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WATERBORNE WASTES OF THE PAINT AND INORGANIC PIGMENTS INDUSTRIES

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WATERBORNE WASTES OF THE PAINT AND INORGANIC PIGMENTS INDUSTRIES

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REVIEW NOTICE

FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

The studies for this report were undertaken to develop the background needed to characterize pollution sources within the subject industries, establish current levels and methods of pollution control and identify specific areas where the Agency's participation in the development of new technology could have maximum effect on the industry's efforts to protect our Nation's water resources.

A. W. Breidenbach, Ph.D.
Director
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ABSTRACT

This report describes a study of the wastewater management practices in the paint and inorganic pigments industries. Information was obtained from 153 plants manufacturing paints, 10 titanium dioxide plants, and 10 plants that produce other inorganic pigments. The data were analyzed to identify the sources and characteristics of wastewater from the manufacturing processes of these plants, to determine the practices for wastewater control and treatment that are presently employed, and to identify deficiencies in technology that require research and development to improve control and treatment methods.

The major findings of the study indicate that although the paint industry uses approximately 300 million liters (80 million gal.) of water per day, only a small portion of this, less than 5%, is necessarily contaminated by virtue of its use. Suspended solids, consisting of pigments and resin particles, are the major wastewater contaminants of the paint industry. The wastewaters from plants that produce titanium dioxide or other inorganic pigments generally contain a high level of dissolved solids and acids for which no entirely satisfactory control and treatment methods exist.

The report includes conclusions and recommendations that may be useful to the industries in meeting anticipated Environmental Protection Agency regulations. In addition, the data reported should be of value to the Environmental Protection Agency in establishing effluent guidelines for the paint industry.

This report was prepared by Southern Research Institute in fulfillment of Project No. R-800602 under the sponsorship of the Office of Research and Development, Environmental Protection Agency. The work was completed in July 1973.

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SECTION I

CONCLUSIONS

PAINT MANUFACTURING INDUSTRY

1. The major source of contaminated wastewater in the paint manufacturing industry is water used in the cleaning of equipment. This source represents a relatively small volume of the total water discharged by the industry, probably less than 2%. At typical plants that have fewer than 50 employees—about 80% of the industry's plants—the cleanup water discharged amounts to less than 1,000 liters (250 gal.) per day. At larger plants, the volume of cleanup water may amount to as much as 40,000 liters (10,000 gal.) per day.

2. Other sources of contaminated wastewater at some of the larger plants are air pollution control equipment and resin manufacturing operations that use process water.

3. The largest use of water is for cooling purposes. This use is exclusively non-contact; thus, the water is not contaminated with process wastes when discharged unless process and cooling discharge streams are combined.

4. The major contaminant generated by the industry is suspended solids, which can be reduced considerably by the efficient application of conventional treatment methods practiced in the industry.

5. Heavy metals, present in at least trace quantities in pigments, drying agents, and fungicides, occur in the industry's wastewater, but the effectiveness of treatment methods presently employed by the industry to control them could not be determined from data obtained in this study.

6. The major portion of the industry consists of many small plants with limited treatment capabilities. About 50% of the plants with fewer than 50 employees discharge all of their wastes to municipal sewers. Most other small plants are able to dispose of their contaminated wastewaters by landfill, evaporation, or other methods. About 10% of the small plants have no wastewater discharges.

7. No advanced treatment technology was identified as being practiced in the industry, although advanced filtration procedures and carbon adsorption have been reported to be used in new installations.

TITANIUM DIOXIDE MANUFACTURING INDUSTRY

1. The principal sources of contaminated water in the titanium dioxide industry are process equipment, air pollution control equipment, and some contact cooling.

2. Waste loadings at plants employing the sulfate process are much higher than those at chloride-process plants.

3. The major contaminants are sulfate and chloride salts of iron and other metals, waste acids, and lost titanium dioxide fines.

4. Effective treatment to control pH and remove suspended solids is practiced to some extent in the industry. Because no effective alternatives or practical treatment methods exist at present, wastes high in dissolved solids and acids are disposed of by deep-well injection or barging to the ocean.

5. Improved technology for reuse of acid wastes has not yet progressed to the commercial stage.

MANUFACTURE OF OTHER INORGANIC PIGMENTS

1. The major use of water and the major source of contamination in the manufacture of other inorganic pigments is process water from synthesis, filtration, washing, and grinding.

2. Contaminants consist of dissolved solids from reactants or by-products formed in the synthesis of pigments. The dissolved solids include heavy metals derived from the raw materials and products. Wastewaters are generally acidic and contain some suspended solids as well. The nature of the suspended solids is such that conventional sedimentation techniques are only partially effective.

3. Present treatment technology practiced in the industry is limited to control of pH and removal of suspended solids by conventional techniques.

4. One advanced treatment method, the use of ion-exchange resins for the removal of chromium salts, was identified. This method appears promising for controlling a portion of the dissolved solids and heavy metal ions generated by the industry.

SECTION II

RECOMMENDATIONS

The following recommendations relate to problems that have been identified in the industries and suggest activities that may be undertaken by the industries—or in their behalf—to alleviate these problems. The objectives of undertaking such activities would be to reduce waste discharges from the manufacturing plants and to enable the plants to meet anticipated Environmental Protection Agency effluent regulations in the most effective manner.

PAINT INDUSTRY

1. Broader use of in-plant control measures in the industry, including segregation of contaminated wastes from uncontaminated effluents, reduction of volume of water used for cleaning equipment such as through the use of high-pressure sprayers, and reuse of cleanup water.

2. Broader dissemination to the industry of information on applicable treatment practices currently available for removal of suspended solids, including costs, design features, and effectiveness levels.

3. Continued research and development on substitutes for heavy metal compounds in fungicides and driers.

4. Determination of the effectiveness of treatment methods presently available for the removal of heavy metals.

5. Determination of the effects of raw waste from paint plants, especially heavy metals, on municipal treatment facilities, which receive discharges from a large number of plants.

6. Estimation of cost versus effectiveness of various control and treatment alternatives as a function of wastewater volume, including drumming for landfill, evaporation, incineration, pretreatment and direct discharge to municipal treatment systems, and complete self-treatment for discharge to surface waters.

TITANIUM DIOXIDE INDUSTRY

1. A thorough evaluation of potential pollution reduction benefits achievable through the upgrading of ilmenite ore for use in the chloride process (since the chloride process is inherently capable of generating lower waste loadings than the sulfate process) and other methods of raw ore enrichment that may be suitable for use in conjunction with the sulfate process.

2. Identification of transferable technology used in other industries that also generate large volumes of acidic wastes.

INORGANIC PIGMENTS INDUSTRY

1. Broader application of ion exchange technology for recovery of chromium and investigation of its feasibility for other heavy metals, particularly when it will allow reuse of process water.

2. Development of more effective methods for removal of the unique forms of suspended solids common to this industry.

3. Development of additional information concerning specific major pigments and their individual manufacturing processes and wastewater management problems.

SECTION III

INTRODUCTION

This report describes a study of wastewater management practices of the paint manufacturing and inorganic pigments manufacturing industries. The purposes of the study were to identify the sources and characteristics of wastewater in these industries, to determine the wastewater control and treatment practices that are presently employed, and to identify needed improvements in control and treatment technology that would permit these industries to achieve the "best available" control as required by the Water Pollution Control Act of 1972, including, if possible, zero discharge of pollutants.

Although the paint and pigments industries are closely allied in terms of market dependence, the structure of the industries and the manufacturing processes are quite different. In addition, within the inorganic pigments industry the processes employed in the manufacture of titanium dioxide, the most commonly used white pigment, are different from the processes used to manufacture other inorganic pigments. Because of these differences, paint, titanium dioxide, and other inorganic pigments are covered in three separate discussion sections of this report.

Data for this study were obtained from individual manufacturing plants, applications for permits to discharge under the Refuse Act Permit Program, detailed in-plant studies conducted by members of the project staff, and interviews and discussions with industry personnel, trade association committees, and Environmental Protection Agency representatives.

SECTION IV

THE PAINT INDUSTRY

The paint industry (SIC Group 2851) consists of about 1,500 companies with about 1,700 plants. In 1971, total industry employment was about 63,000 and the total number of production workers was about 35,000.[33] Because of the relatively simple technology and low capital investment required, the industry contains many small companies. The distribution of plants by size is given in Table 1.

Table 1. DISTRIBUTION OF PAINT PLANTS (SIC 2851) BY SIZE[a]

Size of plant (total number of employees)	Number of plants	Total number of production workers	Value of shipments, millions of dollars
Fewer than 10	710	1,700	104.9
10 to 19	311	2,500	180.3
20 to 49	350	6,100	441.9
50 to 99	171	6,700	512.6
100 to 249	113	9,200	813.4
250 or more	46	10,100	858.4
Totals	1,701	36,300	2,911.5

[a]Reference 4 (1967 data).

About 42% of the plants have fewer than 10 employees. In 1967, these small companies accounted for less than 5% of the industry sales, whereas the four largest companies accounted for about 22% of sales.[4]

Although the industry is spread over a wide geographical area, it is concentrated in heavily industrialized areas. Ten states accounted for about 80% of the value of shipments in 1967.[12] A map illustrating the geographical distribution of the industry is given in Figure 1.

The major products of the industry consist of trade-sales paints, which are primarily off-the-shelf exterior and interior paints for houses and buildings, and industrial finishes sold as custom products to manufacturers of such products as automobiles, aircraft, appliances, furniture, machinery, and metal containers.

