resins can be manufactured by either batch or continuous processes. Most of the larger producers utilize a continuous process for this material as well as batch processes for the lower volume products. Figure III-2 shows a schematic flowsheet of a typical continuous process. Bisphenol A, with a large mole excess of epichlorohydrin, is introduced into the polymerizer where, under the influence of the catalyst and caustic conditions, the reaction takes place. The excess epichlorohydrin is vaporized from the material and recycled.

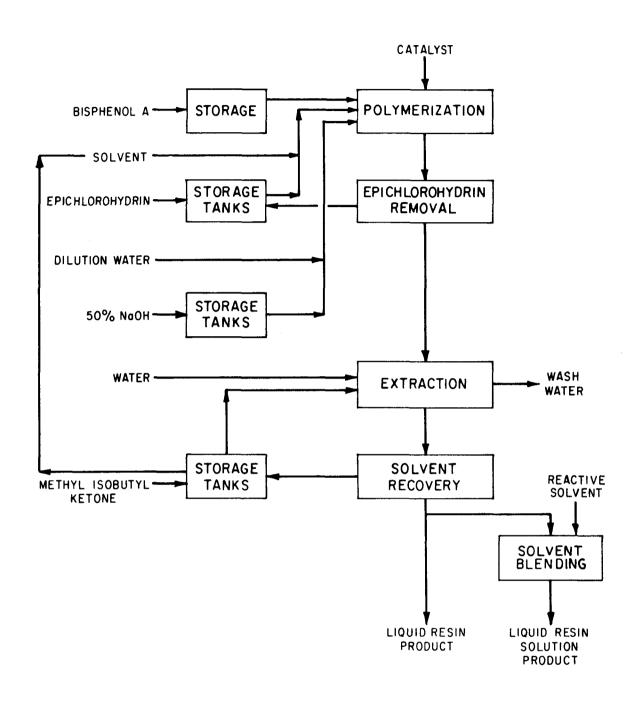


FIGURE III-2 LIQUID EPOXY RESIN PRODUCTION

A solvent, usually a ketone such as methylisobutyl ketone, is then added together with additional caustic and water. The epoxidation of the resin takes place with the formation of salt.

A solution of resin in the ketone solvent is water-washed to remove the final traces of salt, the decanted water is sent to waste, and the solvent is removed by vaporization. The liquid epoxy resin product is then sent to storage. Some resins are redissolved in solvent to produce a liquid resin solution product. Liquid resins are also produced in batch reactors, with reactant ratios similar to the above description of the continuous process, but in the equipment and processing steps as described below.

Batch Process, Liquid and Solid Resins - The solid resins, which have a high molecular weight, are produced by batch techniques in resin kettles. In producing these materials where the repeating part of the epoxy chain is a high number ranging from 1.8 to 16, the mole ratio of epichlorohydrin to bisphenol A charged to the kettle is less than 2. No excess epichlorohydrin is used in this case. The process is shown schematically in Figure III-3. Aqueous sodium or potassium hydroxide is added to serve both as a catalytic agent and as one of the reactants to form the epoxy links during the polymerization reaction. Upon completion of the polymerization reaction, the water-containing salt and a very small amount of excess caustic are decanted to the process waste water system.

A solvent such as methylisobutyl ketone is then added to dissolve the resin, and the solution is washed with water to remove the remaining amounts of sodium chloride and other salts which may be present. This water is decanted to the process waste system, and then the methylisobutyl ketone is vaporized and recovered from the resin. The resins have melting points ranging from about 70-150°C (158-302°F), if a solid resin is being made, and the final temperature is such that the resin is molten. It is then drained and cooled to form a solid mass which is crushed to provide the final granular solid product, or blended with a solvent to make a solid resin solution product.

If a liquid resin is being made, after recovery of the solvent, the resin is either packaged directly as a liquid resin or a solvent is introduced to provide a liquid resin solution.

Batch Fusion and Solid Resin - A third process used by both the basic epoxy resin producer and by those customers tailoring the resin to various end uses is a nonaqueous fusion reaction involving the thermoplastic epoxy resin, a reactive diluent and a catalyst as shown in Figure III-4. Additional water of reaction is produced, and the waste water load is primarily due to the barometric condenser water (used to develop the vacuum in the reactor), vent scrubbers (when not reacting under vacuum), and housekeeping and maintenance water. The result is a low waste water volume that contains a significant quantity of pollutants.

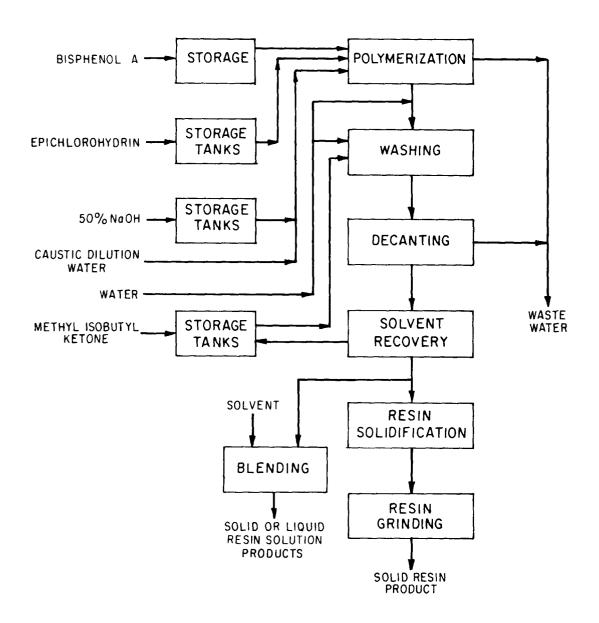


FIGURE III-3 BATCH EPOXY RESIN PRODUCTION

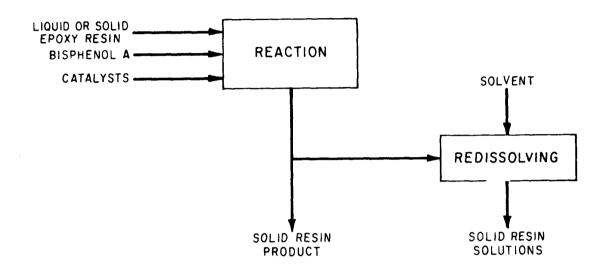


FIGURE III-4 BATCH FUSION SOLID EPOXY RESIN PRODUCTION

Phenolic Resins

The family of phenolic resins includes the oldest synthetic polymers. The term is used to describe a broad variety of materials, all of which are based upon the reaction between phenol, or a substituted phenol such as creosol or resorcinol, and an aldehyde such as formaldehyde or acetaldehyde. Nearly all industrially significant resins, however, are based upon the reaction of phenol with formaldehyde.

Phenol, commonly known as carbolic acid, is a solid at rocm temperature but melts at between 42 and 43°C (107-109°F). It is usually shipped and handled as a liquid by keeping it above its melting point. Formaldehyde is normally a gas. Its most common commercial form is formalin, a 37 percent by weight solution of formaldehyde and water.

There are two broad types of resins produced by this industry: resols and novolaks.

<u>Resols</u> are formed from a mixture of phenol and formaldehyde which contains an excess of formaldehyde. Often the mole ratio is about 1.5 to 1. An alkali such as sodium hydroxide is used to catalyze the polymerization which takes place at a pH of between 8 and 11. The reaction is shown in Figure III-5.

The reacting mixture contains sufficient formaldehyde so that, if allowed to proceed to completion, a cross-linked thermo-set resin would be formed. The reaction, however, is stopped short of completion at an average molecular weight of the polymer appropriate for the end use of the material. Three classes of products are produced under the general grouping of "resols":

- The least degree of reaction produces a water soluble bonding resin which is either sold "as is" or neutralized and partially dehydrated.
- 2. Further reaction produces a water-insoluble resin which is vacuum dehydrated and dissolved in solvents to produce laminating resins and varnishes, using much less basic catalyst than in making bonding resins. Some resols, such as varnishes that are used in rubber cement, require washing of the resin to remove salts; most other resins do not require washing.
- 3. The third class of product is similar to 2, but the water is removed and the reaction carried even further to make a "one-stage" solid resin that is then vacuum dehydrated and dropped from the reactor for cooling and solidification.

 These "one-stage" resins are then compounded into
 - a. bonding compounds and surface coatings,

FIGURE III-5 TYPICAL REACTION TO FORM ONE-STEP RESINS OR RESOLS

by adding catalysts and lubricants:

b. thermosetting molding powders by adding catalysts, lubricants, pigments and fillers. The compounding is sometimes performed in the same facilities where the resin is produced, but more often the resin is shipped to custom compounders. Compounding is a dry operation and adds negligible wastes to the resin manufacturing waste generation.

The material already contains sufficient formaldehyde to completely cross-link the ultimate product so that it can be thermally set into an infusable material by the application of heat at the customer's facilities. Since cooling the mixture in its partially polymerized form does not completely stop further polymerization but merely retards it, these materials have a somewhat limited shelf life (in the order of 60 days for many types).

Novolaks are the second category of phenolic resins. These are formed from a reacting mixture which contains a deficiency of formaldehyde. The normal commercial range for this mole ratio is between 0.75 and 0.90. To produce this material, polymerization is carried out in an acid medium using a catalyst such as sulfuric acid. The pH of the reaction usually ranges from 0.5 to 1.5. For special uses where high ortho linkage is desired, the polymerization may be carried out at a pH of from 4 to 7, but this is not typical. The reaction is shown in Figure III-6. Since the reacting mixture contains a deficiency of formaldehyde, essentially all of the formaldehyde is consumed during polymerization. Since no further polymerization can take place, the product is a low molecular weight, thermoplastic, stable material. The water which enters with the formaldehyde plus the water of reaction is removed under vacuum at the end of the reaction, and a solid, meltable material results.

In order to complete the polymerization, the user must add additional formaldehyde. Sometimes this is done by using paraformaldehyde, a solid polymer of formaldehyde, but the extremely irritating nature of this material has limited its use. Most users complete the reaction by using hexamethylenetetramine. With this material ammonia is evolved from the reacting mass, leaving the same types of methylene linkages as can be obtained by using additional formaldehyde.

The basic resins described above are sometimes modified by the use of materials such as drying oils or epoxy compounds in the final stages of polymerization. These modified phenolics find many specialty uses but do not affect the basic manufacturing processes to any significant degree.

ОН

FIGURE III-6 TYPICAL REACTION TO FORM NOVOLAK RESIN

Manufacture and Waste Water Generation for Typical Phenolic Resins

Although continuous processes for the production of phenolic resins have been developed, they are seldom used. The production of these continuous units must be high, and the industry calls for such a wide variety of materials that it is seldom possible to have a large enough run on a single grade of polymer to justify their use.

The standard producing unit of the industry is typically a batch resin kettle arrangement, such as is shown in Figure III-7. The heart of the process, the resin kettle, varies in size from 7.6 to 38 cu m (2,000 to 10,000 gal.). These are jacketed, and in the larger sizes internal cooling coils are used in order to provide sufficient surface-to-volume ratio to remove the considerable amount of heat generated during polymerization. The kettles are agitated and can operate under either pressure or vacuum conditions.

The feed system generally consists of two weigh tanks which weigh in the required amounts of phenol and formaldehyde solution. Commercial formaldehyde solution is available at 37 percent by weight formaldehyde, but other concentrations are used, such as 44 or 50 percent. This solution often contains about 5 percent methanol (from incomplete conversion or separation in formaldehyde manufacture) which acts as a stabilizer. Other stabilizers are now sometimes used.

The kettle is equipped with a water-cooled condenser, which is also joined to a vacuum system.

Figure III-8 shows the basic manufacturing steps and the resulting products for resol and novelak production.

Resol Manufacture - In a typical production cycle for a resol resin, the phenol is charged in a molten form to the kettle followed by formaldehyde, which washes any residual phenol out of the lines leading to the kettle. A sodium hydroxide catalyst solution is then added, and the kettle is heated to bring the mixture to a temperature of about 60°C (140°F). During this period the condensation reaction starts and the reaction becomes highly excthermic so that a change is made from supplying steam to the coils to supplying cooling water. The mixture is held at a temperature ranging from 60°C to about 80°C (140-176°F) for a period of three to five hours. During this period temperature is controlled by circulating cooling water through the coils as well by using total reflux returning from the water-cooled condenser mounted above the kettle. When the polymerization has reached the desired degree, as shown by laboratory tests, the mixture is cooled to about 35°C (95°F) to essentially stop further reaction. At this point the caustic may be neutralized addition of sulfuric acid, which brings the mixture to a by the pH of about 7.