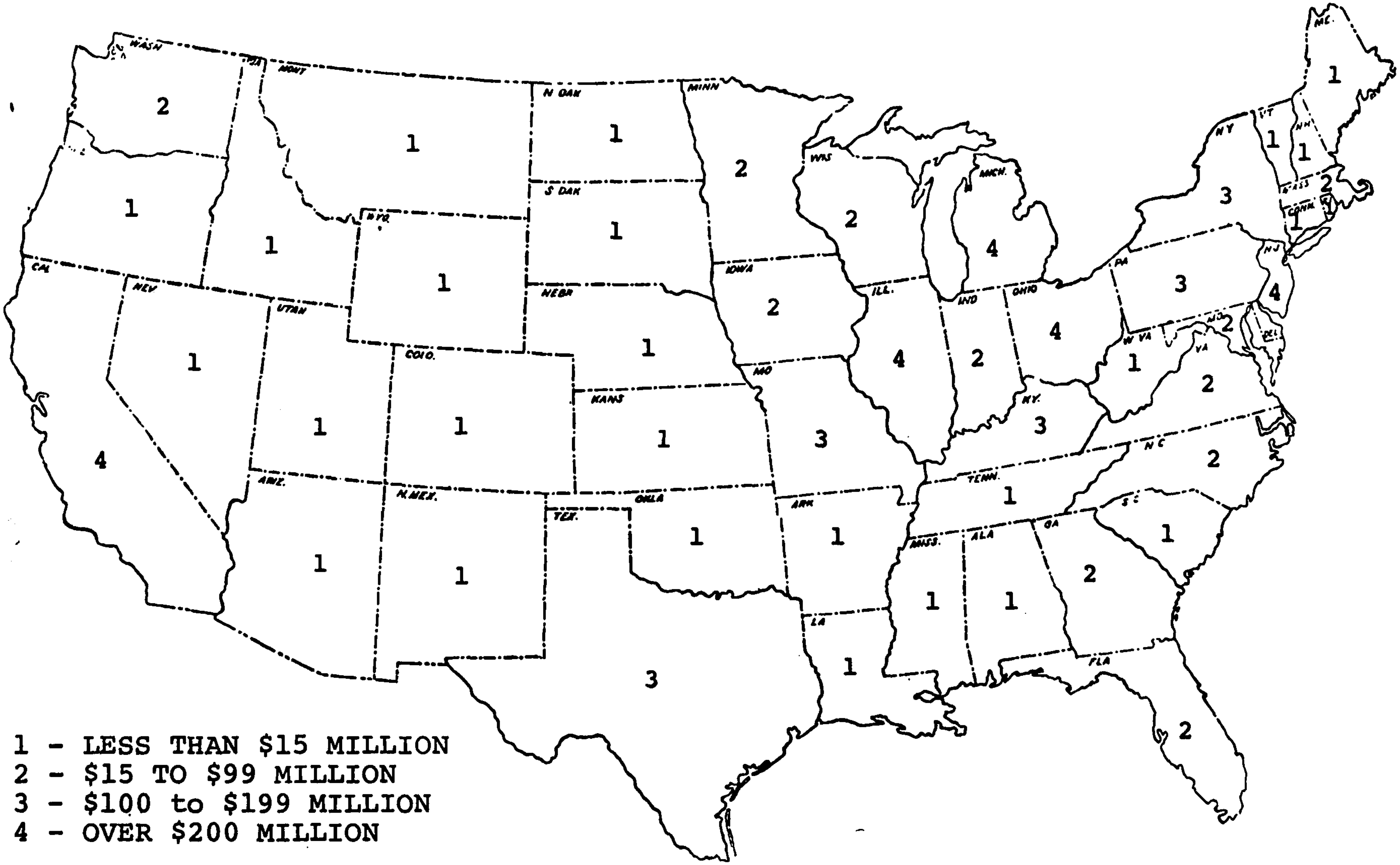

Figure 1. U. S. shipments of paint and allied products by state, 1967[a]

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[a]1967 Census.

In 1971, the value of trade-sales paints amounted to $1,563 million and that of industrial finishes was $1,268 million.[12] Between now and 1980 the value of these products is expected to increase at an average annual rate of 7.5%.[33] The historical and projected growth of these products is illustrated in Figure 2.

PRODUCTS AND RAW MATERIALS

The major products of the paint industry are paints, varnishes, and lacquers, all of which consist of film-forming binders (resins or drying oils) dissolved in volatile organic solvents or dispersed in water. In addition, all paints and most lacquers contain pigments and extenders. The industry also produces putty, caulking compounds, sealants, paint and varnish removers, and thinners, which have been excluded from this study. Some plants produce resins for their internal consumption. The quantity and value of shipments of trade-sales paints in 1971 are shown in Table 2. A breakdown of industrial finishes by type of product is not available.

Table 2. SHIPMENTS OF TRADE-SALES PAINTS, 1971[a]

Type of product	Volume		Value,
	Millions of liters	Millions of gallons	millions of dollars
Water-based paint products	833	220	730
Solvent-based paint products	303	80	340
Stains, varnishes, and other coatings	132	35	145
Other trade sales products	231	61	223
Primers and sealers	76	20	65
Enamels	57	15	60
Totals	1631	431	1563

[a]Reference 12.

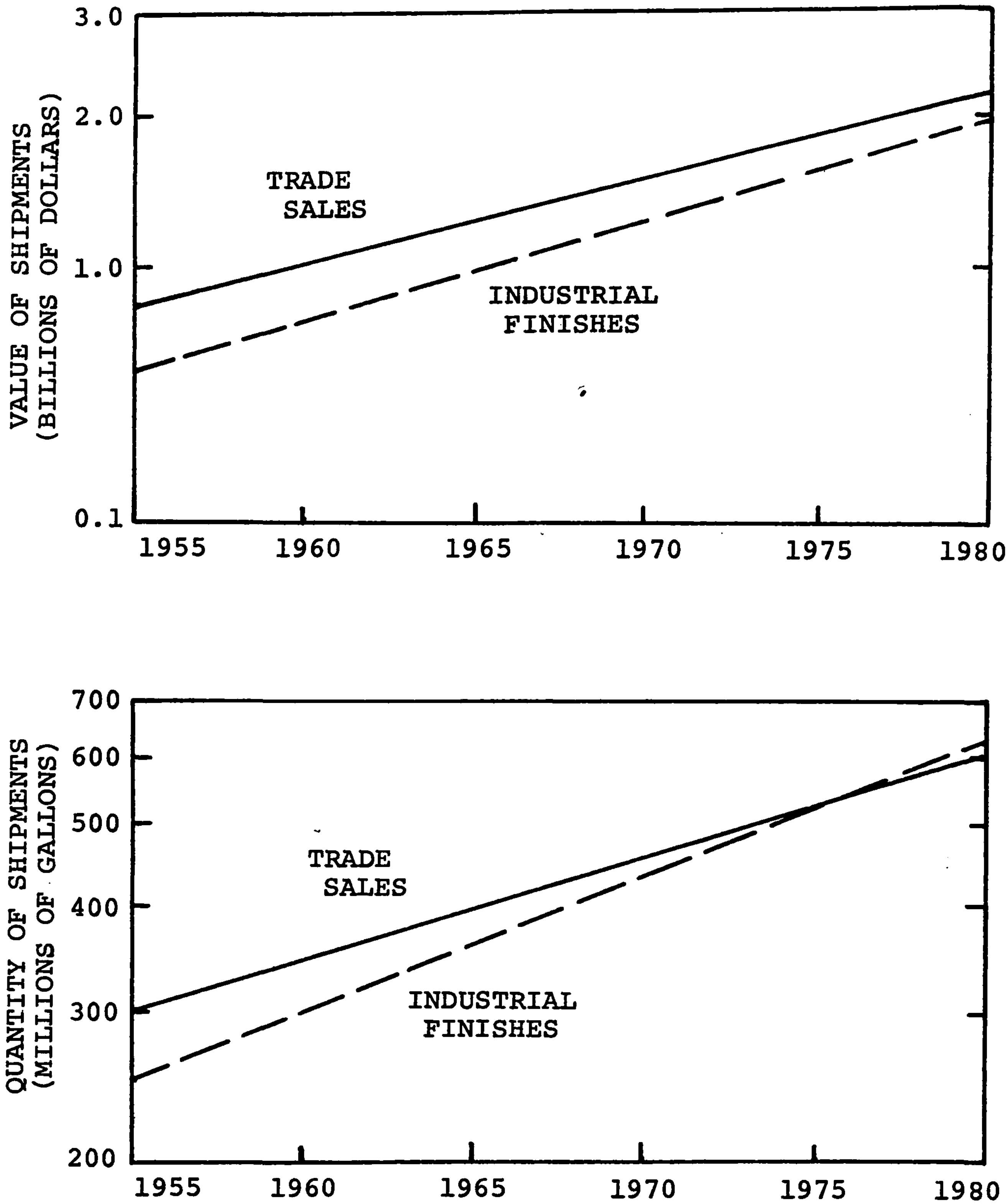

Figure 2. Historical and projected growth of coating products, 1955 to 1980[a]

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[a]Reference 12.

The principal raw materials consumed by the industry are oils, resins, pigments, and solvents. Drying oils, such as linseed oil, are used as the film-forming binder in some oil-based paints. Semi-drying oils, such as soybean oil, are used in the manufacture of alkyd resins, which are the principal binders in all oil-based paints. Acrylic resins are used in the manufacture of water-base (latex) paints. Some industrial water-base paints contain a third type of resin, the water-soluble alkyd resins. Pigments are used to impart opacity and color to the coatings. The pigment particles must be finely divided to provide good dispersibility in the oil or water medium and to provide opacity. The four basic types of pigments are prime white pigments, colored inorganic and organic pigments, filler and extender pigments, and metallic powders. Not surprisingly, the paint industry is the largest consumer of titanium dioxide (55% of total production in 1970) and inorganic pigments (60%).

The paint industry is also a large consumer of solvents, which are used as the volatile vehicles in all coatings except water-base paints. The major solvents used are mineral spirits, toluene, xylene, naphtha, ketones, esters, alcohols, and glycols.

Consumption of the principal raw materials used by the industry is shown in Table 3. In addition, the industry consumes a wide variety of other additives such as driers, bactericides and fungicides, defoamers, antisettling agents, and thickeners.

MANUFACTURING PROCESSES

Paint is manufactured by a batch process in quantities up to 23,000 liters (6,000 gal.) per batch. Most plants manufacture too many different formulations to make continuous processes feasible. There are three major steps in the paint manufacturing process: mixing and grinding of raw materials, tinting and thinning, and filling operations. The flow diagram in Figure 3 illustrates these steps.

At most plants, the mixing and grinding of raw materials is accomplished in one production step. The pigments and a portion of the binder and liquid base or wetting agent are mixed into a paste of a specified consistency. This paste is fed to a grinder or high-speed mixer which disperses the pigments (by breaking down particle aggregates, rather than by reducing the particle size). The pebble or steel-ball mills, or roll-type mills traditionally used for this purpose are generally being replaced by more modern equipment.

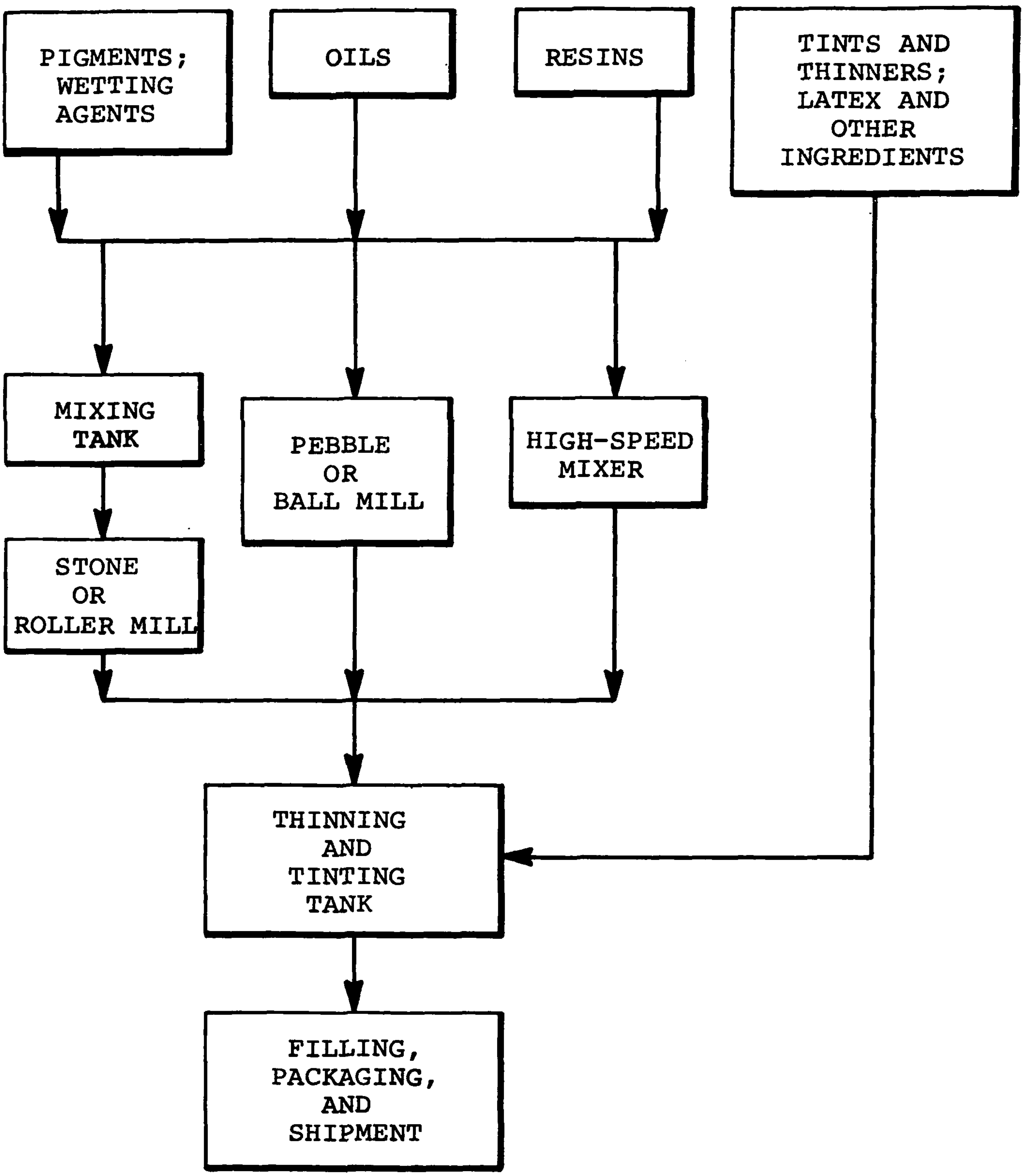

Figure 3. Flow diagram of paint manufacturing process

Table 3. PRINCIPAL RAW MATERIALS USED IN THE MANUFACTURE OF PAINTS, 1970[a]

Raw material	Volume: Thousands of tons	Volume: Thousands of metric tons
Pigments		
Prime white		
Titanium dioxide	360.8	327.4
Zinc oxide	27.0	24.5
White lead	4.0	3.6
Extenders and fillers	333.0	302.0
Red lead	8.0	7.3
Carbon black	7.1	6.4
Oils in paint	133.9	121.5
Oils in paint resins	76.5	69.4
Natural resins	21.0	19.0
Total selected solvents[b]	482.2	437.6

[a]Reference 12.
[b]Includes glycol esters, alcohols, ketones, and esters, but omits mineral spirits (probably the major solvent used), for which data are not available.

In the next stage of production the paint premix is transferred to tinting and thinning tanks, occasionally by means of portable transfer tanks, but more commonly by gravity feed or pump. Here the remaining binder and liquid are added, as well as various additives and tinting colors. The paint is analyzed and the composition is adjusted as necessary to obtain the correct formulation for the type of paint being produced. The finished product is then transferred to a filling operation where it is packaged and labeled.

Some of the larger paint plants manufacture the resins used, either the usual alkyd types or a water-soluble alkyd resin. The manufacture of either type involves the reaction of polybasic acids and polyhydric alcohols to form a condensation product, which may be modified by the addition of various oils or fatty acids. The raw materials are fed into a large reactor (kettle) equipped with an agitator. The kettle is then heated to the specified reaction temperature. Most alkyd resins are manufactured at around 200°C. When the reaction is complete, the resins are filtered and stored for use in paint production or for sale.

WATER USAGE AND WASTE CHARACTERIZATION

The methodology used in obtaining the data on water usage and waste characterization and the significance of the industry sample from which the data were obtained are discussed in Section VII. In most instances, the data were adjusted to reflect differences in coverage of the various size groups in the industry sample. It is recognized, however, that the data may not reflect with complete accuracy the input from plants of different sizes.

On the basis of data sheets on plants representing 26% of the total industry's paint production and 38% of the total industry's production employees, the water usage for the entire industry is estimated at 284 to 310 million liters (75 to 82 million gal.) per day. The principal uses and sources of water are presented in Table 4. For this table, percentages were calculated from the actual data provided in the data sheets representing the sample of the industry described above. As shown in the table, cooling is the largest single use of water, accounting for about 83% of the total usage.

Table 4. WATER USAGE BY SOURCE

Use	Percent of total water used, by source				Total
	Municipal or public supply	Surface water	Well water	Recycle	
Boiler feed	1.9	0.03	1.3	0.5	3.7
Cooling	30.5	21.3	28.6	2.6	83.0
Sanitary	5.2	0	0.3	0	5.6
Cleanup	1.1	0.15	0.2	0	1.4
Consumed in product	1.1	0	0.1	0.01	1.2
Air pollution control	1.2	0	0.8	0.5	2.5
Other	0.3	0	1.0	0	1.3
Unaccounted for	1.3	0.15	0	0	1.4
Totals	42.7	21.5	32.3	3.6	100.1

The major source of water is municipal or public supply, which accounts for about 43% of the total intake. Well water and surface water account for about 21% and 32%, respectively. Only about 4% of the total water used is recycled; however, the reported figures are probably somewhat low because some plants did not include the water used in recirculating cooling systems.

Table 5 shows the distribution of water uses for plants in various size groups. Small plants appear to use much less water per production employee than large plants. For example, plants with fewer than 50 employees have 28.4% of the total industry employees and account for 25% of sales, but use only 4.1% of the total water; plants with 250 or more employees have nearly the same proportion (27.8%) of total industry employees and 30% of sales, but use nearly 70% of the total water. The larger plants use a higher portion of their total water for cooling purposes than do the smaller plants, while the smaller plants use a higher portion for sanitary purposes and for formulation of product.

Disposition of wastewater from the various uses in the paint industry is shown in Table 6. The relative proportions for each use are about the same as shown in Table 4 for uses by source, which indicates consistency in the reported data. Since cooling water normally does not contact the product or raw material, it should not become contaminated if properly handled. On the other hand, water used for cleanup and air pollution control, which accounts for about 4% of the total discharge, necessarily becomes contaminated in use and its use can result in the discharge of pollutants. Thus, although Table 6 shows that about 70% of the total wastewater is discharged untreated, only about 2% (from cleanup and air pollution control, excluding sanitary use) is likely to be contaminated and most of this goes to municipal treatment systems. A somewhat higher level of recycling is shown in Table 6 than in Table 4, and, as discussed above, is probably more consistent with actual industry practice. It is also worth noting that approximately 25% of the industry's wastewater is not discharged, but is disposed of by evaporation, recycling, or by some other method.

The number of plants reporting the discharge of contaminated wastewater is shown in Table 7, which gives the source of contamination for plants of various sizes. Nearly all plants report cleanup water as a source of contamination while only larger plants show other sources, such as air pollution control or process water from resin manufacturing.

Most cleanup waste results from cleaning the equipment used to manufacture water-based paints. The specific kinds of equipment and the amounts of water used are shown in Table 8. The types of equipment most frequently cleaned are filling machines, tinting and thinning tanks, and mixers.

Other sources of wastewater generated in cleanup operations include the washing of equipment used in the preparation of solvent-based paints, resins, and other products. The equipment used to prepare these products is frequently cleaned

Table 5. WATER USES IN PAINT PLANTS BY PLANT SIZE

	Percent, by size of plant (number of employees)						Use, % of total for all size groups
	Fewer than 10	10 to 19	20 to 49	50 to 99	100 to 249	250 or more	
Production employees in size group, % of total	4.7	6.9	16.8	18.5	25.3	27.8	-
Total use, % of total industry usage	0.3	0.6	3.2	6.7	20.4	68.7	100
Uses, % of total for size group:							
Boiler	0	0.7	5	2	8.4	2.5	3.7
Cooling	25	48	74	75	72	87	83
Sanitary	58	16	6	6	7.0	6.2	5.6
Cleanup	3	4	1.2	1.7	1.5	1.4	1.5
Consumed in product	11	14	2	4	1.2	0.7	1.2
Air pollution control	0	2	1.6	1.1	3.2	2.4	2.5
Other	0.6	12	0.8	0.5	5.2	0.01	1.3
Unspecified	2.3	3.3	9.4	9.7	1.6	-	1.2

Table 6. DISPOSITION OF WASTEWATER IN PAINT PLANTS

Use	Total use, as % of total wastewater	Disposition, percent of use						
		Discharged				Not discharged		
		Untreated		Treated				
		To sanitary sewer	To surface receiving body	To sanitary sewer	Other	Evaporated	Recycled	Other[a]
Boiler feed	3.4	34.2	39.4	0.8	0	8.6	14.2	2.8
Cooling	79.0	20.5	56.7	0.1	0.4	0.3	4.1	17.9
Sanitary	6.5	95.0	0	0	0	2.9	0	2.1
Cleanup	1.5	47.2	0.3	30.7	0.3	12.3	2.5	6.7
Air pollution control	2.5	39.1	3.7	19.2	0	0.6	14.4	23.1
Other	1.4	0.3	2.3	17.0	0	2.6	0	77.7
Unaccounted for	5.7	0.7	0	0	0	1.3	3.2	0
Total disposition as % of total wastewater	100.0	26.9	46.1	1.3	0.3	4.2	11.8	9.4

[a]Includes landfill, hauling, incineration, septic tanks, etc.

Table 7. PAINT PLANTS REPORTING DISCHARGE OF CONTAMINATED WASTEWATER

	Number of plants, by size (number of employees)						Total
	Fewer than 10	10 to 19	20 to 49	50 to 99	100 to 249	250 or more	
Number of plants reporting	12	15	11	13	19	18	89
Source of contamination:							
Cleanup	12	15	11	8	17	16	80
Air pollution control	-	1	2	7	9	11	30
Resin manufacturing	-	-	-	2	1	5	8
Intake water treatment backwash	-	-	-	1	1	-	2

Table 8. WASTEWATER GENERATED BY PROCESS EQUIPMENT IN THE MANUFACTURE OF WATER-BASED PAINTS

Type of equipment	Average unit volume of wastewater per unit volume of product	Number of plants reporting
Feed tanks	0.22	7
Mixers	0.09	21
Mills	0.06	13
Tinting and thinning tanks	0.31	28
Transfer tanks	0.16	4
Filling machines	0.06	35

with solvent. When water is used, it is often as a caustic solution, which requires further treatment (neutralization) prior to discharge.

The total volume of cleanup water discharged for plants of various sizes is shown in Table 9. For small plants—those with fewer than 50 employees—the volume discharged is relatively small, less than 1000 liters (260 gal.) per day. At plants with more than 250 employees, the average volume of cleanup water is about 40,000 liters/day (11,000 gal./day).

Table 9. AVERAGE VOLUME OF CLEANUP WATER DISCHARGED FOR PLANTS OF VARIOUS SIZES

Size of plant (total number of employees)	Number of plants reporting	Cleanup water discharged	
		Liter/day	Gal./day
Fewer than 10	24	292	77
10 to 19	30	769	200
20 to 49	34	983	260
50 to 99	21	4,679	1,200
100 to 249	22	11,957	3,200
250 or more	20	40,490	11,000

Relatively concentrated wastewaters are generated through general plant cleanup (housekeeping), spills, and disposal of off-specification batches, as well as through routine equipment cleanup. It is not possible to estimate accurately the volumes of wastewater arising from these operations. Table 10, however, shows how these wastes are handled in terms of the number of plants reporting the use of a specific disposal method. About half of the plants reported that floor drains do not exist or have been sealed or plugged. In about one-third of the plants that have floor drains the wastes pass to settling tanks prior to discharge, and in about two-thirds of these plants the wastes are discharged directly to sewers without any treatment. Some plants indicated that they have no disposal problems resulting from spills or off-specification batches; some of these plants manufacture no water-based paints. Most other plants dispose of spills and off-specification batches by hauling the wastes to an off-site landfill or, in a few instances, to an incinerator. The hauling is usually done by a contractor. Many plants recover off-specification batches for reuse or sale.