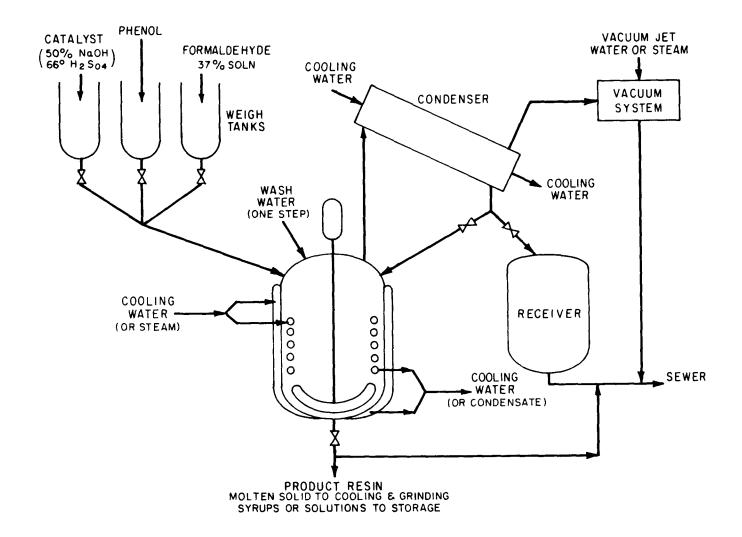


FIGURE III-7 PHENOLIC RESIN PRODUCTION



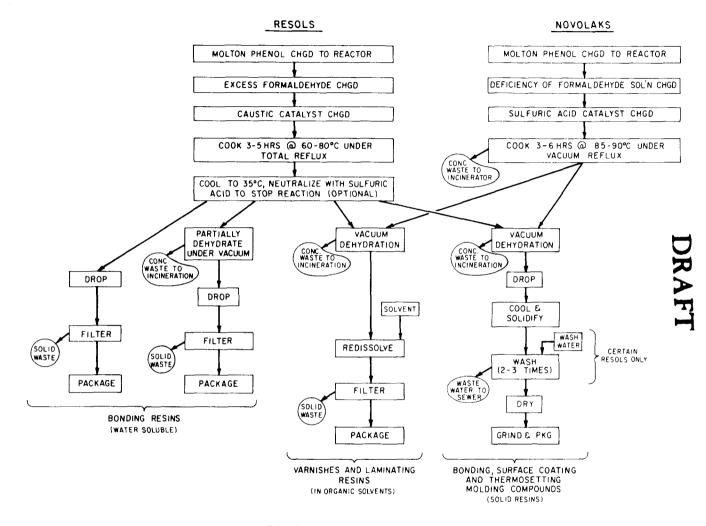


FIGURE III-8 PHENOLIC RESIN PROCESSING

The mixture is then heated by admitting steam to the coil, and the resin is purified by distillation. The water from this distillation is a concentrated waste which contains unreacted formaldehyde and phenol and low molecular weight resin, and may be segregated for disposal by incineration.

The batch is then dumped. A few resins, such as varnish type resols used as tackifiers for rubber cement, are washed two or three times, thereby resulting in a considerable increase in waste water and contaminants.

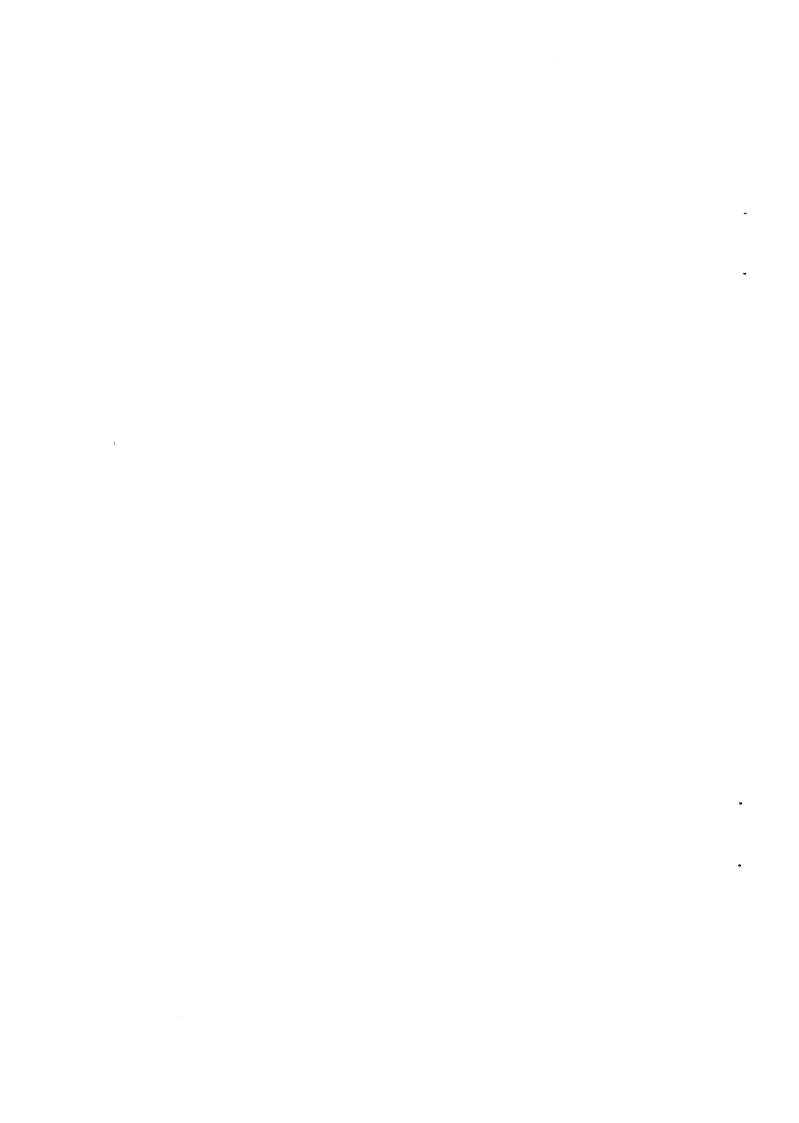
If a resin is required which contains a very small amount of water such that it cannot be dehydrated at a temperature low enough to prevent further polymerization, a vacuum is applied during the latter part of the dehydration cycle. This technique can be used to produce an essentially anhydrous melt of a single-step resin.

The molten resin must be quickly discharged from the bottom of the kettle through cooling plates for a quick quench in order to prevent the mass from setting up into an insoluble, infusible material. The cast material, when solidified, can be broken up and crushed for shipment as a powder.

Novolak Resin Manufacture - The manufacture of novolak resins is entirely analogous except that an acid catalyst, such as sulfuric acid, is added at the start of the batch. With strongly acid catalysts it is necessary to utilize a vacuum reflux in order to maintain temperatures at 85 to 90°C (185°F-194°F), a slightly higher temperature range than that used for the one-step reaction. Under milder reaction conditions, atmospheric reflux is adequate to control the temperature.

At the end of the reflux period, three to six hours after initiating the reaction, the condensate is switched to the receiver and water is removed from the batch. When the temperature reaches the order of 120 to 150°C (248-302°F) the vacuum is applied to aid in removing the final traces of water and part of any unreacted phenol. Final temperatures may rise to about 160°C (320°F) under a vacuum of 63.5 to 68.5 cm (25 to 27 in.) of mercury. These higher temperatures are possible since the reaction has proceeded to completion and, therefore, no further polymerization can be carried out until additional formaldehyde is added. The completed batch is dumped in the molten form onto cooling pans where it solidifies, or onto a flaker. If the product is needed in solution form, solvent is added at the end of the batch as it cools in the kettle and the solution discharged from the kettle to storage tanks for drumming.

The finished products may be shipped to customers as such or may be compounded with additives at the resin-producing point. The solid resins may be ground, and wood fillers, pigmenting materials and hexamethylenetetramine added to form a finished



molding compound. These processes all involve solids-handling and do not normally give rise to waste water generation.

The term "amino resins" is used to describe a broad group of polymers formed from formaldehyde and various nitrogen containing organic chemicals. The nitrogen group is in the form of the NH4 radical. Although called amino resins most of the compounds used are more of the nature of amides than true amines. The resins are characterized as being thermo-setting, amorphous materials which are insoluble in most solvents. Although many amino compounds are used in the formation of amino resins, the two of primary commercial significance are urea and melamine. Specialty materials are formed from other amino compounds such as thiourea, acrylomide or aniline. These, however, are produced only in small volumes and have little significance in the total amino resin market.

Formaldehyde, the common raw material in all types of amino resins, is normally a gas but is handled industrially as an aqueous solution. It is infinitely miscible with water. Urea, a solid under normal conditions, is highly soluble in water. Melamine could be described as sparingly soluble and is also a solid under the usual conditions, melting at the high temperature of 355°C (671°F).

Another characteristic of the group of amino resins is that the polymerization reaction proceeds in two distinct stages. In the first of these, as indicated in Figure III-9, Equations 1 and 2 urea (depending upon the mole ratio of the reactants) forms materials such as monomethylol urea and dimethylol urea which are the reactive monomers involved in the final polymer. As indicated in Equation 3, these materials may react among themselves to form dimers. Although the structure of just one dimer is shown, a consideration of the active hydrogen groups involved shows that many other dimers containing both methylene and ether linkages are possible. The initial reaction is an addition reaction with no water formed as a result of the combination. The condensation reaction, as indicated by Equation 3, involves the formation of one mole of water for each linkage formed.

As shown in Figure III-10, the reactions in the case of melamine and formaldehyde are entirely analagous to those shown for ureaformaldehyde. It should be noted, however, that since melamine contains three NH2 groups, permutations are much greater than is the case for urea. Again, the first two reactions indicate initial step of the polymerization. This consists of formation of reactive monomers between melamine and formaldehyde. The further reactions, as indicated schematically by Equation 3. can involve the reaction of an additional mole of melamine with one of the monomers, shown in this case as trimethylol melamine, to form condensation compounds which involve the elimination of Although not shown, it can be readily water of reaction. visualized that a mole of trimethylolamine could react with an additional mole of trimethylolamine to eliminate water and form an ether linkage as contrasted to the methylene linkage formed between the trimethylolamine and another molecule of melamine.

(1)
$$H_2 N - C - NH_2 + CH_2 O \longrightarrow H_2 N - C - NH - CH_2 OH$$
Urea Formaldehyde Monomethylolurea

(2) $H_2 N - C - NH_2 + 2CH_2 O \longrightarrow HOCH_2 - NH - C - NH - CH_2 OH$
Dimethylolurea

(3) $H_2 N - C - NH - CH_2 OH + HOCH_2 - NH - C - NH - CH_2 OH$

$$HOCH_2 OH$$

$$OH_2 N - C - NH - CH_2 OH + H_2 OH$$

$$HOCH_2 OH$$

$$OH_2 N - C - NH - CH_2 OH + H_2 OH$$

FIGURE III-9 TYPICAL POLYMERIZATION FOR UREA AND FORMALDEHYDE

FIGURE III-10 TYPICAL POLYMERIZATION REACTIONS FOR MELAMINE AND FORMALDEHYDE

These reactions are catalyzed by hydrogen ions and, in general, are moderated or slowed down by hydroxyl ions. Thus, the proper pH selection is an important consideration in determining the structure of the ultimate polymer formed.

The basic amino resin manufacturing process is generally stopped with the formation of a predetermined amount of monomers, dimers and trimers depending upon the specifications desired for the ultimate resin. This mixture of materials is then utilized by the customer to form the final thermoset resin which is an insoluble, heat resistant material. This is contrasted with the mixture of very low molecular weight materials produced by the basic manufacturer which are usually water soluble, very heat sensitive materials.

Consideration of the equations presented above will show there are numerous possibilities for cross-linking the various monomers, dimers and trimers which would be involved in the initial stages of the reaction. The ultimate customer forms these cross-links between the molecules by the application of heat and pressure, sometimes with the aid of a catalyst depending upon the nature of the application.

The ultimate markets for the amino resins are approximately as shown in Table III-3.

TABLE III-3

MARKETS FOR AMING RESINS

Percentage of Total Consumption

Application Am	ino Resins
Adhesives Textile and Paper Treating and Coating Laminating and Protective Coatings Moulding Compounds and All Other Applications	36 22 18 24
	100

For most of these applications the resin is used in the form of either an aqueous solution or a mixture of an aqueous and alcohol solution, ethanol being the usual alcohol. For moulding compounds and some of the others, a solid material is utilized. In nearly all of these applications, the melamine part of the amino resin family has superior properties. Because of its higher cost, however, it is utilized principally where these superior properties are necessary. The urea formaldehyde resins, which are lower cost, are equally applicable in other instances.

Since, as mentioned above, the reactive monomers, polymers, trimers and low molecular weight material formed by the basic resin manufacturer contain all of the reactive groups necessary to further crosslink, the solution materials have a limited shelf

life, in the order of 60 days. Thus the users who have a large volume requirement for solution forms, such as paper mills, textile mills, and the like, may purchase material made in solution form by the manufacturer since they will utilize it quickly and not have a residual inventory. Other users, where the shelf life of the product is of considerable importance, will purchase the material in an anhydrous solid form which has a relatively indefinite shelf life. Often, before the final use, the solid may be re-dissolved in either water or alcohol or mixtures thereof if a solution form is utilized in the application.

Manufacture and Waste Water Generation

Since amino resins are produced in many specialty grades with each run being a relatively modest volume, continuous processes are not in general use in the industry. The typical process is a standard tatch polymer kettle arrangement. As shown in Figure III-ll, the normal arrangement consists of a jacketed polymer kettle ranged in size from about 7.6 to 38 cu m (2,000 to 10,000 gal.). The larger sizes contain internal coils for additional heating and cooling surface in order to provide a reasonable surface-to-volume ratio. The kettles are agitated and can operate under either pressure or vacuum conditions.

The kettle is equipped with a water-cooled condenser and tied into a vacuum system so that the operating temperature can be controlled through the use of both reflux and cooling or heating in the jacket and coils of the kettle. The feed system consists generally of weigh tanks for the batch operation of the kettle.