The major contaminants of wastewater reported by 71 plants of various sizes are listed in Table 11. As would be expected, these contaminants, except for caustics used in cleaning, are components of paint. The materials listed most frequently by plants as major contaminants are pigments and latex. The presence of one or both of these materials in the wastewater was reported by about 90% of the 71 plants. Over half of the plants also reported the presence of such materials as oils, resins, driers, and dispersing agents. Only four plants listed solvents as a major contaminant of the wastewater. Eleven plants reported heavy metals and fungicides. However, the presence of heavy metals is probably more extensive than indicated in the table because of varying interpretations of what constitutes a "major" contaminant, and because most pigments and drying agents are likely to contain heavy metals.

Table 10. SUMMARY OF DISPOSITION OF WASTE MATERIALS FROM FLOOR DRAINS, SPILLS, AND OFF-SPECIFICATION BATCHES

Disposition of wastes	Number of plants reporting the indicated disposition of wastes		
	Floor drains	Spills	Off-specification batches
Plants reporting no wastes from these sources	78	24	24
Direct to municipal sewer without treatment	34	10	3
Direct to storm sewer without treatment	10	3	0
Use of settling tanks for preliminary treatment	22	15	2
Use of treatment methods other than or in addition to settling	6	2	0
Direct to septic tanks or evaporation ponds	4	3	0
Off-site disposal to landfill or incinerator	2	80	81
Wastes recovered, reused, or sold	0	9	43

The amount and quality of the waste parameter data reported were so limited that interpretation was difficult. Although 48 (about 30%) plants reported that routine effluent analyses were conducted by plant staff or outside laboratories, only 33 (about 20%) reported any data on the results of the analyses. Of these 33 plants, two gave mercury data only; two gave oil and grease only; and six gave total suspended solids, BOD or COD, and oil and grease. Thirteen plants listed only five or fewer parameters. Only 12 plants listed 10 or more parameters. Several of the analyses reported were on single samples only, and some plants did not indicate either the source of the sample or the frequency of sampling. Of the 33 plants providing some waste parameter data, 19 gave values for total dissolved solids, 23 for total suspended solids,

Table 11. MAJOR CONTAMINANTS IN WASTEWATER DISCHARGES

	Number of plants, by size (number of employees)						Total
	Fewer than 10	10 to 19	20 to 49	50 to 99	100 to 249	250 or more	
Number of plants reporting	12	14	16	7	12	10	71
Major contaminants:							
Pigments	6	9	6	4	8	3	36
Latex	6	6	5	3	5	1	26
Driers and wetting agents	2	1	2	2	5	3	15
Oils	1	2	2	1	3	3	12
Resins	3	4	2	1	0	1	11
Caustics	0	1	0	0	3	4	8
Fungicides (including mercury)	2	0	1	1	1	1	6
Heavy metals (excluding mercury)	0	0	0	1	1	3	5
Solvents	0	0	1	2	1	0	4
Other	3	2	1	6	5	5	22

22 for BOD, 21 for COD, 21 for oil and grease, 25 for one or more of the heavy metals, and lesser numbers gave values for other parameters.

The more complete waste parameter data were supplied generally by the larger plants. Of the 48 plants stating that effluent analyses were conducted routinely, 19 had fewer than 100 employees; nine of these plants supplied some data and 10 supplied no data. Thirteen plants had 100 to 249 employees; ten of these supplied some data and three supplied no data. Sixteen plants had more than 250 employees; 14 supplied data and two did not.

Approximately 100 plants stated that effluent analyses were not conducted routinely. Many of these plants stated that they have no wastewater effluent. Typical reasons given for the absence of effluent discharges were: "consumed in product"; "incinerated and hauled to landfill"; "drummed for commercial disposal"; or, simply, "no wastewater". Comments from other plants that have discharges but conduct no analyses included these: "analyzed by city"; "cooling (or sanitary, or boiler) water only"; "never requested"; "not contaminated"; and "no contaminants other than pigments". Several plants stated that they were planning, or had just begun, a systematic program of analysis.

The waste parameter data acquired in this project are insufficient for making any accurate estimates of the paint industry's total waste loadings. The best estimates that can be made with the data available are given in Table 12. These data were taken from information supplied by nine plants. Most of the data represent the raw waste characteristics of combined effluents; thus, calculations of the waste loadings in relation to production of particular products—such as water-based paints or resins, for example—were not possible. The loadings are therefore expressed in kg/day or g/day, rather than in the preferred units of weight per unit of product. Although 68 plants (see Table 13) reported that all or part of their wastewater was subjected to some degree of treatment in the plant, only about 20 plants reported data on treated effluents. Most of these effluents were from cleanup operations. However, no meaningful conclusions could be drawn from the analyses of treated effluents because of the limited amount of data presented and because too few plants used the same treatment methods.

As indicated in Table 12, suspended solids, primarily from pigments and resin particles, is the most significant parameter. The next highest parameter is dissolved solids. However, the high loading of dissolved solids is not readily explainable in terms of the ingredients used in paint or the soluble constituents shown in the table that would constitute the dissolved solids. A substantial portion of the dissolved solids may, however, be derived from once-through cooling water. Loadings of BOD and COD, principally from biodegradable oils, resins, and solvents, are not as high as those of suspended and dissolved solids. While oil and grease contents appear high, it should be noted that the standard test gives erroneously high results for oil and grease in the effluents from this industry because resin particles that are present are at least partially extracted by the solvent used in the test. The relatively high loadings of metals are due principally to the pigments, drying agents, and preservatives. Mercury is still present in some preservatives, although the industry is attempting to replace mercury biocides when possible. In addition to lead and zinc, shown in the table, some drying agents also contain cobalt and manganese. All of the heavy metals shown in the table, and a number of others, are commonly present in at least trace quantities in inorganic

Table 12. DAILY RAW WASTE LOADING FOR PAINT PLANTS

Parameter	Waste loading, kg/day (or g/day)[a]			Number of plants reporting
	Average	Low	High	
Total dissolved solids	220	9	483	7
Total suspended solids	377	3	3,233	9
Volatile suspended solids	40	15	61	3
Acidity/Alkalinity	17	2	47	5
BOD_5 (acclimated seed)	20	4	77	9
Chemical oxygen demand	28	13	44	6
Total organic carbon	15	6	23	2
Chloride	43	0.4	125	3
Oil and grease	224	0.8	1,327	6
Sulfate	14	0.4	40	3
Sulfide	0.12	<0.02	0.4	3
Organic nitrogen	0.4	-	-	1
Nitrogen, as N	6	0.4	18	4
Ammonia	2	0.02	10	5
Phosphorus	0.2	<0.02	0.5	4
Mercury	0.2	<0.2	0.4	5
Lead	77	24	120	7
Cadmium	8	2	120	6
Chromium	112	10	217	3
Zinc	4,713	28	10,840	5
Iron	2,919	426	9,636	4
Titanium	933	52	1,205	4

[a]The waste loading is in g/day for the seven metals listed.

pigments. The averages shown in the table are not necessarily representative of the industry because of the small number of samples and the wide range of concentrations.

CONTROL AND TREATMENT TECHNOLOGY

The extent of control and treatment technology reported by plants of various sizes is shown in Table 13. About 20% of all plants reported that they generate no wastewater on a routine, daily basis, other than sanitary, non-contact cooling, and boiler blowdown water. Most of the plants generating no wastewater manufacture little or no water-based paint; however, the few of those that do manufacture some water-based products are able to recycle and reuse virtually all cleanup water generated. Most of the plants that either

Table 13. EXTENT OF CONTROL AND TREATMENT PRACTICED IN PAINT PLANTS

	Number and percentage of plants in group reporting, by size (number of employees)												Total	
	Fewer than 10		10 to 19		20 to 49		50 to 99		100 to 249		250 or more			
	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%	No.	%
Plants in group	25	16	29	19	34	22	22	15	22	15	20	13	152	100
Plants generating no wastewater	7	28	5	17	11	33	5	23	2	9	1	5	31	20
Plants controlling all wastewater	6	24	9	30	12	35	4	18	1	5	1	5	33	22
Plants self-treating all wastewater	5	20	10	33	5	15	5	23	10	45	10	50	45	30
Plants partially self-treating or controlling wastewater	2	8	2	7	4	11	5	18	6	27	4	20	23	15
Plants not treating or controlling wastewater	5	20	3	10	2	6	3	14	3	14	4	20	20	13

do not generate wastewater or control all wastewater have fewer than 50 employees. About half of the plants in this size group discharge all of their wastes to municipal sewers.

An additional 22% of the plants, while generating some wastewater, do not discharge wastewater, but control or dispose of it by some nondischarge method.

Of the remaining 58% of the plants that discharge wastewater, 30% treat all wastewater, including spills, 15% control or treat some of their wastewater, and 13% discharge without using any control or treatment. Thus, about 87% of the plants either do not generate any wastewater or are treating or controlling at least some of it.

Table 14 summarizes the treatment and disposal methods employed in plants of various sizes. Sedimentation is the most common treatment method employed, which is to be expected in view of the high level of suspended solids characteristic of the wastewater of this industry. In about half of the plants employing sedimentation, flocculation is also used to increase the effectiveness of removing suspended and some dissolved solids. Neutralization, principally of caustic cleaning solutions, is reported at eight plants. Of the remaining treatment methods, none is widely employed. Off-site disposal, such as landfill, is the most common disposal (nontreatment) method, and is practiced at 32 plants. Reuse of cleanup water in products is practiced at 26 plants. Ten plants evaporate wastewater and three plants use incineration to dispose of specific wastes.

Table 15 is a summary of practices reported as planned or recently initiated for the control or treatment of wastewater. About a third of the plants report reduction of wastewater volume by recycling, or by conservation of water, by the use of high-pressure nozzles for cleaning or other conservation methods. Twenty plants reported current or planned enlargement or improvement of existing treatment facilities, and seven plants reported installation of new treatment facilities where none existed previously. Sedimentation and flocculation continue to be the most common treatment practices being installed, although increased use of chemical treatment and filtration are also reported.

A total of 87 plants reported on the adequacy of treatment facilities. This number is larger than the number of plants reporting treatment facilities, because some respondents interpreted the question as applying to their wastewater management practices. Of these 87, 56 consider their practices adequate, while 14 consider them inadequate. At the remaining 17 plants, the adequacy is unknown, probably because of uncertainties regarding local effluent requirements.

Table 14. WASTEWATER TREATMENT AND DISPOSAL METHODS EMPLOYED IN THE PAINT INDUSTRY

	Number of plants reporting, by size (number of employees)						Total
	Fewer than 10	10 to 19	20 to 49	50 to 99	100 to 249	250 or more	
Treatment method:							
Sedimentation	5	9	5	3	9	8	39
Flocculation	0	3	3	1	5	5	17
Neutralization	0	1	0	2	3	2	8
Flotation	0	1	0	1	1	0	3
Aerated lagoon	1	0	0	0	0	1	2
Filtration	0	1	0	0	1	0	2
Equalization	0	0	0	1	0	0	1
Odor control	0	0	1	0	0	0	1
Activated sludge	0	0	0	0	0	1	1
Chemical treatment	0	1	0	0	0	0	1
Unspecified or other	0	1	1	3	2	2	9
Disposal method:							
Off-site disposal	3	5	7	9	5	3	32
Reused in product	1	8	4	6	1	6	26
Evaporation	4	3	2	0	1	0	10
Incineration	0	0	2	0	0	1	3

Table 15. SUMMARY OF PLANNED OR RECENTLY INITIATED WASTEWATER CONTROL AND TREATMENT PRACTICES

Control practice	Number of plants reporting	Treatment practice	Number of plants reporting
Recycling of water, including reuse of cleanup water	34	Improvement or enlargement of existing facility	20
Reduction of volume of wastewater	12	Treatment methods added or enlarged:	
		Sedimentation	11
Use of high-pressure nozzles for cleaning	6	Flocculation	7
		Chemical treatment	5
		Filtration	4
Elimination of use of mercury compounds	4	Cooling tower	3
		Improved automation	2
		Aeration	1
Segregation of contaminated streams	4	Carbon sorption	1
Removal of floor drains	2	Installations by plants having no previous facility	7
Off-site disposal	2		
Elimination of wet scrubbers	1		

For those plants that reported data on the costs of treatment facilities, the variations are large. A small proportion of the plants account for most of the expenditure. At 27 plants, the capital cost to 1972 ranges from $250 to $800,000, for a total investment of $1,848,650. The projected additional capital cost through 1977 ranges from $300 to $1,500,000 for 17 plants for a total of $1,895,300. Thus, the plants studied will about double their investment in treatment facilities over the next five years. The cost of operating treatment facilities also varies widely, from $75 to $150,000 per year. The operating cost at 27 plants ranges from $0.001 to $4.49 per 1000 liters of wastewater treated. The reported age of treatment facilities indicates that most of the facilities were installed or modified within the last three years, probably to comply with recent local interest in pollution abatement.

The effectiveness of the treatment facilities employed by the paint industry is difficult to judge on the basis of available data. However, the most significant parameter, suspended solids, is amenable to treatment by the conventional sedimentation methods used—if effectively operated. As in other industries, dissolved solids are not treated and no practical treatment methods exist. This probably constitutes the major area that will require development of new technology before "zero discharge" of pollutants can be effected in the paint industry.

EXAMPLES OF PAINT PLANTS EMPLOYING CONTROL AND TREATMENT TECHNOLOGY

In the following section, four plants are discussed to illustrate examples of control and treatment technology employed in the paint industry.

Plant A—Small Plant with No Wastewater Discharge

This plant employs fewer than 50 production workers. The principal products are solvent-based coatings, with water-based products representing only a small portion of the total production.

Only sanitary effluent and non-contact cooling water are discharged to the municipal sewer. Floor drains have been sealed at this plant, and solvents used for cleaning are recovered for reuse. No caustic cleaning is used, and the small amount of wastewater generated in cleanup of equipment used for making water-based paint is drummed and hauled away.

Plant B—Medium-Size Plant Employing Sedimentation for Pre-Treatment of Cleanup Water

This plant employs fewer than 100 production workers and manufactures about 23,000 liters (6,000 gal.) of paint per day, of which about 65% is water-based product.

Non-contact cooling water is discharged directly to surface water bodies without reuse. Wastewater from cleanup operations is pumped from a holding sump to an 11,000 liter (3,000 gal.) tank (formerly used for production), where lime, sodium sulfite, alum, and a polyelectrolyte are added. The wastewater from the tank is pumped to a 53,000 liter (14,000 gal.) two-stage settling pond with about 4 days' retention time before discharge to the sanitary sewer. Sludge is pumped from the pond to an adjacent landfill about every 2 months. This system was designed to precipitate mercury compounds and is reported to be effective. Plans are underway for routing floor drains and runoff from the latex storage area into the treatment system.

Plant C—Large Plant Employing Reuse and Pretreatment of Wastewater in Tank-Form Facilities

This plant employs about 250 production workers, manufactures alkyd and latex resins, and produces a wide range of solvent-based and water-based products. Non-contact cooling water, boiler blowdown, and surface runoff are discharged to surface waters without treatment. Floor drains have been sealed and precautions taken to prevent spills from entering storm drains. Other non-contaminated wastewater is segregated and discharged directly to sanitary sewers.

Wastewater from the paint and resin plants and a tank cleaning station is pumped to an in-plant treatment facility. Sumps are located in each of these areas and collected sludge is removed weekly by a private contractor. Portable collectors are located near each sump to contain overflow in the event of pump failure. Waste from the resin plant consists of spent caustic cleaning solution and wastewater fron condensers. Paint plant waste consists of cleanup water and, occasionally, waste from caustic cleaning of mills. The first wash of filling machines is drummed and reused as make-up water in later batches of similar paint; although mercurials are no longer used, this practice, adopted to eliminate the discharge of mercury compounds, is still used.

The treatment facility consists of a series of tanks surrounded by a dike to contain any spills. Wastewater is pumped to a 19,000 liter (5,000 gal.) tank where it is agitated by a continuous pumping until the volume reaches a specified level. It is then fed to a smaller tank where sulfuric acid and a flocculating agent ($FeSO_4$) are added. Addition of sulfuric acid is controlled by a pH probe. Following these additions, the mixture is pressurized in a smaller tank to dissolve a quantity of air, which is subsequently released in another 19,000 liter (5,000 gal.) tank. In this tank, the resulting froth is skimmed off and the solids settle out. The remaining liquid is discharged into the sanitary sewer after pH measurement and analysis. The system meets the requirements of the local control agency.

Plant D—Large Plant Employing Pretreatment of Wastewater in an Aerated Lagoon System

This plant has more than 250 employees and manufactures resins and water-based paints. Non-contact cooling water, boiler blowdown, and sanitary wastes are discharged directly to the municipal sewer. Wastewater from cleanup operations in the paint plant amounts to 23,000 to 45,000 liters (6,000 to 12,000 gal.) per day. Wastewater from wet scrubbers, tank washing, filtering, and decanter wastes in the resin plant amounts to 38,000 to 113,000 liters (10,000 to 30,000 gal.) per day. The total wastewater from these two sources contains about 900 kg (2,000 lb) per day of suspended solids and has a COD of about 1,800 to 1,700 kg/day (4,000 to 6,000 lb/day).

Paint plant wastes are collected in large tanks where a polyelectrolyte is added. Once the polyelectrolyte is thoroughly mixed with the waste based on the volume needed to flocculate the solids, the mixture is pumped to one of two clarifiers for settling. After settling, the underflow is pumped to a 3,800,000 liter (1,000,000 gal.) sludge drying lagoon. The overflow is sent to a 11,400,000 liter (3,000,000 gal.) three-stage, aerated lagoon where it is mixed with the wastes from the resin plant and the run-off from the yard. The yard is equipped with collection sumps to prevent the run-off from going into the stream. The aerated lagoon is equipped with aerators that reduce the influent COD by approximately 90% during a 20-day retention time. At this plant the influent and effluent are monitored daily.

Effluent discharge to the municipal sewer contains about 45 kg (100 lb) per day of suspended solids and has a COD of about 180 to 230 kg (400 to 500 lb) per day. This system is considered exemplary by the local control agency.

SECTION V

THE TITANIUM DIOXIDE INDUSTRY

There are seven companies with eleven plants currently producing titanium dioxide (TiO_2) in the United States. Total annual capacity in 1972 was 756,000 metric tons (833,000 tons) with planned expansions at three plants expected to bring the annual capacity to 929,000 metric tons (1,024,000 tons) by 1975.[32] The eleven plants and their capacities are listed in Table 16.

The principal market for TiO_2 is in the manufacture of paints and lacquers, which accounts for more than half of consumption. Other markets include paper and paper board, plastics and fibers, rubber, floor coverings, printing inks, and ceramics. Together, these uses accounted for a consumption of about 700,000 metric tons (780,000 tons) in 1972. About 11% of this amount was imported.[32] Thus, production in 1972 is estimated at about 623,000 metric tons (687,000 tons).

PRODUCTS

Titanium dioxide may be made in two crystalline forms—anatase and rutile. Because its index of refraction is higher, the rutile form is preferred in paints where it offers advantages in hiding power and opacity. The anatase form is generally whiter, although advances in the production techniques for making the rutile form have led to improvements in color, which, combined with superior brightness and hiding power, make rutile the preferred form. Anatase is used principally in paper manufacturing where whiteness is important.

MANUFACTURING PROCESSES

There are two basic processes for the manufacture of titanium dioxide—the sulfate process and the chloride process. In the sulfate process, which is outlined in Figure 4, finely ground ore, usually ilmenite (which contains 40 to 65% TiO_2 and 30 to 50% FeO and Fe_2O_3 and smaller amounts of other metal oxides), is digested with concentrated sulfuric acid to convert the ore to the soluble sulfates. Excess iron is

Table 16. DOMESTIC PRODUCTION CAPACITY, TITANIUM DIOXIDE[a]

Company	Capacity, thousands of metric tons (thousands of tons)					
	1972			1975		
	Sulfate	Chloride	Total	Sulfate	Chloride	Total
American Cyanamid Savannah, Georgia	65 (72)	36 (40)	102 (112)	65 (72)	36 (40)	102 (112)
E. I. du Pont de Nemours Antioch, California	0 (0)	25 (27)	25 (27)	0 (0)	25 (27)	25 (27)
E. I. du Pont de Nemours Edgemoor, Delaware	45 (50)	45 (50)	91 (100)	0 (0)	136 (150)	136 (150)
E. I. du Pont de Nemours New Johnsonville, Tennessee	0 (0)	128 (141)	128 (141)	0 (0)	207 (228)	207 (228)
Glidden-Durkee Baltimore, Maryland	50 (55)	23 (25)	73 (80)	50 (55)	23 (25)	73 (80)
Kerr-McGee Hamilton, Mississippi	0 (0)	34 (37)	34 (37)	0 (0)	50 (55)	50 (55)
NL Industries St. Louis, Missouri	104 (115)	0 (0)	104 (115)	104 115	0 (0)	104 (115)
NL Industries Sayreville, New Jersey	113 (124)	0 (0)	113 (124)	113 (124)	33 (36)	145 (160)
New Jersey Zinc Gloucester City, New Jersey	39 (43)	0 (0)	39 (43)	39 (43)	0 (0)	39 (43)
New Jersey Zinc Ashtabula, Ohio	0 (0)	25 (27)	25 (27)	0 (0)	25 (27)	25 (27)
Sherwin Williams Ashtabula, Ohio	0 (0)	25 (27)	25 (27)	0 (0)	25 (27)	25 (27)
Totals	416 (459)	340 (374)	756 (833)	371 (409)	558 (615)	929 (1024)

[a]Reference 32.