The techniques used are very similar for both melamine or urea types of formaldehyde amino resins. As a typical example, production of a plywood adhesive grade urea formaldehyde resin is Formaldehyde as a 30 percent solution is added to follows. the kettle and the pH adjusted to about 7 to 7.8. Boric acid, the catalyst, is then added, and then urea in the form of a solid fed into the reaction vessel. The pH of the mixture is again brought back to approximately neutral and the mixture heated to (212°F) under atmospheric reflux conditions. During this initial heating period the pH drops to about 4 as the reaction between urea and formaldehyde takes place to form di- and trimethylol urea. Atmospheric reflux is maintained for a period about two hours. Then the vacuum is applied, and the system temperature drops to approximately 40°C (104°F). maintained at this level for approximately five hours. During this period of time there is a small amount of condensation reactions taking place between the various monomers formed Simultaneously with this further reaction, water is removed from the system so that the final water content, in the case of this particular adhesive formulation, is about The water in the system comes from two sources - that introduced with the 30 percent formaldehyde solution used as a raw material, and that produced by the reaction between the

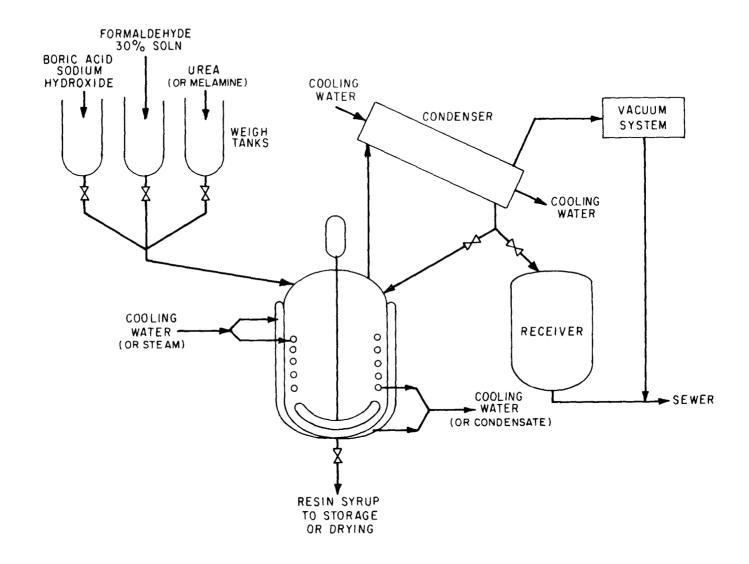


FIGURE III-11 AMINO FORMALDEHYDE RESIN PRODUCTION

monomers, which eliminates a mole of water for each pair of monomers or trimers reacting.

At the end of the vacuum reflux period, the system is put on total reflux and the pH adjusted to slightly alkaline conditions. The reactor is then returned to atmospheric pressure, and the product is ready to be removed. The total cycle time is about 10 hours.

The mixture, at this point in the form of a thick syrup, is drained to storage where quality checks are made to determine the exact condition of the polymers. The material may be shipped in this form for further polymerization by the customer or it may be dried to be shipped as a solid which, as mentioned earlier, has a much longer shelf life. If the material is to be dried, it is fed to either a belt drier or a spray drier where the remaining water is removed at low temperature in order to prevent further polymerization. As mentioned earlier, the final adjustment of the pH also helps prevent further condensation reaction and polymerization of the monomers. The water removed during these final drying operations is vented to the atmosphere.

Depending upon the end-use requirements, the final solid product may be milled with pigments, dyes and fillers to provide a moulding compound suitable for the particular end use desired.

The equipment used for the production of the first-step amino resins is often used for other materials, such as phenolics. Between these different uses, and indeed between production batches of melamine and urea resins or between batches of significantly different resins, it is customary to clean the equipment by utilizing a hot dilute caustic solution. This material is drained as process waste.

SECTION IV

INDUSTRY CATEGORIZATION

The most effective means of categorizing the plastics industry for setting effluent guidelines is based on the characteristics of the waste water. In particular, the two most relevant characteristice are (1) raw waste load, expressed in kg of pollutant/kkg of product, and (2) attainable BOD5 concentrations as demonstrated by plastics and synthetics plants using technologies which are defined as the basis for BPCTCA. The data on treated waste water characteristics obtained from manufacturers of epoxy, melamine, phenolic and urea resins are summarized in Table IV-1 along with data obtained on other synthetic resins. They are grouped in four major subcategories representing combinations of the waste characteristics discussed above.

Major Subcategory I - A low raw waste load; raw waste load less than 10 units/1000 units of product; attainable low BOD5 concentrations - less than 20 mg/liter.

Major Subcategory II - High raw waste load; raw waste load greater than 10 units/1000 units of product; attainable low BOD5 concentrations.

Major Subcategory III - High raw waste load; attainable medium BOD5 concentrations - in the 30-75 mg/liter range.

Major Subcategory IV- High raw waste load; attainable high BOD5 concentrations over 75 mg/liter.

The attainable BOD5 concentration in the effluent is influenced by the treatability and, for a specific plant, by the variations in the influent concentrations. In major subcategory I, where raw waste loads are less than 10 units/1000 units and where hydraulic flows ranged from 8.3 to 29.3 cu/m/kkg (1000 to 3500 gal/1000 lb), the influent concentrations ranged from 33 to 530 mg/liter. Disregarding the low influent concentration of the high density polyethylene plant, the influent concentrations varied over nearly a five-fold range while the effluents varied over a two-fold range. This indicates that practicable waste water treatment plants should be capable of attaining effluent BOD5 average concentrations in the vicinity of 15 mg/liter when using properly designed and well operated biological systems. The major subcategory II plants are characterized by high raw waste loads, but the waste waters can be treated to low attainable BOD5 concentrations. Raw and effluent loads are a factor of 10 higher than for the major subcategory I plants, largely because of the high water usage for rayon and cellophane and the high BOD5 influent concentration for ABS/SAN resins. Major subcategory III plants are characterized by high raw waste loads and moderate observed flows, which lead to high influent concentrations. The waste treatment plants achieve BOD5 removals

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TABLE IV-1
PERFORMANCE OF OBSERVED WASTEWATER TREATMENT PLANTS

	В	OD	C	OD	S:	S
	Inlet (mg/liter)	Outlet (mg/liter)	Inlet (mg/liter)	Outlet (mg/liter)	Inlet (mg/liter)	Outlet (mg/liter)
						
Category III						
*Epoxy, Batch & Cont. (liquid, solid and solution)	793	36	2063	363		84
*Epoxy, Batch Fusion (solid & solu.)	793	36	2063	363		84
Category IV						
**Urea & Melamine (liquid)	1310	28	6460	406		50
**Phenolic Resin	1466	450	5139	677	298	8

^{*} These values were derived from raw waste data from the individual process combined with treatability efficiencies observed immulti-product chemical complex treatment plants where the epoxy wastes were a significant portion of the total load.

^{**} These values were calculated from expected wastes in a multi-product plant and using the treatability demonstrated for the total wastes shown in Table VII-1 and VII-2.

ranging from 96.5 to 99.3 percent, which are high efficiencies by general standards of industrial waste treatment. Even with these high removal efficiencies, effluent concentrations are moderate due to the high concentration of the raw wastes. Major subcategory IV plants have relatively high raw waste loads and the observed attainable BOD5 concentrations were found to be high.

The design bases and operational modes of these plants are such as to indicate that practicable waste water treatment technology (e.g., two-stage biological treatment) might reduce the effluent concentrations by a factor of nearly two which would make them comparable to the plants appearing in major subcategory III. However, attainable BOD5 concentrations below these levels has not been documented.

Additional subcategorization within the above four major subcategories was necessary to account for the waste water generation which is specific to the individual products and their various processing methods. The separation of each individual product into separate subcategories simplifies the application of the effluent limitations guidelines and standards of performance by providing clear and unambiguous direction as to the proper standard application to that product. The substantial advantage of clarity appears to outweigh any technical advantage of product grouping.

Further subdivisions were found desirable for these resins. For epoxy resins these were (1) batch and continuous manufacture of liquid resins and the manufacture of solids and solution resins manufacture by batch fusion. and (2) Phenolics were subdivided: the guidelines were developed for a process employing what we believe is maximum water and probably close to maximum pollutant generation, due to product washings and Some plants that do not wash the resin after reaction changes. will have considerably lower waste water generation as well as pollutant discharge. Melamines and urea were combined and treated similarly to phenolics. Guidelines were developed for all subdivisions except solids or solution manufacture of melamines, phenolics and urea; data were not made available for these latter subdivisions.

The performance of observed waste water treatment plants in the group of resins reported upon in this addendum report is shown in Table IV-1. The resulting major industry subcategories and product and process subdivisions for the groups of plastics and synthetic material are reported in EPA 440/1-73/010 plus those reported in this addendum. (See Table IV-2)

The exemplary treatment plant for phenolics manufacture employs neutralization, settling and activated carbon treatment; this system should be capable of achieving major subcategory IV guideline limitations with the addition of biological oxidation.

TABLE IV-2

INDUSTRY SUBCATEGORIZATION

Major Subcategory III Major Subcategory IV

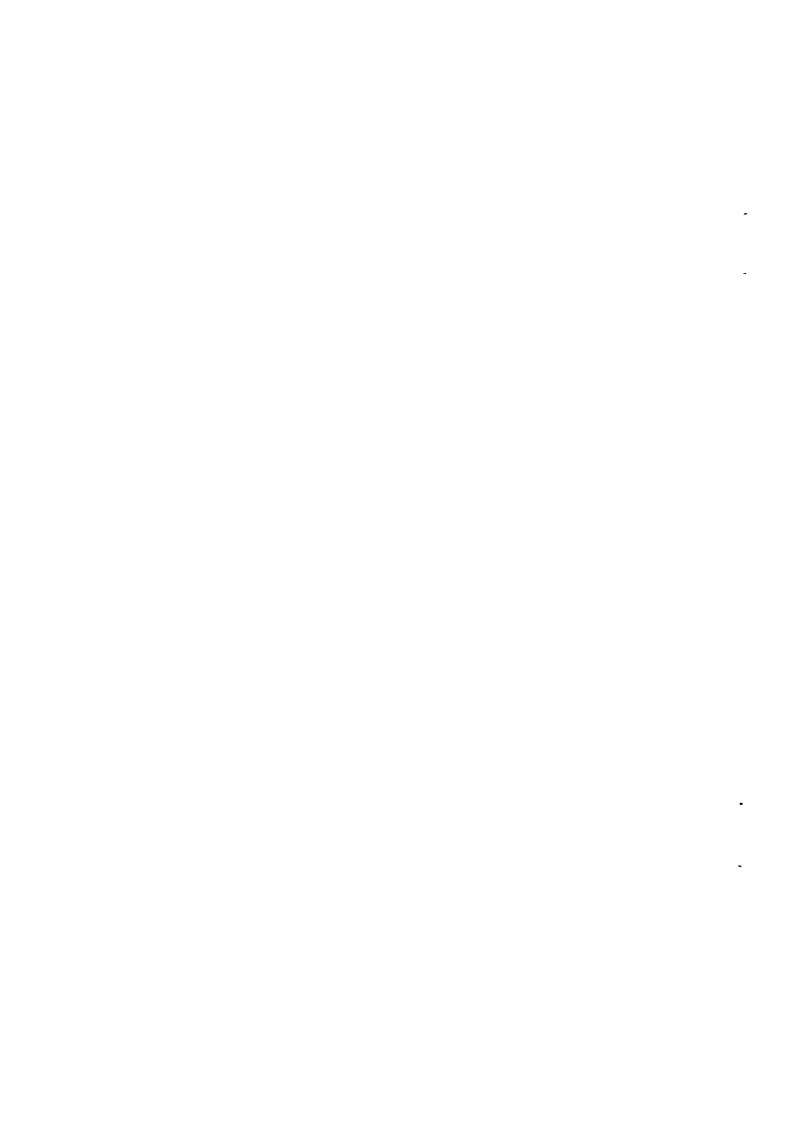
Epoxy Resin (batch, & cont., liquid solid & solution)

Phenolic Resin

Epoxy Resin (batch, fusion, solid & solution)

Urea & Melamine Resin
 (liquid)

Several other methods of subcategorization of the industry were considered. These included plant size, plant age, raw materials and products, and air pollution and solid waste generation. rate of higher unit treatment costs on smaller plants or their potential for utilizing municipal systems was examined in the was not sufficient to economic analysis but warrant categorization. The age of the plants in this industry are determined by obsolescence due to size or process changes and not physical age. Similar raw materials are often used to make dissimilar products. The impact of air pollution control and solid waste disposal is not sufficient to warrant segmentation. For those reasons, none of the above-mentioned factors had sufficient impact on categorization of the industry to be considered further.



SECTION V

WASTE CHARACTERIZATION

The general process flow diagrams in Section III indicate the major waste water generation points for individual processes as furnished by the manufacturers. Flow rates and compositions of process waste water streams were limited in number and are usually based on either estimates established in conjunction with operating personnel or limited measurements. In the manufacture of epoxy, melamine, phenolic and urea resins, there is a significant volume of waste water from housekeeping and other nonprocess sources such as the cleaning of reactors.

Raw Waste Loads

The waste water loadings for these resins are shown in Table V-1, and the ranges of raw waste loads are recorded in Table V-2. Other pollutants which may occur from the manufacture of resins are listed in Table V-3.

TABLE V-1
WASTEWATER LOADING FOR THE PLASTICS AND SYNTHETICS INDUSTRY

		Wastewate	r Loading	Wastewater Loading	
	Product	(cu m Observed <u>Flow</u>	/kkg) Reported <u>Range</u>	(gal./l Observed <u>Flow</u>	000 lbs) Reported Range
	Epoxy Resins				
46	Batch & Continuous (liquid, solid & solution)	24.2	-	2,900	2,200-4,200
	Batch Fusion (solids & solution)	7.1	-	850	600-1,100
	Phenolic Resins	6.9	0.5-20	830	60-2400
	Urea & Melamine Resins				
	Batch (liquid)	1.0	_	150	

46

4

.

TABLE V-2 PLASTICS AND SYNTHETICS INDUSTRY RAW WASTE LOADS

All units expressed as kg/kkg (1b/1000 lb) of production

			OD5		OD	S	
	Product					*Reported	Observed
		Range	Value	Range	Value	Range	Value
	Epoxy Resins						
47	Batch & Continuous (liquid, solid & solution)	57-82	15–150	30–127	65-618	5-24	-
	Batch Fusion (solids and solution)	57-82	0-25	30–127	0-100	5-24	-
	Phenolic Resins	**15-51	***20-72	**90-64 *	* **52-18 8	**0.5-7	1.2-21
	Urea & Melamine Resins						
	Batch (liquid)	-	13	-	60	_	-

^{*} From survey by the Manufacturing Chemist Association and Celanese Corporation studies.