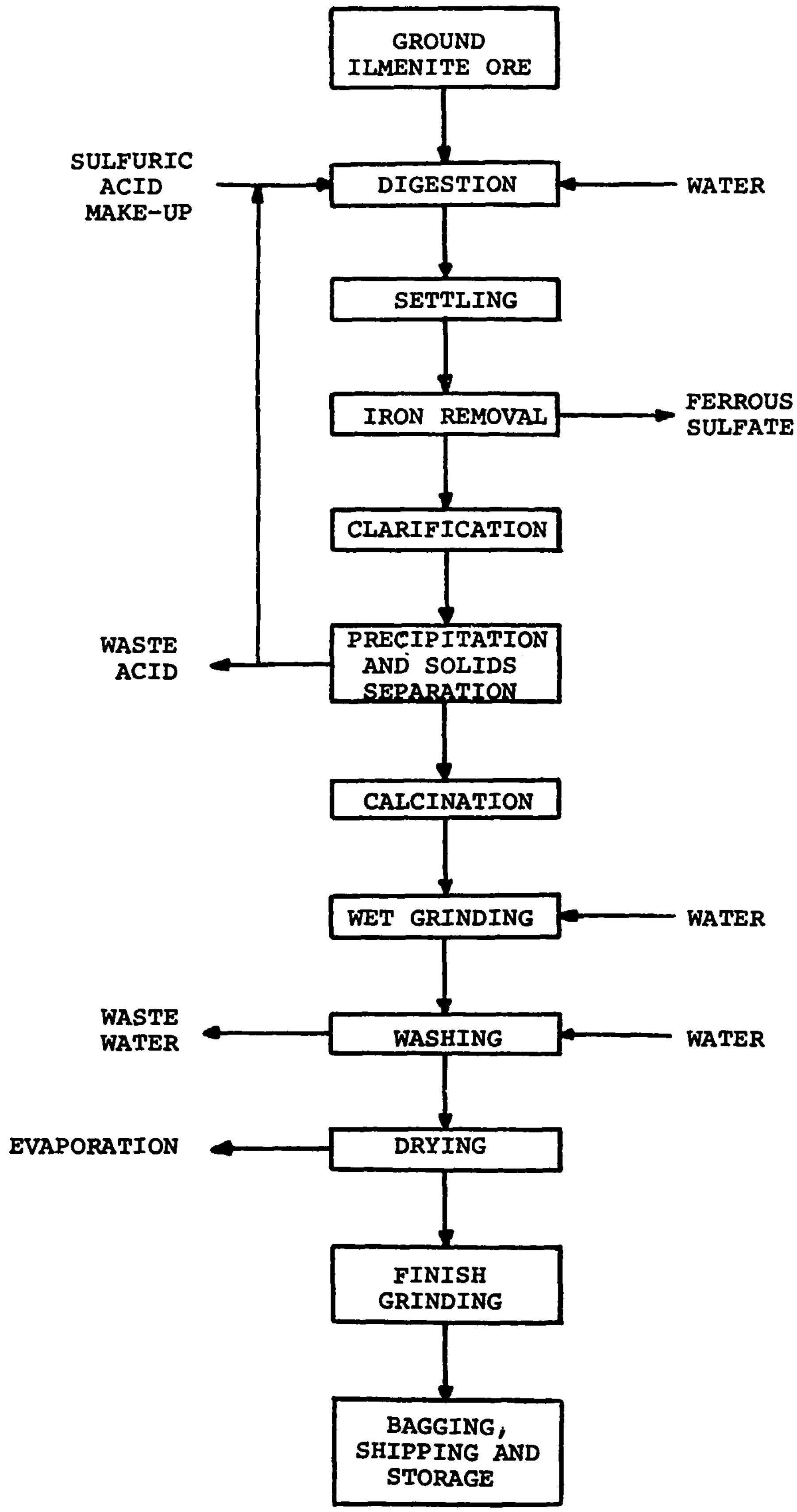

Figure 4. Sulfate process for producing titanium dioxide

introduced to convert a small amount of titanium to the trivalent state and thus prevent later reoxidation of the ferrous iron. The iron salts are removed by vacuum crystallization and the TiO_2 is precipitated after hydrolysis of the $Ti(SO_4)_2$ at an elevated temperature. The precipitate, in the hydrous oxide form, is filtered, washed, dried, and calcined in a rotary kiln where it is converted from the amorphous state to the desired crystalline form.

The chloride process, outlined in Figure 5, requires a raw material of higher TiO_2 content; rutile ore, slag, or beneficiated ilmenite may be used. In this process, liquid titanium tetrachloride, produced by the reaction of ore with gaseous chlorine in the presence of coke, is purified by distillation and oxidized in a flame to TiO_2 which condenses as a fume with the evolution of chlorine.

The TiO_2 that is formed in either process may be given a chemical surface treatment to impart wettability or other properties. This additional treatment involves further filtration, washing, and drying.

The choice of process is dictated by the technology of the company and the availability of raw materials. Although the chloride process is preferred because of its simplicity relative to the sulfate process and the purer, more uniform product, it requires higher-grade ore. Wastewater problems are much greater in the sulfate process, which generates large quantities of ferrous sulfate and spent sulfuric acid. Processes for the beneficiation of ilmenite ore result in a suitable raw material for the chloride process, but the wastewater problems may only be shifted to the beneficiation plant. Presently, the industry is divided on the question of process preference; Du Pont is planning to switch its production to the chloride process, while NL Industries has closed down the chloride process operation at its Sayreville, New Jersey, plant.

WATER USE AND WASTE CHARACTERIZATION

A composite flow sheet of water sources, uses, and waste disposal for a titanium dioxide manufacturing plant representing the overall industry is shown in Figure 6. This composite is based on averages of data reported by seven plants that use a total of 870 million liters (230 million gal.) of water per day. Both sulfate and chloride process plants are included in the seven plants. The data available were not sufficient to prepare separate flow sheets for each process. By far the largest source of water is surface water, which accounts for about 63% of the total water used. Less than 6% of the water

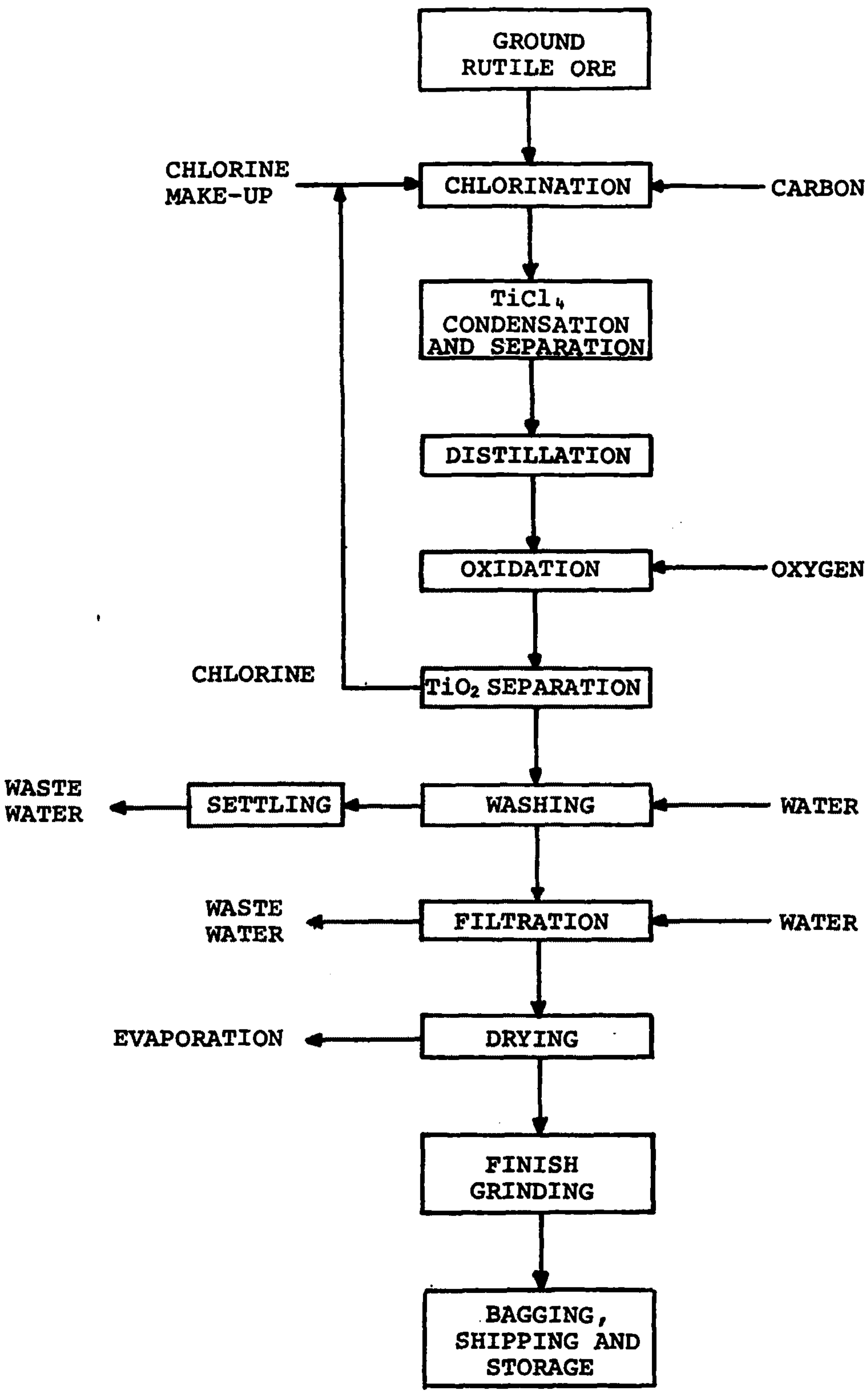

Figure 5. Chloride process for producing titanium dioxide

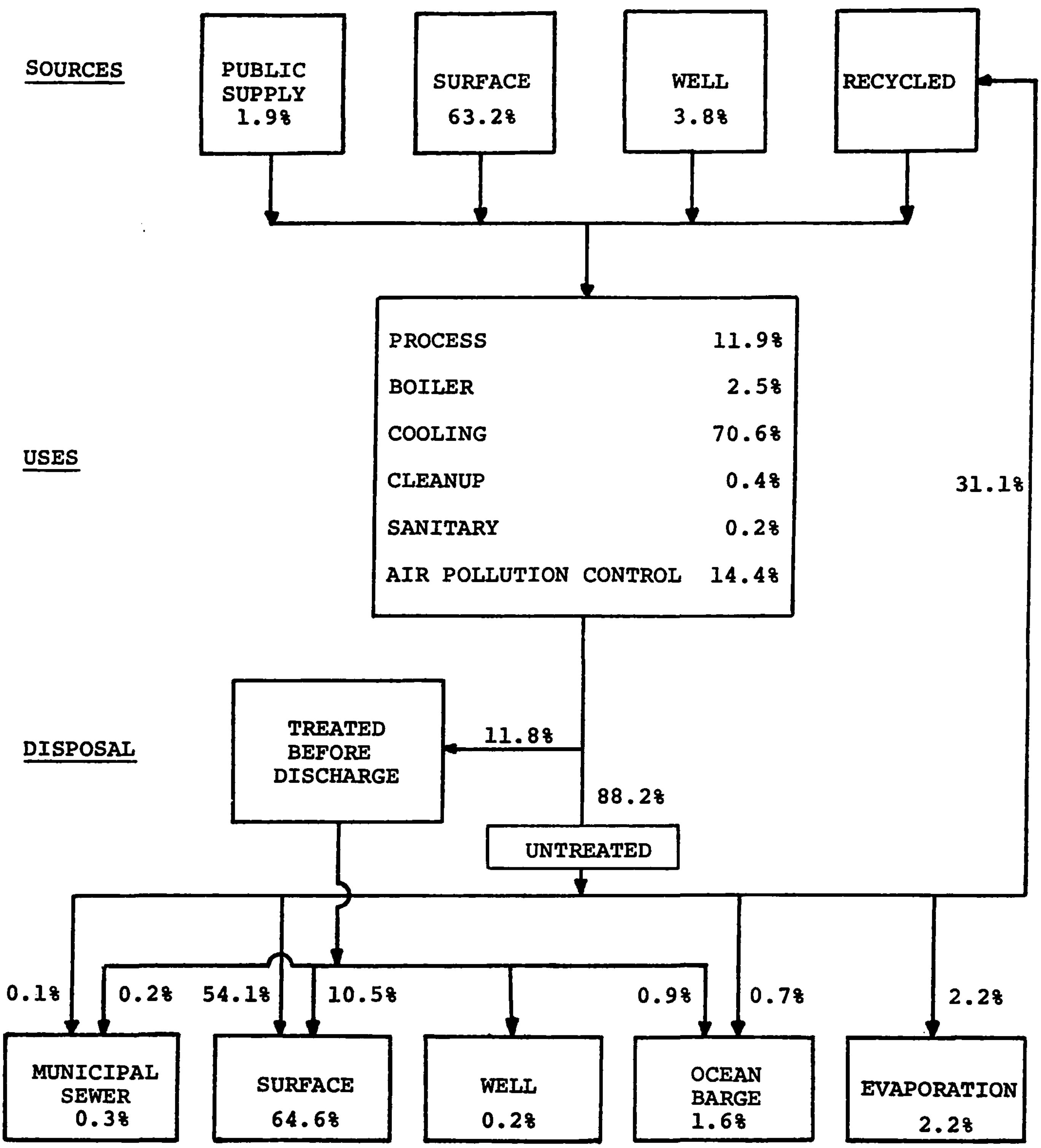

Figure 6. Water data for typical titanium dioxide plant[a]

[a]Composite based on average of seven plants reporting information on data sheets.

used is from wells or public water supplies. The remaining 31% is recycled and is mostly used for cooling, which accounts for 70% of the total water used. Process water accounts for 12%, and 14% is used for air pollution control equipment. The remaining 3% is used for boiler feed, cleanup, and sanitary purposes. In addition to the 31% of the water that is recycled, 4% is disposed of by evaporation, ocean barging, and subsurface disposal. Virtually all of the remaining 65% is presently discharged to surface waters. A total of only 12% of the wastewater is treated prior to discharge.

Although some contamination of water occurs through cleanup, use of air pollution control devices, and some contact cooling, most of the contamination results from process uses. A summary of the volume of process wastewater generated in various operations, the major contaminants introduced in these operations, and the disposition of process wastewater is shown in Table 17 for the sulfate process and Table 18 for the chloride process. As shown in these tables, fewer contaminants and smaller volumes of wastewater are generated in the chloride process than in the sulfate process.

Table 19 summarizes waste discharge data for nine titanium dioxide plants. These data were obtained from both discharge permit applications and data sheets. Four of the plants use the chloride process only, three use the sulfate process only, and two use both processes. It is not feasible to tabulate data for the industry as a whole because of variations in the manner in which data are presented by the different plants and variations in their methods of handling wastes. Three of the plants in this group dispose of part of their wastes in landfills, two discharge part in the ocean by barge transport, and one uses deep-well injection. For six of the plants the data in Table 19 represent the total discharge of plant effluents to streams and to landfill, deep well, or ocean. Parameter data on discharge other than that to streams were lacking for the other three plants; for these three plants, therefore, the data given in the table represent only a part of the total wastes. The treatment of wastes discharged to streams varies considerably, but all of the nine plants use sedimentation methods and some use several other treatment methods in addition to sedimentation. Most of these plants reported that their waste disposal systems were in the process of being modified or improved. The parameter loadings in Table 19 were calculated from reported daily average concentrations, discharge flow rates, and annual production rates. It was assumed for the purposes of computation that each plant operated for 350 days during the year.

Table 17. PROCESS WASTEWATER INFORMATION FOR PLANTS PRODUCING TITANIUM DIOXIDE BY THE SULFATE PROCESS

	Digestion/ reduction	Thickening	Separation of iron salts	Concentrating
Discharge, liters/metric ton of product (gal./ton):				
Average	18,000 (4,500)	2,200 (520)	1,900 (450)	10,800 (2,600)
Maximum	67,000 (16,000)	3,000 (720)	2,700 (650)	40,000 (9,700)
Minimum	500 (120)	1,350 (325)	1,000 (250)	1,200 (300)
Number of plants reporting	4	3	2	4
Major contaminants:				
H_2SO_4	+[a]	+	+	+
$FeSO_4$		+	+	+
Other SO_4 salts				
SO_2	+			
TiO_2				
Ore/gangue	+	+		
Method of disposal of waste:				
Surface	+[a]	+	+	+
Ocean barging		+	+	+
Evaporation	+			
Landfill		+		
Number of plants treating wastes prior to discharge	1	2	1	0

[a]"+" indicates presence of indicated major contaminant or use of indicated method of disposal.

(Continued)

Table 17 (Continued). PROCESS WASTEWATER INFORMATION FOR PLANTS PRODUCING TITANIUM DIOXIDE BY THE SULFATE PROCESS

	Filtering	Washing	Kiln	Thickening/ filtering
Discharge, liters/metric ton of product (gal./ton):				
Average	5,000 (1,200)	34,000 (8,300)	6,200 (1,500)	13,000 (3,300)
Maximum	7,400 (1,800)	70,000 (17,000)	13,000 (3,200)	27,000 (6,500)
Minimum	1,900 (455)	18,000 (4,300)	1,700 (410)	8,100 (1,950)
Number of plants reporting	4	4	4	4
Major contaminants:				
H_2SO_4	+[a]	+	+	+
$FeSO_4$	+	+		
Other SO_4 salts	+			+
SO_2			+	+
TiO_2			+	+
Ore/gangue				
Method of disposal of waste:				
Surface	+[a]	+	+	+
Ocean barging	+	+		
Evaporation			+	+
Sewer			+	
Number of plants treating wastes prior to discharge	2	2	2	3

[a] "+" indicates presence of indicated major contaminant or use of indicated method of disposal.

Table 18. PROCESS WASTEWATER INFORMATION FOR PLANTS PRODUCING TITANIUM DIOXIDE BY THE CHLORIDE PROCESS

	Chlorination	Filtering/ washing	Drying
Discharge, liters/metric ton of product (gal./ton):			
Average	4,200 (1,000)	12,500 (3,000)	3,300 (800)
Maximum	5,000 (1,200)	27,000 (6,480)	5,000 (1,200)
Minimum	2,800 (675)	5,800 (1,400)	1,500 (360)
Number of plants reporting	4	4	2
Major contaminants:			
HCl	+[a]		
$FeCl_x$	+		
Other chloride salts	+		
Other salts		+	
TiO_2		+	+
Method of disposal of waste:			
Surface	+[a]	+	+
Ocean barging	+		
Evaporation	+		
Landfill	+	+	
Number of plants treating wastes prior to discharge	4	4	2

[a]"+" indicates presence of indicated major contaminant or use of indicated method of disposal.

Table 19. WASTE DISCHARGE DATA FOR TITANIUM DIOXIDE PLANTS[a]

Parameter	Waste loading, kg/metric ton of product[b,c]								
	Plant A Cl, SO_4	Plant B SO_4	Plant C[d] Cl, SO_4	Plant D[d] SO_4	Plant E[d] Cl	Plant F Cl	Plant G Cl	Plant H Cl	Plant I Cl, SO_4
Average wastewater discharge, millions of liters/day	112	35.2	135	146	11.0	134	2.8	2.6	109
Total dissolved solids	2,650	2,274	3,720	7,240	601	1,330	175	169	-
Total suspended solids	46	24	53	595	7.1	15	-	0.2	-
Total volatile solids	1,043	-	-	1,060	-	-	-	4.4	-
Acidity/alkalinity	1,652	-	-	20	15	-	-	2.2	-
BOD_5	4.6	0.6	0	2.1	0.6	-	-	<0.4	-
COD	40	26	28	-	9.1	-	-	1.1	-
Oil and grease	3.3	0	0	-	<0.1	-	-	-	1.0
Total organic carbon	1.5	-	-	2.2	3.5	-	-	0.6	2.0
Total organic nitrogen	1.0	1.3	0	1.4	0.3	-	-	0.01	0.6
Ammonia, as N	0.4	7.7	0	<0.1	0.7	-	-	<0.01	-
Chloride	316	13	35	3,540	453	877	181	47	853
Fluoride	-	-	-	-	0.2	-	-	0.05	0.2
Nitrate	-	-	-	-	-	-	-	0.05	-
Sulfate	484	980	3,170	205	32	26	35	16	486
Sulfide	-	-	1.0	<0.08	0.008	-	-	<0.02	0
Phosphorus, total	0.2	0.5	0.06	0.05	0.2	-	-	0.002	-
Iron	449	656	192	7	0.05	330	27	11	144
Titanium	26	19	40	0.9	9.8	-	1.4	<0.02	25
Antimony	300	-	-	-	-	-	-	20	-
Arsenic	-	-	-	-	-	-	-	10	20
Cadmium	3	0	-	<1	<0.6	-	-	<2	0
Chromium	440	1,100	1,900	30	50	-	0.2	1,800	800
Lead	150	0	200	<0.3	3	-	-	<0.4	0
Manganese	14,000	-	-	-	-	-	-	0.4	4,000
Mercury	0.04	0	0	<0.3	<0.1	-	0.02	<0.02	0
Nickel	-	-	-	-	10	-	1	-	90
Selenium	500	-	-	-	<0.6	-	-	-	-
Zinc	600	1,100	600	40	3	-	-	2,100	700

[a] Data from Corps of Engineers discharge permit applications and data sheets.
[b] A zero indicates that the constituent was reported as "absent" or "not detected"; a dash indicates that no information was reported on the concentration of the constituent.
[c] Waste loadings for the ten metals listed in the lower part of the table are in g/metric ton of product.
[d] Plants C, D, and E dispose of part of their wastes by methods other than discharge to streams, but did not provide data on these disposal methods. The data given for these plants represent only discharges to streams.

Total solids, almost all in the form of dissolved solids, is the most significant parameter for both processes. The pH of discharged process water ranges from 3 to 7.5. Since the raw materials used in the sulfate process contain up to 50% of impurities that are removed in the digestion with sulfuric acid, all of the other parameters are explainable as by-products of these impurities and sulfuric acid. In the chloride process higher-grade raw materials are used, and this fact is reflected by lower loadings. In addition to process waste, the industry discharges a large volume of cooling water at an elevated temperature that must be considered as part of the overall environmental problem. Some cooling water is also used for contact cooling and therefore becomes contaminated.

CONTROL AND TREATMENT TECHNOLOGY

Waste abatement practices currently employed in the industry include disposal of some process wastes, particularly iron sulfate and sulfuric acid, by ocean barging, deep-well disposal, and landfill. In-plant control measures consist of recycling and reuse of wastewater, reuse of sulfuric acid, segregation and concentration of waste streams, and, more recently, process and raw material changes designed to reduce the waste loading. Reuse of sulfuric acid appears to be limited to one plant, which recovers "some of the dilute sulfuric acid".

All seven plants reporting information on wastewater treatment facilities employ sedimentation to reduce suspended solids. Three of these plants use flocculation to increase the effectiveness of sedimentation, and two also employ filtration. In view of the relatively low level of suspended solids in the discharge reported by the industry (Table 19), these methods appear to be effective for removal of suspended solids.

Neutralization of acidic wastes is practiced at four of the seven plants and planned at one other, and one plant employs an additional, unspecified chemical treatment before final discharge. The treatment methods employed by these plants are considered adequate by three, inadequate by three, and unknown by one plant.