^{**} Presumed to include all raw waste load.

^{***} Assumes concentrated wastes from reactor does not appear in wastewaters.

TABLE V-3

OTHER ELEMENTS, COMPOUNDS AND PARAMETERS

pН

Color

Turbidity

Alkalinity

Temperature

Nitrogenous Compounds (organic, ammonias and nitrates)

Oils and Greases

Dissolved Solids - principally inorganic chemicals

Phosphates

Phenolic Compounds

Sulfides

Cyanides

Fluorides

Mercury

Chromium

Copper

Lead

Zinc

Iron

Cobalt

Cadmium

Manganese

Aluminum

Magnesium

Molybdenum

Nickel

Vanadium

Antimony

Numerous Organic Chemicals

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

The rationale for the selection of pollutant parameters has been discussed in EPA Document 440/1-73/010 and remains the same for these resins. Other elements and compounds specific to epoxy, melamine, phenolic and urea resins are given in Table VI-1.

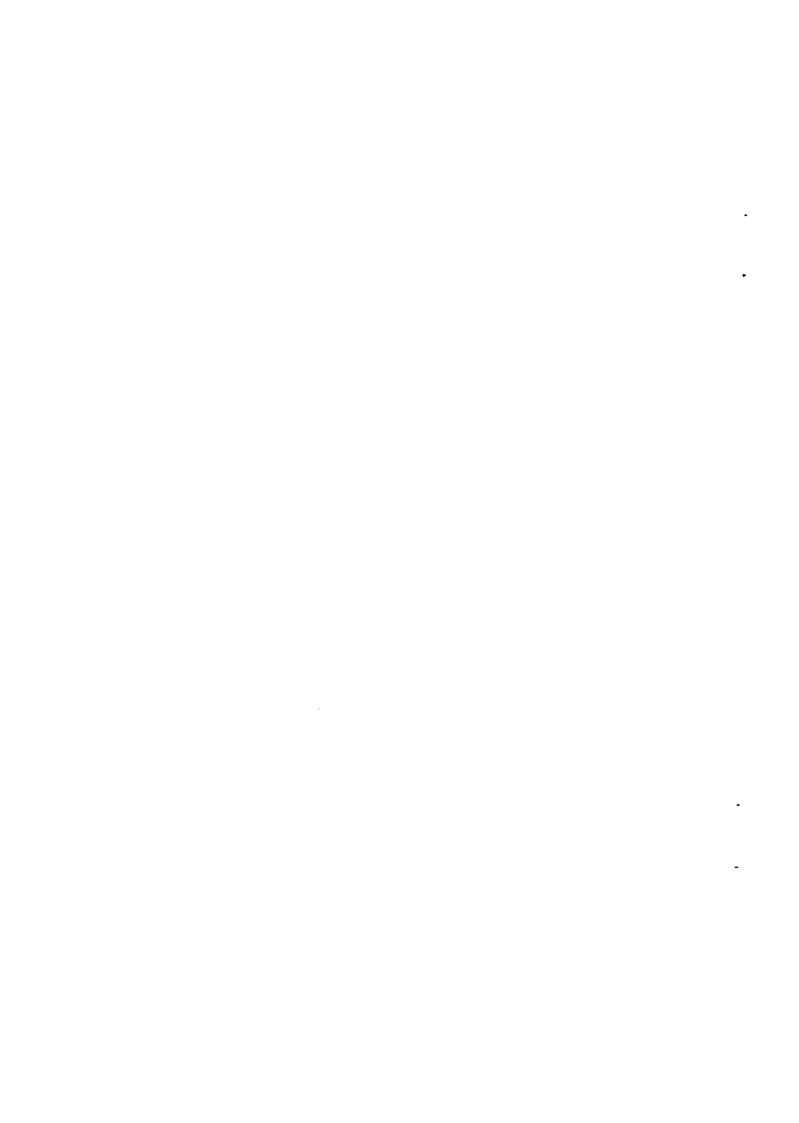
TABLE VI-1

OTHER ELEMENTS AND COMPCUNDS SPECIFIC TO EPOXY, PHENOLIC, UREA AND MELAMINE RESINS

Subcategory Other Element or Compound

Epoxy Resins Phenolic Compounds
Phenolic Resins Phenolic Compounds
Urea & Melamine

Resins Organic Nitrogen



SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

The control and treatment technology applicable to the waste waters from epoxy, melamine, phenolic and urea resin manufacture is similar to that discussed in the EPA Document 440/1-73/010. The operational parameters of waste water treatment facilities for these resins are given in Tables VII-1 and VII-2.

Pollutional parameters of special significance to this group of resins are (1) phenolic compounds from the epoxy and phenolic resins and (2) nitrogenous compounds from melamine and urea resin manufacture. Otherwise, the waste water treatment parameters are the same as for other resin manufacturing operations.

Presently Used Waste Water Treatment Technology

Since the bulk of these resins are produced in batch processes where the probability of spills or had batches tend to be higher than with continuous processes, shock loads on treatment facilities are of particular concern; hence, good current practice includes not only equalization basins but also holding capacity to absorb the surges of the concentrated wastes which are subsequently slowly bled into the treatment plant.

Neutralization is also generally practiced since acids or bases are common catalysts used in the polymerization reactions.

Initial treatment frequently consists of removal of solid polymeric materials which are not significantly affected by biological systems.

The concentrated wastes obtained from decanting the reactor products from liquid phenolics manufacture are usually segregated and do not appear in waste water streams.

The phenolics compounds in waste water from epoxy and phenolic resin manufacture are treated by both biological and activated carbon systems. The biological treatment plants observed handle mixed wastes from chemical complexes; consequently insufficient data was obtained to establish the effectiveness of biological treatment on wastes from a plant producing only one of these resins. The phenolics plant where activated carbon is used for waste water treatment was essentially manufacturing a single product.

The urea and melamine compounds contained in the waste streams from those processes present a particularly difficult problem in biological treatment plants since they oxidize slowly and, therefore, need long retention times to be adequately degraded. In addition, the excess of nitrogenous compounds requires the controlled addition of phosphorous to maintain the proper balance of nutrients. Control of this balance is difficult due to the

TABLE VII-1 OPERATIONAL PARAMETERS OF WASTEWATER TREATMENT PLANTS (Metric Units)

	Type of Plant	Epoxy Resins (4)	Phenolic Resins (4)	tirea Resins (4)
1.	Type of Treatment	Oil Sep., Neut. Chem. Coag., Flotation, Bio-ox., Clarifier	Settling, Neut., Chem. Coag., Equal., Clarif., Act. Carbon	Equal., 2-stage Bio-ox., Clarif. Polish
2.	Hydraulic Load (cu m/day)	27,252	1,041	246
3.	Residence Time (hrs)	30	43	354(3)
4.	BOD ₅ (kg removed/day/cu m)	0.65	0.54	0.088
5.	COD (kgremoved/ day/cu m)	1.56	3.15	0,41
6.	Power (hp/cu m)	0.079	-	0.029
7.	BOD ₅ (kg removed/ hp-hr)	0.36	-	0.11
8.	Suspended Solids (mg/liter)	84	10	50
9.	Clarifier Overflow (m/day)	10.6		21.1
10.	Biomass (mg/liter)	3,500	-	4,000
11.	BOD ₅ (kg removed/day/ kg MLSS)	0.23	-	0.03
12.	Typical Values NH ₃ -N out (mg/liter)	(1)	-	1.8
13.	Typical Values TKN out (mg/liter)	(1)	-	16.6
14.	BOD ₅ in (mg/liter)	837	1,466	131
15.	BOD ₅ out (mg/liter)	36	450	2.8
16.	COD/BOD ₅ in	2.7	3.5	4.9
17.	COD in (mg/liter)	2,255	5,139	646
18.	COD out (mg/liter)	363	677	41
19.	COD/BOD ₅ out	10.1	1.5	14.7
20.	Efficiency, BOD ₅ (%)	95	70 ⁽²⁾	98
21.	Efficiency, COD (%)	82	87	94
22.	Phenolics in (mg/liter)	200	159	-
23.	Phenolics out (mg/liter)	1.4	39	0.018
24.	Efficiency, Phenolics (%	99	76	-

Nutrients added.
 No bio-oxidation, primary and tertiary treatment only.
 Residence time is 40 days (960 hours) if total volume of system is included:
 urea compounds are slow-release chemicals.
 Data are from wastewater treatment facilities handling effluents from multi-product plants.

TABLE VII-2 OPERATIONAL PARAMETERS OF WASTEWATER TREATMENT PLANTS (English Units)

Туре е	f Fiant	Epoxy Resins (4)	Phenolic Resins (4)	Urea Resins (4)
1. Type of 7	reatment	Oil Sep., Neut. Chem. Coag., Flotation, Bio-ox., Clarifier	Settling, Neut., Chem Coag., Equal., Clarif., Act. Carbon	Equal., 2-stage Bio-ox., Clarif. Polish
2. Hydraulic	Lead (MGD)	7.2	0.275	0.065
3. Residence	Time (hours)	30	43	354(3)
4. BOD (#re 1000 ft ³)	moved/day/	40	33	5.4
5. COD (# 50 1000 ft ³)	moved/day/	96	194	25.5
6. Power (HP	/1000 ft ³)	2.2	-	0.8
7. BOD ₅ (# r	emoved/day/ 000 ft ³)	0.8	-	0.24
3. Suspended (mg/liter	Solids	84	10	50
Clarifier (GPD/ft ²)	Overflow	260	-	517
O. Biomass (mg/liter)	3,500	*	4,000
11. BOD ₅ (# r MLSS)	emoved/day/#	0.23	-	0.03
12. Typical V N-out (mg	alues ^{NH} 3 /liter)	(1)	-	18.4
13. Typical V (mg/liter	alues TKN out)	(1)	-	166
14. BOD ₅ in (mg/liter)	837	1,466	1,310
.5. BOD ₅ out	(mg/liter)	36	450	28
16. COD/BOD ₅	in	2.7	3.5	4.9
7. COD in (m	g/liter)	2,255	5,139	6,460
18. COD out (mg/liter)	363	677	406
19. COD/BOD ₅ 0	ut	10.1	1.5	14.5
O. Efficienc	y, BOD ₅ (%)	95	70 ⁽²⁾	98
l. Efficienc	y, COD (%)	82	87	94
22. Phenolics	in (mg/liter)	200	159	-
23. Phenolics	out (mg/liter)	1.4	39	0.018
24. Efficienc	y, Phenolics (%) 99	76	-

Nutrients added.
 No bio-oxidation, primary and tertiary treatment only.
 Residence time is 40 days (960 hours) if total volume of system is included: urea compounds are slow-release chemicals.
 Data are from wastewater treatment facilities handling effuents from multi-product plants.

lack of a good on-line measurement. Further discussion of this problem is found in Section VII of EPA 440/1-73/010.

During the course of the survey on this group of resins, four plant visits were made and three companies were contacted by telephone to obtain information relative to waste loads and treatability. The visits were made to companies who had expressed dissatisfaction with the original guidelines and who offered assistance to obtain a better data base. Even with this new base, considerable judgment was required to develop guidelines since most plants were part of chemical plant complexes.

It was found that the principal differences between this new data base and that used in developing the original guidelines were due to a greater hydraulic and pollutant load that arises from housekeeping, equipment cleaning and once-through barometric condensers and coolers. In addition, further subcategorization appeared reasonable. Although no completely independent exemplary waste water treatment plants were found for this section of the industry, the data provided were presumed to be the best available and guidelines were developed accordingly.

Potentially Usable Waste Water Treatment Technology

The discussion in EPA 440/1-73/010 of potentially usable waste water treatment technology applies to the subgroups considered in this addendum. The use of activated carbon for removal of phenolic compounds from the waste waters of phenolic resin plants was found to be in practical operation as well as the use of extended aeration for the degradation of the slowly oxidizable wastes from urea resin manufacture.

SECTION VIII

COST, ENERGY, AND NONWATER QUALITY ASPECTS

Approximately 100 company operations participate in the manufacture of the four products for which guidelines and standards are recommended. Some of the 100 company operations include multi-plant divisions; some represent multi-product plants.

Total production in 1972 for these products was estimated at 1.0 million kkg or 2.2 billion pounds per year. Overall, production of these products is expected to grow at 8 percent per year. Current water usage (1972) is estimated at 20 thousand cubic meters per day (5.3 MGD). Assuming that hydraulic loads (unit of flow/unit of production) remain constant, water usage is expected to grow to 29 thousand cubic meters per day (7.5 MGD) or at 7.2 percent per year through 1977. Approximately 10 percent of current discharge from the production of these products was estimated to be treated in municipal systems.

The first part of this section (Tables VIII-1 to VIII-4) summarizes the costs (necessarily generalized) of end-of-pipe treatment systems either currently in use or recommended for future use in synthetic polymers production facilities. In order to reflect the different treatment economics of existing versus new plants, large versus small plants, free-standing versus joint treatment facilities, or municipal versus industrial facilities, costs have been developed typically for more than one plant situation in each product subcategory. These product-specific analyses are presented in Tables VIII-4/1 to VIII-4/9.

Cost Models of Treatment Technologies

Information on treatment cost experience for these products was scarce. In large part this was due to the small number of free-standing plants in this industry. Much of the wastes resulting from these products are treated in the central facilities of the large chemical complexes in which they are located.

Consequently, the basic data for estimating the costs of treating the wastes was that developed in the first study. These cost models were developed around standard waste water treatment practice and compared to actual data from a dozen resin plants. That comparison resulted in deviations within \pm 20 percent of model values. For details on the basis of the cost models and their assumptions, see the cost section of the earlier development document for the resins industry.

Annual Cost Perspectives

The expected annual costs for existing plants in 1977 consistent with best practicable technology was estimated at \$2.0 million.

This estimate (Table VIII-2) was the result of the following considerations: the production volumes and waste loads for each of the product groups; the average costs of treatment for different plant sizes; or the costs to be expected from handling these wastes as part of a larger municipal or industrial system. Similarly, by 1983, the estimated costs (Table VIII-2) for existing plants using best available technology were \$6.4 million. It is noted that these costs were associated with end-of-pipe treatment only. Costs for in-plant additions or modifications were not included.

The above annual cost estimates for existing plants for 1977 and 1983 indicate average increases of 21 percent per year between 1977 and 1983. To the costs for existing plants must be added the costs associated with new plants - governed by BADT-NSPS. Assuming the production volume of new plants to be equal to the expected growth in production, the potential annual cost associated with new plants in 1977 was estimated at \$1.9 million (Table VIII-2).

Cost Per Unit Perspectives

Another measure by which to gauge the importance of the costs in Table VIII-2 is to relate them to the sales price of the products as is done in Table VIII-3. The average range of water pollution control costs under BPCTCA was estimated at 0.4 percent to 1.0 percent of current sales prices. On average, the range of costs for applying BATEA to existing plants was 1.4 to 3.5 percent of sales price. The cost of BADT-NSPS was estimated at 1.4 percent of sales price.

Waste Water Treatment Cost Estimates

The average range of water pollution control costs (Table VIII-4) under BPCTCA, BATEA, and BADT-NSPS technologies respectively was: \$0.34 (\$1.29), \$1.06 (\$4.00), and \$0.75 (\$2.85) per cubic meter (per thousand gallons).

Table VIII-4 and its 9 associated tables portray the costs of major treatment steps required to achieve the recommended technologies. Where municipal user charges are not considered directly, the appropriate charge would be \$0.39 or \$0.63 per thousand gallons depending on the size economies of the representative municipal system.

In each of the representative plant cost analyses, typical plant situations were identified in terms of production capacity, hydraulic load, and treatment plant size. Capital costs have been assumed to be a constant percentage (8 percent of fixed investment. Depreciation costs have been calculated consistent with the faster write-off (financial life) allowed for these facilities (10 percent per year) over 10 years even though the physical life is longer. Cost-effectiveness relationships are implicit in the calculation of these costs together with the effluent levels achieved by each treatment step in each major

relevant pollutant dimension. These effluent levels are indicated at the bottom of each representative plant sheet.

Industrial Waste Treatment Model Data

In Table VIII-5 the total discharges for each product subcategory are estimated for 1972 and 1977. The quality of effluents remaining untreated in 1977 is indicated as that consistent with the application of EPCTCA technology. Finally, the current status of treatment in the product group is estimated in terms of the proportion utilizing primary treatment and that utilizing a form of biological treatment - whether industrial or municipal.

Energy Cost Perspectives

Each of the representative plant analyses in the 9 tables summarized by Table VIII-4 includes an estimate of energy costs (of control). The basis for these energy cost estimates was explained in the earlier development document for resins production. The most important assumption therein was one of 1972 energy prices. That assumption has been retained, for purposes of comparison, in this analysis.

Generally, the biological treatment systems employed by industries and municipalities are not large consumers of energy. By the cost models employed in this report, the energy costs of BPCTCA and BADT-NSPS technologies in this industry were estimated at about 2 percent of the total annual waste water treatment costs in Table VIII-2. The add-on technologies for BATEA compliance, however, were estimated to raise that proportion to 6 percent (physical-chemical) or 24 percent (incineration) by 1983.

Nonwater Quality Effects

The nonwater quality aspects of the treatment and control technology found in the synthetics and plastics industry are related to (1) the disposal of solids or slurries resulting from waste water treatment and in-process plant control methods, (2) the generation of a by-product of commercial value, (3) disposal of off-specification and scrap products, and (4) the creation of problems of air pollution and land utilization. These effects were discussed in the development document for resins production.

Other nonwater quality aspects of treatment and pollution control are minimal in this industry and largely depend upon the type of waste water treatment technology employed. In general, noise levels from typical waste water treatment plants are not excessive. If incineration of waste sludges is employed, there is potential for air pollution, principally particulates and possibly nitrogen oxides, although the latter should be minimal because incineration of sludges does not normally take place at temperature levels where the greatest amounts of nitrogen oxide are generated. There are no radioactive nuclides used within the industry, other than in instrumentation, so that no radiation problems will be encountered. Odors from the waste water

treatment plants may cause occasional problems since waste waters are sometimes such that heavy, stable foams occur on aerated basins and septicity is present. But, in general, odors are not expected to be a significant problem when compared with odor emissions possible from other plant sources.

Alternative Treatment Technologies

The range of components used or needed to effect best practicable control technology current available (BPCTCA), best available technology economically achievable (BATEA), and best available demonstrated technology for new source performance standards (BADT-NSPS) in this portion of the plastics and synthetics industry have been combined into eight alternative end-of-pipe treatment steps. These are as follows:

- A. <u>Initial Treatment</u>: For removal of suspended solids and heavy metals. Includes equalization, neutralization, chemical coagulation or precipitation, API separators, and primary clarification.
- B. <u>Biological Treatment</u>: Primarily for removal of BOL. Includes activated sludge (or aerated stabilization basins), sludge disposal, and final clarification.
- C. <u>Multi-Stage Biological</u>: For further removal of BOD loadings. Either another biological treatment system in series or a long-residence-time polishing lagoon.
- D. <u>Granular Media Filtration</u>: For further removal of suspended solids (and heavy metals) from biological treatment effluents. Includes some chemical coagulation as well as granular media filtration.
- E. <u>Physical-Chemical Treatment</u>: For further removal of COD, primarily that attributable to refractory organics, e.g., with activated carbon adsorption.
- F. <u>Liquid Waste Incineration</u>: For complete treatment of small volume wastes.
- H. <u>Phenol Extraction</u>: For removal of phenol compounds, e.g., from epoxy, acrylics, and phenolics wastes.
- M. <u>Municipal Treatment</u>: Conventional municipal treatment of industrial discharge into sewer collection systems. Primary settling and secondary biological stages assumed.

TABLE VIII-1

PERSPECTIVES ON THE PLASTICS AND SYNTHETICS INDUSTRY
- WATER USAGE -

Product	Number of Company Operations(1)	Percent Of Total 18 Product Production(2)	Percent of Water Used by 18 Products	Percent of Growth in Water Usage of 18 Products(3)
Epoxies	8	0.7	0.6	0.7
Melamine/Urea	11	3.5	0.2	0.4
Phenolics	81	4.7	1.1	1.0
Subtotal	100	8.9	1.9	2.1
Total - 18 Resins	s 280	100.0	100.0	100.0

- (1) Number of companies producing each of the products; the number of plants is greater because of multiple sites for any one company.
- (2) Estimated 18-product production in 1972: 12 million kkg (26 billion 1bs).
- (3) Result of projected product growth at current hydraulic loads.

TABLE VIII-2

PERSPECTIVES ON THE PLASTICS AND SYNTHETICS INDUSTRY

- TREATMENT COSTS -

	Tota	l Annual	Costs, \$ Million
	Existir	ng Plants	New Plants
Product	1977	1983	1973 - 1977
Epoxies	0.3	1.0	0.1
Melamines/Ureas	0.6	1.5	0.5
Phenolics	1.1	3.9	1.3
Subtotal	2.0	6.4	1.9
Total - 18 Resins	62.5	177.1	34.9

TABLE VIII-3

PERSPECTIVES ON THE PLASTICS AND SYNTHETICS INDUSTRY
- COST IMPACT -

P ₁	rice Level	Control Cost	Range as % of	Sales Price
Product	¢/1b	BPCTCA	BATEA	BADT-NSPS
		7,	 %	%
Epoxies	60	0.2-0.8	0.7-2.3	0.7
Melamine/Urea	20	0.3-0.4	0.7-0.8	0.7
Phenolics	22	0.6-1.9	2.7-7.3	2.7
II				
Unweighted Average - 14 other Resins		0.7-3.1	1.7-8.7	1.0

TABLE VIII-4

SUMMARY OF WATER EFFLUENT TREATMENT COSTS
COST PER UNIT VOLUME BASIS

Product	BI	PCTCA	BA	TEA	BADT		
	\$/cu m	\$/1000 gal	\$/cu m	\$/1000 gal	\$ cu m	\$/1000 gal	
Epoxies	0.12-0.41	0.45-1.55	0.44-1.28	1.51-4.83	0.14	0.52	
Melamines/ Ureas	0.96-1.06	3.63-4.00	2.32-2.43	8.78-9.21	1.03	3.88	
Phenolics	0.25-0.46	0.94-1.74	1.05-1.78	3.97-6.73	1.05	3.97	

WATER EFFLUENT TREATMENT COSTS PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Epo

Plant Description: Small Plant - in industrial complex

Batch and/or continuous (liquid, solid, & solution)

Representative Plant Capacity

million kilograms (pounds) per year: 11.3 (25)

Hydraulic Load

cubic meters/metric ton of product: 24 (2.9)

(ga1/1b)

Treatment Plant Size

thousand cubic meters per day (MGD): 8.3 (2.2)*

<u>Costs</u> - \$1000	Alte	rnative	Treatm	ent Steps
	<u>A</u>	<u>B</u>	D	E
Initial Investment	57	147	29	167
Annual Costs:				
Capital Costs (8%)	5	12	2	13
Depreciation (10%)	6	15	3	17
Operation and Maintenance	0.8	13	0.3	15
Energy and Power	0.2	2		2
Total Annual Costs	12	42	8.3	47

	Raw Waste Load	Resulting Effluent Levels			
		(un	its per	1000	units of product)
		A	В	$\overline{\mathbf{D}}$	E
B.O.D.	34	_	1.1	_	0.6
C.O.D.	141	_	16	-	9
Suspended Solids	N/A	0.8		0.2	-
Phenolics	N/A	-	0.012	_	0.0023

^{*} The epoxy contribution is 0.83 thousand cubic meters per day (0.22 mgd), this is approximately 10% of the total flow to be treated.

WATER EFFLUENT TREATMENT COSTS PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:	Epoxies		
Plant Description:	Small Plant Batch Fusion		•
Representative Plant Capac million kilograms (pou	ity	·	(25)
Hydraulic Load cubic meters/metric to (gal/lb)	on of product:	2.5	(0.3)
Treatment Plant Size thousand cubic meters	per day (MGD)	0.76	(0.2)*
Costs - \$1000		Alternative	Treatment Ste

<u>Costs</u> - \$1000	Alter	native	Treatme	nt Steps
	<u>A</u>	<u>B</u>	<u>D</u>	<u>E</u>
Initial Investment	11	28	8	56
Annual Costs:				
Capital Costs (8%)	0.9	2	0.6	4
Depreciation (10%)	1.1	3	0.8	6
Operation and Maintenance	0.2	4	0.2	12
Energy and Power	0.1	0.3	-	1
Total Annual Costs	2.3	9.3	1.6	23

	Raw Waste Load	Resulting Effluent Levels				
		(uni	ts per	1000	units of	product)
		<u>A</u>	<u>B</u>	<u>D</u>	E	
B.O.D.	12.5	-	0.3	_	0.1	
C.O.D.	50	-	5	-	2	
Suspended Solids	N/A	0.2	-	0.05	-	
Phenolics	N/A	-	0.003	5 -	0.00048	3

^{*} The epoxy contribution is 0.08 thousand cubic meters per day (0.02 mgd), this is approximately 10% of the total flow to be treated.

WATER EFFLUENT TREATMENT COSTS PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:

Epoxies

Plant Description:

Large Plant in industrial complex

Batch and/or Continuous (liquid, solid & solution)

Representative Plant Capacity

million kilograms (pounds) per year: 45.4 (100)

Hydraulic Load

cubic meters/metric ton of product: 24 (2.9)

(gal/1b)

Treatment Plant Size

thousand cubic meters per day (MGD): 16.7

7 (4.4)*

<u>Costs</u> - \$1000	Alte	rnative	Treatr	ment Steps
	<u>A</u>	<u>B</u>	<u>D</u>	E
Initial Investment	180	440	96	716
Annual Costs:				
Capital Costs (8%)	14	35	8	57
Depreciation (10%)	18	44	10	72
Operation and Maintenance	1.6	26	0.8	152
Energy and Power	0.4	2	-	47
Total Annual Costs	34	107	18.8	328

	Raw Waste Load	Resulting Effluent Levels				zels
		(un	its per	1000	units of	product)
		A	В	D	E	
B.O.D.	34	-	1.1		0.6	
C.O.D.	141	-	16	-	9	
Suspended Solids	N/A	0.8	-	0.2	_	
Phenolics	N/A	_	0.012	-	0.0023	

^{*} The epoxy contribution is 3.3 thousand cubic meters per day (0.88 mgd), this is approximately 20% of the total flow to be treated.

WATER EFFLUENT TREATMENT COSTS PLASTICS AND SYNTHETICS INDUSTRY

Industry	Subcategory:	Phenolics

Plant Description: Small plant in industrial complex

Batch (liquid)

Representative Plant Capacity

million kilograms (pounds) per year: 11.3 (25)

Hydraulic Load

cubic meters/metric ton of product: 7.1 (0.85)

(gal/1b)

Treatment Plant Size

thousand cubic meters per day (MGD): 0.49 (0.13)*

Costs - \$1000	Altern	ative Tr	eatment	Steps
	<u>A</u>	<u>B</u>	<u>F</u> **	
Initial Investment	22	116	500	
Annual Costs:				
Capital Costs (8%) Depreciation (10%)	1.8	9 12	40 50	
Operation and Maintenance Energy and Power	1	10	19 34	
Total Annual Costs	5	32	143	

	Raw Waste Load	Resulting Effluent Levels			zels	
		(units	per 10	00 units	of	product)
		Α	В	F		
B.O.D.	0.045	_	0.1	0		
C.O.D.	0.091	_	0.5	0		
Suspended Solids	N/A	0.3	_	0		
Phenolics	N/A	-	0.0035	0		

^{*} The phenalic contribution is 0.24 thousand cubic meters per day (0.064 mgd), this is approximately 50% of the total flow to be treated.

^{**} Based upon assumption that flow will be reduced to 10% and incinerated.

WATER EFFLUENT TREATMENT COSTS PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory: Phenolics

Plant Description: Small Plant in industrial complex Batch (solid and solution)

Representative Plant Capacity million kilograms (pounds) per year: 11.3 (25)

Hydraulic Load cubic meters/metric ton of product: 12.5 (1.5) (gal/lb)

Treatment Plant Size thousand cubic meters per day (MGD): 0.83 (0.22)*

Costs - \$1000 Alternative Treatment Steps Α <u>B</u> F** Initial Investment 54 136 700 Annual Costs: Capital Costs (8%) 4 11 56 Depreciation (10%) 5 14 70 Operation and Maintenance 1 17 19 Energy and Power 2 57 Total Annual Costs 10 44 202

	Raw Waste Load	Resulting Effluent Levels
		(units per 1000 units of product)
B.O.D.	N/A	
C.O.D.	N/A	No Coordia Cuidalina
Suspended Solids	N/A	No Specific Guidelines
Phenolics	N/A	

^{*} The phenolic contribution is 0.42 thousand cubic meters per day (0.11 mgd), this is approximately 50% of the total flow to be treated.

^{**} Based upon the assumption that the flow will be reduced to 10% and incinerated.

WATER EFFLUENT TREATMENT COSTS PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:

Phenolics

Plant Description:

Large plant in industrial complex

Batch (liquid)

Representative Plant Capacity

million kilograms (pounds) per year: 45.4 (100)

Hydraulic Load

cubic meters/metric ton of product: 7.1 (0.85)

(ga1/1b)

Treatment Plant Size

thousand cubic meters per day (MGD):

1.97

(0.52)*

Costs - \$1000	Alteri	native	Treatment	Steps
	A	<u>B</u>	<u>F**</u>	
Initial Investment	133	350	1300	
Annual Costs:				
Capital Costs (8%) Depreciation (10%) Operation and Maintenance Energy and Power	11 13 2 1	28 35 33 4	104 130 36 113	
Total Annual Costs	27	100	383	

	Raw Waste Load	Res	ulting Ef	Levels		
		(units	per 1000	units	of product)	
		Α	В	\mathbf{F}		
B.O.D.	0.045	_	0.1^{-1}	<u>0</u>		
C.O.D.	0.091	_	0.5	0		
Suspended Solids	N/A	0.3	-	0		
Phenolics	N/A	_	0.0035	0		

^{*} The phenolic contribution is 0.98 thousand cubic meters per day (0.26 mgd), this is approximately 50% of the total flow to be treated.

^{**} Based upon the assumption that flow will be reduced to 10% and incinerated.

WATER EFFLUENT TREATMENT COSTS PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:

Phenolics

Plant Description:

Large plant in industrial complex

Batch (solid and solution)

Representative Plant Capacity

million kilograms (pounds) per year: 45.4 (100)

Hydraulic Load

cubic meters/metric ton of product: 12.5 (1.5)

(gal/1b)

Treatment Plant Size

thousand cubic meters per day (MGD):

3.4

(0.9)*

<u>Costs</u> - \$1000	Alterna	tive	Treatment	Steps	
		70	n.t.t.		
	A	<u>B</u>	<u>F</u> **		
Initial Investment	153	392	1800		
Annual Costs:					
Capital Costs (8%)	12	31	144		
Depreciation (10%)	15	39	180		
Operation and Maintenance	2.5	35	56		
Energy and Power	0.5	6	215		
Total Annual Costs	30	111	595		

	Raw Waste Load	Resulting Effluent Levels
		(units per 1000 units of product)
B.O.D.	N/A	
C.O.D.	N/A	No Consider Outland
Suspended Solids	N/A	No Specific Guidelines
Phenolics	N/A	

^{*} The phenolic contribution is 1.7 thousand cubic meters per day (0.45 mgd), this is approximately 50% of the total flow to be treated.

^{**} Based upon the assumption that the flow will be reduced to 10% and incinerated.

WATER EFFLUENT TREATMENT COSTS PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:	Urea and Melami	ine	
Plant Description:	Small plant in Batch (liquid)	industrial	complex
Representative Plant Capac million kilograms (pou	•	6.8	(15)
Hydraulic Load cubic meters/metric to (gal/lb)	n of product:	1.25	(0.15)
Treatment Plant Size thousand cubic meters	per day (MGD):	0.53	(0.14)*

<u>Costs</u> - \$1000	Alternative Treatment Steps				
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
Initial Investment	5	13	13	3	24
Annual Costs: Capital Costs (8%) Depreciation (10%) Operation and Maintenance Energy and Power	0.5	1.0 1.3 1.6	1.3	0.2	2.4
Total Annual Costs	1	4	4	0.6	11

	Raw Waste Load	Resulting Effluent Levels				vels
		(unit	s per	1000 ur	its of	product)
		<u>A</u>	<u>B</u>	C	D	E
B.O.D.	13	-	-	0.05	=	0.03
C.O.D.	60	-	_	0.8	-	0.4
Suspended Solids	N/A	0.04	-	-	0.01	-

^{*} The urea and/or melamine contribution is 0.03 thousand cubic meters per day (0.07 mgd), this is approximately 5% of the total flow to be treated.

WATER EFFLUENT TREATMENT COSTS PLASTICS AND SYNTHETICS INDUSTRY

Industry Subcategory:	Urea and Melami	ine	
Plant Description:	Large plant in Batch (liquid)	industrial	complex
Representative Plant Capac	<u>-</u>		
million kilograms (pou	nds) per year:	27.2	(60)
Hydraulic Load cubic meters/metric to (gal/lb)	n of product:	1.25	(0.15)
Treatment Plant Size thousand cubic meters	per day (MGD):	0.42	(0.11)*
- 44000			

Costs - \$1000	Alternative Treatment Steps			<u>s</u>	
	<u>A</u>	<u>B</u>	<u>C</u>	$\overline{\mathbf{D}}$	E
Initial Investment	23	53	53	10	101
Annual Costs:					
Capital Costs (8%)	1.8	4.2	4.2	0.8	8.1
Depreciation (10%)	2.3	5.3	5.3	1.0	10.1
Operation and Maintenance	0.5	4.2	4.2	0.5	25
Energy and Power	0.1	0.3	0.3		0.8
Total Annual Costs	4.7	14	14	2.3	44

	Raw Waste Load	Resulting Effluent Levels			els	
		(unit	s per	1000 uni	lts of	product)
		<u>A</u>	B	<u>C</u>	D	E
B.O.D.	13	_	-	0.05	_	0.03
C.O.D.	60	_	-	0.8	-	0.4
Suspended Solids	N/A	0.04	-	-	0.01	-

^{*} The urea and/or melamine contribution is 0.1 thousand cubic meters per day (0.027 mgd), this is approximately 25% of the total flow to be treated.

TABLE VIII-5

INDUSTRIAL WASTE TREATMENT MODEL DATA PLASTICS AND SYNTHETICS INDUSTRY

	Product Subcategory			
	Epoxies	Melamine/Urea	Phenolics	
Total Industry Discharge				
1000 cubic meters/day or (million gallons/day)				
1972	6.0(1.6)	2.3(0.6)	11.8(3.1)	
1977	8.9(2.3)	3.8(1.0)	15.8(4.2)	

Flow through Components Employed

One hundred percent of total flow in each industry subcategory is assumed to pass through each treatment step or component.

Quality of Untreated Wastewater in 1977

(Expressed in terms of monthly average limits)

Parameters:

(in units/1000 units of product)

B.O.D.	1.1	0.05	0.1
C.O.D.	16	0.8	0.5
S.S.	0.8	0.04	0.3

Number of Companies in Subcategory

(in percent now treated)

C) 1	.1. 8	7
C) 1	. 1) I

Percent of Treatment in 1972

Treatment Steps:

Α.	Primary Treatment	55
В.	Secondary Treatment	30

Estimate

SECTION IX

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE GUIDELINES AND LIMITATIONS

Definition of Best Practicable Control Technology Currently Available (EPCTCA)

Based on the analysis of the information presented in Sections IV-VIII the basis for BPCTCA is defined herein as it was in EPA 440/1-73/010.

Best practicable control technology currently available (BPCTCA) for existing point sources is based on the application of end-of-pipe technology such as biological treatment for BOD5 reduction as typified by equalization, to dampen shock loadings, settling, clarification, and chemical treatment, for removal of suspended solids, oils, other elements, and pH control, and subsequent treatment typified by clarification and polishing processes for additional BOD5 and suspended solids removal, and dephenolizing units for the removal of phenolic compounds. Application of inplant technology and changes which may be helpful in meeting BPCTCA include segregation of contact process waste from noncontact waste waters, elimination of once through barometric condensers, control of leaks, and good housekeeping practices.

The best practicable control technology currently available has been found to be capable of achieving efficient concentrations of BOD5 comparable to the secondary treatment of municipal sewage. For phenolic resins manufacture, activated carbon was found to be required as a pretreatment for phenol extraction: subsequent biological treatment should be capable of treating the residual formaldehyde and phenolics to achieve the quideline limitations. The design and operational conditions of these biological systems are, of course, significantly different than for municipal The capabilities of biological accatment for industrial sewage. wastes are specific to a particular plant's waste waters. However, as discussed in Section VII, end-of-pipe treatment for the removal of biologically active substances from waste waters has been demonstrated successfully in different sections of the plastics and synthetics industry. This technology has proven applicable regardless of the age or size of the manufacturing plant. Depending upon the treatability of the waste waters, it has been demonstrated to be practical in maintaining concentrations of biologically active substances in the effluent stream within reasonable limits. However, variations due to the vagaries of micro-organisms as well as process and climatic conditions are normal for any biological waste water treatment plant. The guidelines for best practicable control technology take these factors into consideration and recognize that certain unique properties such as measured by COD exists in the waste waters from the industry. Besides BOS5, COD, and SS, certain metals, phenolic compounds, and nitrogen compounds are among the parameters of major concern to the industry.

Table 21, Section VII of EFA 44C/1-73/010 describes effluent loadings which are currently being attained by the product subcategories of the industry for BOD5, COD, and suspended solids. The results of this work show that exemplary, practical waste water treatment plants are presently in operation and that their operational procedures are comparable with those of biological systems in other industries. Consequently, the most significant factors in establishing effluent limitation guidelines on a basis of units of pollutants per unit of production are (1) the waste water generation rates per unit of production capacity and (2) the practicable treatment levels of the waste waters from the particular manufacturing process.

The Guidelines

The guidelines in terms of kg of pollutant per kkg of production (lb/1000 lb) are based on attainable effluent concentrations and demonstrated waste water flows for each product and process subcategory.

Attainable Effluent Concentrations

Based on the definition of BPCTCA the following long-term average ${\tt BOD5}$ and SS concentrations were used as a basis for the quidelines.

			mg/liter	
			EOD5	SS
	- 1	_	4 6	2.4
	Subcategory		15	3 C
Major	Subcategory	ΙΙ	20	30
Major	Subcategory	III	45	30
Major	Subcategory	IV	7 5	30

The BOD5 and SS concentrations are based on exemplary plant data presented in Table 18, Section VII, of EPA 440/1-73/010.

The COD characteristics of process wastes in the plastics industry vary significantly from product to product, and within a plant over time. The ratio of CCD to BOD5 in plant effluents is shown in Table IX-1 to range from a low of 1.5 for phenolic resins to a high of 15 for epoxy resins. The CCD limits for BPCTCA are based on levels achieved in the exemplary plants for which data were available. They are expressed as a ratio to the BOD5 limits in Table IX-2.

Considering the variability of the CCD/EOD ratio between plants, the upper limits of COD/BOD of 5, 10, and 15 were used.

There is a real need for more data in most segments of the industry to provide a basis for better understanding of how the COD load can be reduced. In the interim, the purpose of the EPCTCA guidelines is simply to reflect the removal of COD to be expected along with best practicable BOD5 removal.

TABLE IX-1 COD/BOD RATIOS IN EFFLUENT STREAMS

Product	COD/BOD
Epoxy resins	10.1
Phenolic resins	1.5
Urea & melamine resins	14.3

TABLE IX-2 COD/BOD GUIDELINE BASES

Phenol:	ics				5	
Γ	II	1	Melamine	Dantan	15	

The removal of phenolic compounds is based on an attainable concentration level of 0.5 mg/liter monthly limit as demonstrated by dephenolizing units, activated carbon or biological degradation as referenced in EPA 440/1-73/010.

Demonstrated Waste Water Flow

The waste water flow basis for BPCTCA is based on demonstrated waste water flows found within the industry for each product and process subcategory. Waste Water flows observed at exemplary plants were used as the basis when they fell at the approximate middle of the waste water flow ranges reported by previous industry and EPA surveys. When the observed flows fell outside of the middle range, a waste water flow within this range was used as the basis.

The waste water flow basis includes process water, and excludes utility blowdowns and auxiliary facilities such as laboratories, etc., where definable. The waste water flow basis is summarized in Table IX-3. It is essential to note that the waste water flow is often an integral part of the basic design and operation of the plant or the process and may therefore be subject to significant reduction only at large expense. In general, the hydraulic load is larger for older plants. However, the availability of water also influences design as does the philosophy of the company constructing the plant. No simple formula for relating hydraulic load to plant age, size or location can be established. Demonstrated waste water flows which fall in the middle of the reported range of waste water flow is the best available basis for use in determining quidelines.

Statistical Variability of a Properly Designed and Operated Waste Treatment Plant

The effluent from a properly designed and operated treatment plant changes continually due to a variety of factors. Changes in production mix, production rate and reaction chemistry influence the composition of raw wasteload and, therefore, its treatability. Changes in biological factors influence the efficiency of the treatment process. A common indicator of the pollution characteristics of the discharge from a plant is the long-term average of the effluent load. The long-term (e.g., design or yearly) average is not a suitable parameter on which to base an enforcement standard. However, using data which show the variability in the effluent load, statistical analyses can be used to compute short-term limits (monthly or daily) which should never be exceeded, provided that the plant is designed and run in the proper way to achieve the desired long-term average load. It is these short-term limits on which the effluent guidelines are based.

In order to reflect the variabilities associated with properly designed and operated treatment plants for each of the major subcategories as discussed above, a statistical analysis was made

TABLE IX-3
DEMONSTRATED WASTEWATER FLOWS

	Wastewater	Flow Basis
Epoxy Resins		
Batch & Continuous (liquid, solid		
& solution)	24.2	2600
Batch Fusion (solid & solution)	7.1	300
Phenolic Resins		
	6.9	2700
Urea & Melamine Resins	1 OF	150
Batch (liquid)	1.25	150

of plants where sufficient data was available to determine these variances for day-to-day and month-to-month operations. The standard deviations for day-to-day and month-to-month operations were calculated. For the purpose of determining effluent limitation a variability factor was defined as follows:

Standard deviation = Q monthly, Q daily
Long-term average (yearly or design) = x
Variability factor = y monthly, y daily
y monthly = x + 2Q monthly
x
y daily = x + 3Q daily
x

The variability factor is multiplied by the long-term yearly average to determine the effluent limitations guideline for each product subcategory. The monthly effluent limitations guideline is calculated by use of a variability factor based on two standard deviations and is only exceeded 2-3 percent of the time for a plant that is attaining the long-term average. The daily effluent limitations guideline is calculated by the use of a variability factor based on three standard deviations and is exceeded only 0.0-0.5 percent of the time for a plant that is attaining the long term average. Any plant designed to meet the monthly limits should never exceed the daily limits. The data used for the variability analysis came from plants under voluntary operation. By the application of mandatory requirements, the effluent limitations guidelines as discussed in this paragraph should never be exceeded by a properly designed and operated waste treatment facility.

The variability factors in Table IX-5 are based on the data obtained in the synthetic resin segment (16) of the plastics and synthetics industry.

The variability factors for suspended solids removal are the same as used in the resins segment of the industry, i.e., a monthly variability of 2.2 and a daily variability of 4.0.

The variability factors recommended for phenolic compounds are based on the monthly limits and a variability factor of 2.0 for the daily maximum.

Based on the factors discussed in this section, the effluent limitations guidelines for BPCTCA are presented in Tables IX-7 and IX-8.

The following table summarizes the basis for the variability factors.

TABLE IX-4
DEMONSTRATED VARIABILITY

	Influent Concentration	Long Term Effluent Concentration	Variability	Factor
Major Sub- category	mg/liter	mg/liter	Monthly	Daily
I	33	6 9	1.50	2.00
II	380 380	17	1.33 1.80	1.71 2.60
II	1206 91	11 20	1.76 1.77	2.50 2.84
III	1267 793 1503	44 36 182	2.2 4.3	3.0* - 3.85
IV	-	-	2.2*	3.0*

NOTICE

Those are tentative recommendations based upon information in this report and are subject to change based upon comments received and further internal review by EPA.

^{*} Estimated values

Based on the table of demonstrated variability the following variability factors were applied to determine the effluent limitation guidelines for ${\rm BOD}_5.$

TABLE IX-5
VARIABILITY FACTOR

Major Subcategory	Monthly	Daily
I	1.6	3.1
II	1.8	3.7
III	2.2	4.0
IV	2.2	4.0

NOTICE

These are tentative recommendations based upon aformation in this report and are subject to change based upon comments received and further internal review by EPA.

The variability factors for suspended solids removal are based on the variables projected in Table IX-6 for S. S. removal. The monthly variability was calculated at 2.2 and the daily estimated at 4.0.

The variability for phenolic compounds are based on the monthly limits and a variability factor of 2.0 for the daily maximum ${}^{\circ}$

TABLE IX-6

VARIABILITIES PROJECTED FOR SUSPENDED SOLIDS REMOVAL

S. S. Removal	Demo. Monthly Variability
Cellulose Acetate	2.2
Nylon 6	1.7
Polyester	2.2
Nylon 66	2.2
Acrylics	2.6
Polyvinyl Chloride	1.9
Phenolic Resin	3.6*-4.3
Epoxy Resin	2.8

^{*}Daily Variability

TABLE IX-7

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE EFFLUENT LIMITATIONS GUIDELINES (kg/kkg (1b/1000 1b) of Production)

	BOL	5	C	OD	SS		
Subcategory	Maximum average of daily values for any period of thirty consecutive days	Maximum for any one day	Maximum average of daily values for any period of thirty consecutive days	any one day	Maximum average of daily values for any period of thirty consecutive days	Maximum for any one day	
Epoxy Resins							83
Batch & Continuous (liquid, solid & solution)	2.1	3.9	32	58	1.4	2.6	
Batch, Fusion (solid & solution)	0.25	0.45	3.9	6.7	0.17	0.30	
Phenolic Resins	3.7	6.7	19	34	1.5	2.7	
Urea & Melanine Resins							
Batch (liquid)	0.20	0.38	1.5	2.7	0.13	0.25	

TABLE IX-8

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE EFFLUENT LIMITATIONS GUIDELINES (PHENOLIC COMPOUNDS)

			kg/kkg (1b/1000 1b)	of production
m	Product	Parameter	Maximum average of daily values for any period of thirty consecutive days	Maximum for any one day
84	Epoxy Resins			
	Batch & Continuous (líquíd, solid & solution)	Phenolic Cmpds	0.011	0.022
	Batch Fusion (solid & solution)	Phenolic Cmpds	0.0013	0.0025
	Phenolic Resins	Phenolic Cmpds	0.011	0.023

SECTION X

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE

The definition of Best Available Technology Economically Achievable given in EPA 440/1-73/010 is directly applicable to the epoxy, phenolic, urea and melamine resins. Key parameters are summarized in Table X-1. The flow basis is summarized in Table X-2. The BATEA guidelines are presented in Tables X-3 and X-4.

TABLE X-1

KEY PARAMETERS FOR BEST AVAILABLE TECHNOLOGY
ECONOMICALLY ACHIEVABLE

		BOD ₅			Suspended Solids			Phenolics		
_	Group	mg/liter	Monthly Variability	Daily Variability	mg/liter	Monthly Variability	Daily <u>Variability</u>	mg/liter	Monthly Variability	Daily Variability
	I	15	1.6	2.4	10	1.7	2.0	0.1	1.0	2.0
86	II	15	1.8	2.8	10	1.7	2.0	0.1	1.0	2.0
	III	25	2.2	3.0	10	1.7	2.0	0.1	1.0	2.0
	IV	25	2.2	3.0	10	1.7	2.0	0.1	1.0	2.0

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TABLE X-2

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE EFFLUENT LIMITATIONS GUIDELINES

kg/kkg (1b/1000 lb of production)

		во	05	CO		SS		
	Subcategory	Maximum average of daily values for any period of thirty consecutive days	any one day	Maximum average of daily values for any period of thirty consecutive days	any one day	Maximum average of daily values for any period of thirty consecutive days	Maximum for ary one day	
	Epoxy Resins							
	Batch & Continuous (liquid, solid & solution)	0.95	1.3	4.8	6.5	0.28	0.33	
37	Batch, Fusion (solid & solution)	0.12	0.17	0.65	U.88	0.04	0.05	
	Phenolic Resins	0.96	1.3	5	6.8	0.30	0.35	
	Urea & Melamine Resins							
	Batch (liquid)	0.06	0.08	0.09	0.13	0.017	0.021	

TABLE X-3

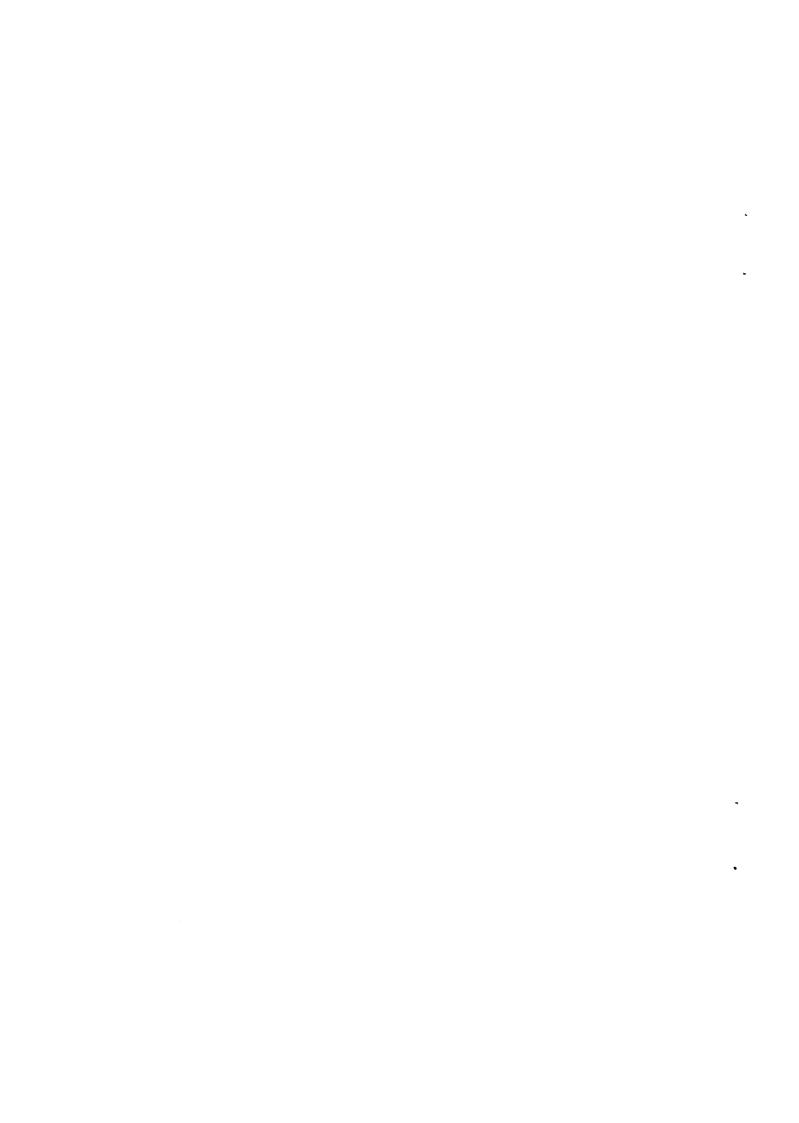
BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE EFFLUENT LIMITATIONS GUIDELINES (PHENOLIC COMPOUNDS)

			kg/kkg (1b/1000 1b	of production)
	Product	Parameter	Maximum average of daily values for any period of thirty consecutive days	Maximum for any one day
	Epoxy Resins			
88	Batch & Continuous (liquid solid & solution)	Phenolic Cmpds	0.0017	0.0033
	Batch, Fusion (solid & solution)	Phenolic Cmpds	0.00022	0.00044
	Phenolic Resins	Phenolic Cmpds	0.0018	0.0035

TABLE X-4

Best Available Technology Economically Achievable - Flow Rate Basis

Subcategory	Flow basis				
	gal/1000 lbs	cum/kkg			
Epoxy Resins Batch Batch-Fusion	2000 265	16.68 2.21			
Phenolic Resins	2100	17.51			
Urea and Melamine Resins	138	1.15			



SECTION XI

NEW SOURCE PERFORMANCE STANDARDS BEST AVAILABLE DEMONSTRATED TECHNOLOGY

The definitions, standards and waste load reduction basis described in EPA 440/1-73/010 are applicable to the epoxy, phenolic, urea and melamine resins.

Key parameters are summarized in Table XI-1. The lowest demonstrated waste water flows are shown in Table XI-2. Effluent Limitation Guidelines for Best Available Demonstrated Technology for New Source Performance Standards (BADT-NSPS) are presented in Tables XI-3 and XI-4.

TABLE XI-1

KEY PARAMETERS FOR NEW SOURCE PERFORMANCE STANDARDS

BEST AVAILABLE DEMONSTRATED TECHNOLOGY

		BOD ₅			Suspended Solids			Phenolics		
	Group	mg/liter	Monthly Variability	Daily Variability	mg/liter	Monthly Variability	Daily Variability	mg/liter	Monthly Variability	Daily Variability
	I	15	1.6	3.1	10	1.7	2.5	0.1	1.0	2.0
92	ΙΙ	15	1.8	3.7	10	1.7	2.5	0.1	1.0	2.0
	III	25	2.2	4.0	10	1.7	2.5	0.1	1.0	2.0
	IV	25	2.2	4.0	10	1.7	2.5	0.1	1.0	2.0

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TABLE XI-2

LOWEST DEMONSTRATED WASTEWATER FLOWS

Epoxy Resins Batch & Continuous (liquid, solid and solution) Batch Fusion Lowest Demonstrated Wastewater Flow cu m/kkg gal/1000 lbs 21.7 1400 22.5 230 Phenolics Resins

1.0

125

Urea & Melamine Resins

TABLE XI-3

BEST AVAILABLE DEMONSTFATED TECHNOLOGY FOR NEW SOURCE PERFORMANCE STANDARDS

kg/kkg (1b/1000 1b of production)

	BOD ₅		COD		SS	
Subcategory	Maximum average of daily values for any period of thirty consecutive days	Maximum for any one day	Maximum average of daily values for any period of thirty consecutive days	Maximum for any one day	Maximum average of daily values for any period of thirty consecutive days	any one day
Epoxy Resins						
Batch & Continuous (liquid, solid & solution)	0.67	1.2	9.2	12.9	0.20	0.30
Batch Fusion (solid & solution)	0.11	ó.19	1.5	2.1	0.03	0.05
Phenolic Resins						
Batch (liquid)	0.69	1.3	19	34	0.21	0.31
Urea & Melamine Resins						
Batch (liquid)	0.06	0.11	0.10	0.18	0.02	0.04

4

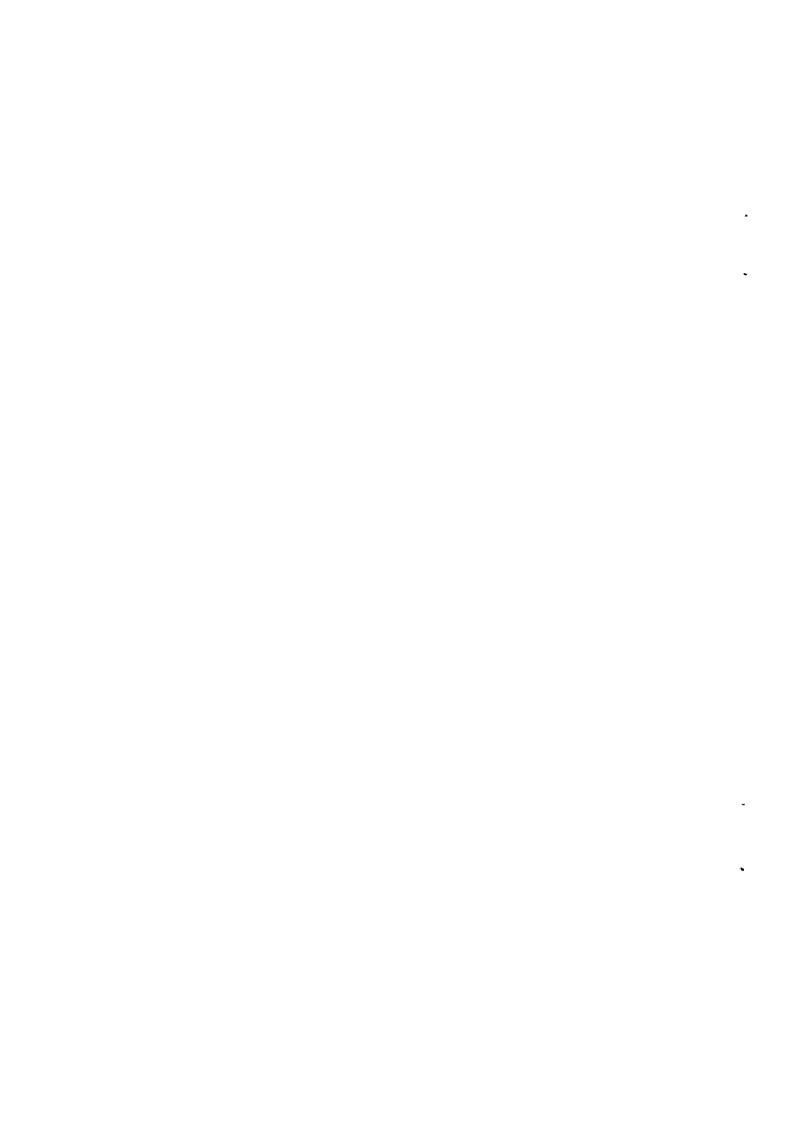
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TABLE XI-4 BEST AVAILABLE DEMONSTRATED TECHNOLOGY FOR NEW SOURCE PERFORMANCE STANDARDS (PHENOLIC COMPOUNDS)

				kg/kkg (1b/1000 1b of production)		
	Product	Parameter	Maximum average of daily values for any period of thirty consecutive days	Maximum for any one day		
95	Epoxy Resins					
	Batch & Continuous (liquid, solid & solution	Phenolic Cmpds	0.0012	0.0024		
	Batch Fusion (solid & solution)	Phenolic Cmpds	0.00019	0.00038		
	Phenolic Resins	Phenolic Cmpds	0.0012	0.0025		



SECTION XII

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Allen Cywin - Effluent Guidelines Division
David Becker - Effluent Guidelines Division (Project Officer)
William Frick - Office of General Counsel
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Robert Wooten - Region IV
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Frank Mayhue - Office of Research and Monitoring (Ada)
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SECTION XIII

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SECTION XIV

GLCSSARY

Acetyl

Refers to that portion of a molecular structure which is derived from acetic acid.

Addition Polymerization

Polymerization without formation of a by-product (in contrast to condensation polymerization).

Aerobic

A living or active biological system in the presence of free, dissolved oxygen.

Alkyl

A general term for monovalent aliphatic hydrocarbons.

Allophanate

A derivative of an acid, NH2CCNHCOOH, which is only known in derivative forms such as esters.

Amerphous

Without apparent crystalline form.

Alumina

The oxide of aluminum.

Anaerobic

Living or active in the absence of free oxygen.

Annealing

A process to reduce strains in a plastic by heating and subsequent cooling.

Aryl

A general term denoting the presence of unsaturated ring structures in the molecular structure of hydrocarbons.

Atactic Polymer

A polymer in which the side chain groups are randomly distributed on one side or the other of the polymer chain. (An atactic polymer can be molded at much lower temperatures and is more

soluble in most solvents than the corresponding isotactic polymer, g.q.).

<u>Autoclave</u>

An enclosed vessel where various conditions of temperature and pressure can be controlled.

Azeotrope

A liquid mixture that is characterized by a constant minimum or maximum boiling point which is lower or higher than that of any of the components and that distills without change in composition.

Bacteriostat

An agent which inhibits the growth of bacteria.

Blowdown

Removal of a portion of a circulating stream to prevent buildup of dissolved solids, e.g., boiler and cooling tower blowdown.

BOD5

Biochemical Oxygen Demand - 5 days as determined by procedures in Standard Methods, 19th Edition, Water Pollution Control Federation, or EPA's Manual 16020-07/71, Methods for Chemical Analysis of Water and Wastes.

Catalyst

A substance which initiates primary polymerization or increases the rate of cure or crosslinking when added in quantities which are minor as compared with the amount of primary reactants.

Caustic Soda

A name for sodium hydroxide.

Chain Terminator

An agent which, when added to the components of a polymerization reaction, will stop the growth of a polymer chain, thereby preventing the addition of MER units.

COD

Chemical Oxygen Demand - Determined by methods explained in the references given under BOD5.

Copolymer

The polymer obtained when two or more monomers are involved in the polymerization reaction.

Cross-link

A comparatively short connecting unit (such as a chemical bond or a chemically bonded atom or group) between neighboring polymer chains.

Crystalline

Having regular arrangement of the atoms in a space lattice -- opposed to amorphous.

Delusterant

A compound (usually an inorganic mineral) added to reduce gloss or surface reflectivity of plastic resins or fibers.

Dialysis

The separation of substances in solution by means of their unequal diffusion through semipermeable membranes.

Diatomaceous Earth

A naturally-occurring material containing the skeletal structures of diatoms - often used as an aid to filtration.

Effluent

The flow of waste waters from a plant or waste water treatment plant.

<u>Emulsifier</u>

An agent which promotes formation and stabilization of an emulsion, usually a surface-active agent.

Emulsion

A suspension of fine droplets of one liquid in another.

Facultative Lagcon or Pond

A combination of aerobic surface and anaerobic bottom existing in a basin holding biologically active waste waters.

Fatty Acids

An organic acid obtained by the hydrolysis (saponification) of natural fats and oils, e.g., stearic and palmitic acids. These acids are monobasic and may or may not contain some double bonds. They usually contain sixteen or more carbon atoms.

Filtration

The removal of particulates from liquids by membranes on in-depth media.

Formalin

A solution of formaldehyde in water.

Free Radical

An atom or a group of atoms, such as triphenyl methyl $(C\underline{6}H\underline{5})\underline{3}C\bullet$, characterized by the presence of at least one unpaired electron. Free radicals are effective in initiating many polymerizations.

Godet Roll

Glass or plastic rollers around which synthetic filaments are passed under tension for stretching.

GPD

Gallons per day.

GPM

Gallons per minute.

<u>Halogen</u>

The chemical group containing chlorine, fluorine, bromine, iodine.

Isotactic Polymer

A polymer in which the side chain groups are all located on one side of the polymer chain. See also "Atactic Polymer."

Lewis Acid

A substance capable of accepting from a base an unshared pair of electrons which then form a covalent bond. Examples are boron fluoride, aluminum chloride.

Homopolymer

A polymer containing only units of one single monomer.

Humectant

An agent which absorbs water. It is often added to resin formulations in order to increase water absorption and thereby minimize problems associated with electrostatic charge.

<u>Influent</u>

The flow of waste waters into a treatment plant.

Μ

Thousands (e.g., thousands metric tons).

MM

Millions (e.g., million pounds).

Monomer

A relatively simple compound which can react to form a polymer.

рΗ

A measure of the relative acidity or alkalinity of water on a scale of 0-14. A pH of 7 indicates a neutral condition, less than 7 an acid condition, greater than 7 an alkaline condition.

Phenol Phenol

Class of cyclic organic derivatives with the basic chemical formula C6H5OH.

Plasticizer

A chemical added to polymers to impart flexibility, workability or distensibility.

Polymer

A high molecular weight organic compound, natural or synthetic, whose structure can be represented by a repeated small unit, the (MER).

Polymerization

A chemical reaction in which the molecules of a monomer are linked together to form large molecules whose molecular weight is a multiple of that of the original substance. When two or more monomers are involved, the process is called copolymerization.

Pretreatment

Treatment of waste waters prior to discharge to a publicly owned waste water treatment plant.

Primary Treatment

First stage in sequential treatment of waste waters - essentially limited to removal of readily settlable solids.

Quenching

Sudden cooling of a warm plastic, usually by air or water.

Reflux

Condensation of a vapor and return of the liquid to the zone from which it was removed.

Resin

Any of a class of solid or semi solid organic products of natural or synthetic origin, generally of high molecular weight with no definite melting point. Most resins are polymers.

Scrubber

Equipment for removing condensable vapors and particulates from gas streams by contacting with water or other liquid.

Secondary Treatment

Removal of biologically active soluble substances by the growth of micro-organisms.

Slurry

Solid particles dispersed in a liquid medium.

Spinnerette

A type of extrusion die consisting of a metal plate with many small holes through which a molten plastic resin is forced to make fibers and filaments.

Staple

Textile fibers of short length, usually one-half to three inches.

Stoichiometric

Characterized by being a proportion of substances exactly right for a specific chemical reaction with no excess of any reactant or product.

TDS

Total dissolved solids - soluble substances as determined by procedures given in reference under EOD5.

<u>Thermoplastic</u>

Having property of softening or fusing when heated and of hardening to a rigid form again when cooled.

Thermosetting

Having the property of becoming permanently hard and rigid when heated or cured.

TOC

Total organic carbon - a method for determining the organic carbon content of waste waters.

<u>**Tow</u>**</u>

A large number of continuous filaments of long length. Tow is the usual form of fibers after spinning and stretching and prior to being chopped into short lengths of staple.

Transesterification

A reaction in which one ester is converted into another.

<u>Vacuum</u>

A condition where the pressure is less than atmospheric.

Ziegler-Natta Catalyst

A catalyst (such as a transition metal halide or an organometallic compound) that promotes an ionic type of polymerization of ethylene or other olefins at atmospheric pressure with the resultant formation of a relatively highmelting polyethylene or similar product.

TABLE XIII-1

METRIC TABLE

CONVERSION TABLE

MULTIPLY (ENGLISH UNITS)

bу

TO OBTAIN (METRIC UNITS)

ENGLISH UNIT	ABBREVIATIO	N CONVERSION	ABBREVIATION	METRIC UNIT
acre	ac	0.405	ha	hectares
acre - feet	ac ft	1233.5	cu m	cubic meters
British Thermal				•
Unit	BTU	0.252	kg cal	kilogram - calories
British Thermal				
Unit/pound	BTU/1b	0.555	kg cal/kg	kilogram calories/kilogram
cubic feet/minute	cfm	0.028	cu m/min	cubic meters/minute
cubic feet/second	cfs	1.7	cu m/min	cubic meters/minute
cubic feet	cu ft	0.028	cu m	cubic meters
cubic feet	cu ft	28.32	1	liters
cubic inches	cu in	16.39	cu cm	cubic centimeters
degree Fahrenheit	°F	0.555(°F-32)	* °C	degree Centigrade
feet	ft	0.3048	m	meters
gallon	gal	3.785	1	liters
gallon/minute	gpm	0.0631	1/sec	liters/second
horsepower	hp	0.7457	kw	killowatts
inches	in	2.54	cm	centimeters
inches of mercury	in Hg	0.03342	atm	atmospheres
pounds	1b	0.454	kg	kilograms
million gallons/day	mgd	3 , 785	cu m/day	cubic meters/day
mile	mi	1.609	km	kilometer
pound/square				
inch (gauge)	psig	(0.06805 psig +1)	t atm	atmospheres (absolute)
square feet	sq ft	0.0929	sq m	square meters
square inches	sq in	6.452	sq cm	square centimeters
ton (short)	ton	0.907	kkg	metric ton (1000 kilograms
yard	yd	0.9144	m	meter

^{*} Actual conversion, not a multiplier

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