The reported investment and operating costs of the treatment facilities, including cost of sludge disposal, ocean barging, and deep-well injection, are summarized in Table 20. Significantly, the anticipated investment in treatment facilities through 1977 reported by these seven plants is nearly equal to the total investment to date. Five of the seven plants

Table 20. SUMMARY OF WASTE TREATMENT AND DISPOSAL COSTS FOR THE TITANIUM DIOXIDE INDUSTRY

	Cost, millions of dollars				Number of plants reporting
	Total	Average	Low	High	
Capital cost to 1973	21.6	3.1	0.3	9.0	7
Capital cost 1973-1977	18.0	3.0	0.7	7.0	6
Annual operating cost	5.9	0.8	0.2	2.0	6

installed treatment facilities when the plants were constructed; all have been enlarged or modified since 1966, six of them within the last three years.

A number of problems related to the control and treatment of plant effluents are reported by six of the seven plants. These range from unique problems at individual plants, such as difficulty in segregating individual waste streams and controlling spills and runoff, to universal agreement that practical methods for treatment of dissolved solids are not available. Practical alternatives are needed for disposal of wastes currently being ocean barged or deep-well injected. These wastes are especially high in dissolved solids. Considerable development of technology to resolve the problem of dissolved solids, including heavy metals, will be required before "no discharge" of pollutants will be feasible.

One plant is reported to be considering an arrangement with another company for the manufacture of gypsum ($CaSO_4$) from limestone ($CaCO_3$) and waste sulfuric acid. The economics of the process appear to be attractive; however, the process has not yet been commercialized. Operating experience will be required before any judgement may be made as to the practicality of this process. In any case, such an arrangement is dependent on minimum shipping costs for one or both materials. At another plant the recovery of sulfuric acid is being evaluated on a pilot scale with EPA assistance (Project No. S801349). Also, the Bureau of Mines has proposed an alternate beneficiation route that uses coal and sodium borate. No data on commercial feasibility is available for any of these procedures at this time.

SECTION VI

THE INORGANIC PIGMENTS INDUSTRY

The manufacture of inorganic pigments is classified by the Department of Commerce as SIC 2816. The products include titanium-, lead-, and zinc-based white pigments, and colored pigments, mostly chrome- and iron-based. There are about 98 manufacturing establishments in the United States in SIC 2816. This number includes the manufacturers of TiO_2 (11 plants, considered separately in this report); manufacturers of pearl essence and carbon blacks, which are not covered in this study since these pigments are considered organic pigments; and manufacturers of extender pigments, which also are excluded from consideration. In the course of this study, about 30 companies having about 35 plants were identified as manufacturers of prime inorganic pigments. The value of total shipments of all inorganic pigments in SIC 2816 have been estimated at 732 million dollars in 1972, compared to 564 million dollars in 1967.[33] For the inorganic pigments that are included in this study, 1967 shipments were 184 million dollars. Assuming that the ratio of these pigments to the total is the same as for 1967, the 1972 shipments are estimated to have a value of about 240 million dollars.

PRODUCTS AND RAW MATERIALS

Colored inorganic pigments consist of a wide variety of inorganic compounds, principally metal oxides and salts. The principal metals are iron, chromium, cadmium, zinc, copper, antimony, and lead. Restrictions on the use of lead have decreased its use in recent years. Table 21 shows a list of common colored pigments and their chemical composition. Raw materials for the manufacture of colored inorganic pigments include naturally-occurring ores, acids, salts, and oxides, as well as metal-organic compounds such as lead acetate.

MANUFACTURING PROCESSES

Each pigment is made by a slightly different process. A detailed discussion of the processes involved is beyond the scope of this report. However, the following five major operations are common in the industry: precipitation, filtration and washing, calcining or roasting, quenching, and grinding and milling. These operations are not necessarily all

Table 21. COMMON INORGANIC COLOR PIGMENTS

Red, Maroon, and Brown Pigments	
Natural red iron oxide	Fe_2O_3
Synthetic iron oxide	Fe_2O_3
Burnt sienna	$Fe_2O_3/SiO_2/Al_2O_3$
Red lead	Pb_3O_4
Cadmium red	$CdS/CdSe$
Cuprous oxide	Cu_2O
Raw and burnt umber	Fe_2O_3/MnO_2
Metallic brown	$Fe_2O_3/SiO_2/Al_2O_3$
Yellow and Orange Pigments	
Ocher	$Fe_2O_3/SiO_2/Al_2O_3$
Raw sienna	$Fe_2O_3/SiO_2/Al_2O_3$
Synthetic hydrated yellow iron oxide	$Fe_2O_3 \cdot H_2O$
Chrome yellow	$PbCrO_4$
Chrome orange	$PbO \cdot PbCrO_4$
Molybdenum orange	$PbCrO_4/PbMoO_4$
Zinc yellow	$ZnCrO_4$
Basic zinc chromate	$4Zn(OH)_2 \cdot ZnCrO_4$
Cadmium yellow	$CdS/BaSO_4$
Green Pigments	
Chrome green	$PbCrO_4/Fe(NH_4)[Fe(CN)_6]$
Chromium oxide green	Cr_2O_3
Hydrated chromium oxide	$Cr_2O_3 \cdot 2H_2O$
Blue Pigments	
Iron blue	$Fe(NH_4)[Fe(CN)_6]$
Ultramarine blue	$SiO_2/Al_2O_3/Na_2O/S$
Blue basic lead sulfate	$PbO/PbSO_4/PbS/PbSO_3/C$

used for any one pigment; for example, red lead (Pb_3O_4) is made by calcining finely-ground litharge (PbO) at 482-509°C (900-950°F) for about 24 hr. Further, other pigments may require operations in addition to those listed above.

Precipitation is the operation most commonly involved in the manufacture of synthetic pigments. Usually, the reactants are dissolved in water and the product is precipitated under carefully controlled conditions of temperature and pH. Careful control is necessary to ensure that the desired crystalline form is obtained in maximum yield. Following precipitation, the product is washed to remove excess reactants and soluble by-products.

Calcining may be done for several reasons, including oxidation, dehydration, modification of crystal structure, and chemical reaction. This operation may involve the use of rotary kilns or furnaces, in either the presence or absence of oxygen. Quenching pigments after they are calcined may be done to cool them under controlled conditions and thus to produce the desired crystalline state.

Before packaging and shipment, pigments may be ground to reduce their particle size as required for use. In addition, surface treatments may be given to impart specific properties.

WATER USE AND WASTE CHARACTERIZATION

A flow sheet of water sources, uses, and disposal for inorganic pigment manufacturing plants is shown in Figure 7. This flow sheet is a composite, based on averages of data reported by only six plants. The principal source of water is public supplies, which accounts for 77% of the water used. Surface water and well water account for 19%, and 4% of the water is recycled.

In contrast to titanium dioxide manufacturing, cooling is a relatively minor use of water in this industry, while process uses account for over 50% of the water used. One industry source noted that about 42 liters (11 gal.) of water are used in the precipitation and washing processes to make 1 kg (2.2 lb) of pigment.

About 80% of the wastewater reported by these six plants is treated in some manner before discharge and most of the wastewater discharged, 60%, goes to surface water bodies. Of the 20% that is not treated after use, nearly half, 8.5%, is either recycled or evaporated.

Table 22 shows some of the more significant waste parameter data reported by six plants. The loading of individual waste constituents varies considerably from plant to plant because of the variety of types of pigments manufactured and differences in the methods and extent of treatment used. Some uncertainties are undoubtedly due to the quality and quantity of the analytical data provided. Most of these plants are expanding and improving their waste treatment facilities.

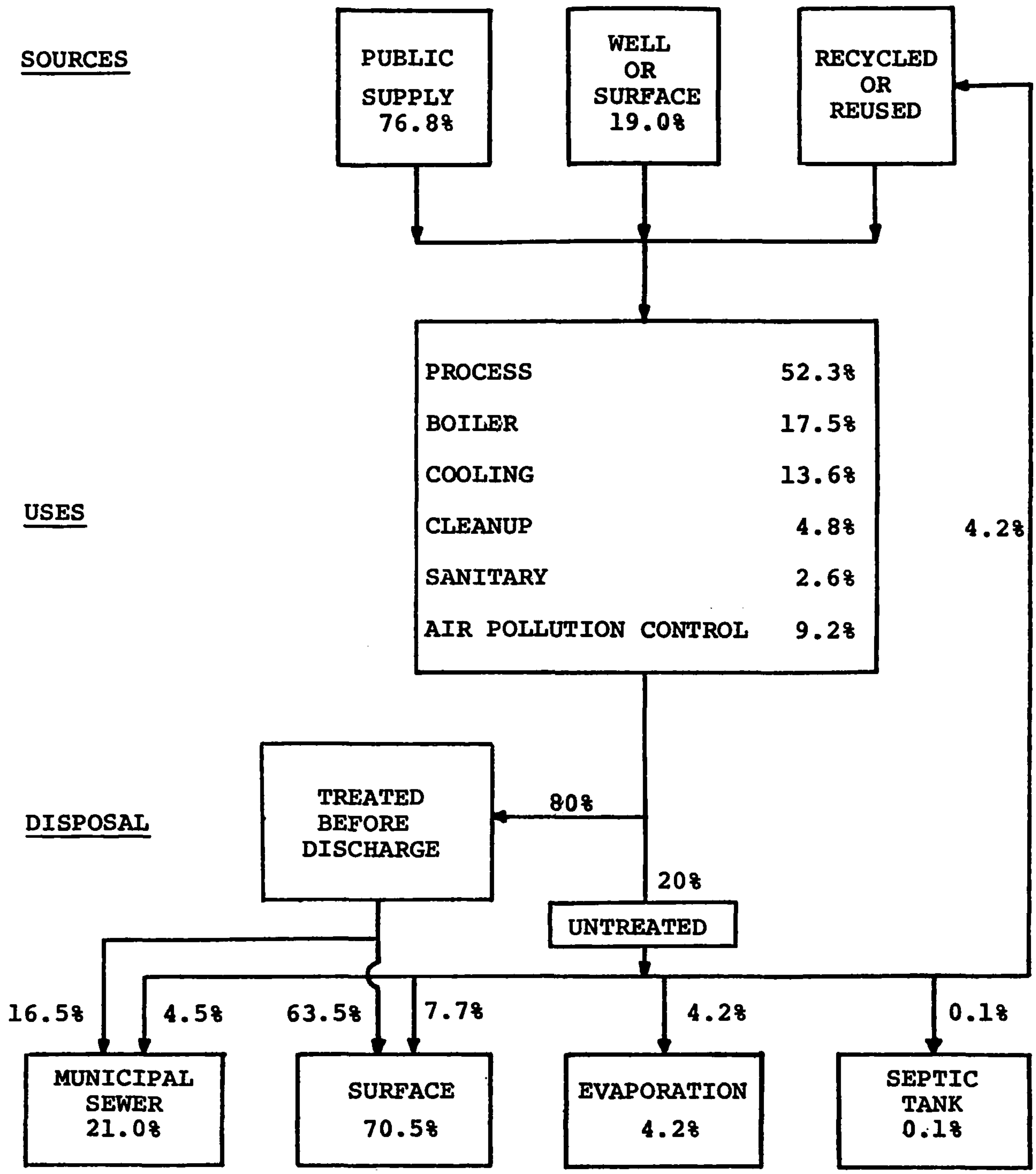

Figure 7. Water data for typical inorganic pigment plant[a]

[a]Composite based on average of six plants reporting information on data sheets.

Table 22. PROCESS WASTE LOADING FOR INORGANIC PIGMENT PLANTS[a]

Parameter	Waste loading, kg/metric ton of product for Plants A-F[b]					
	A Treated	B Combined	C Treated	D Treated	E Untreated	F Treated
Average wastewater discharge, millions of liters/day	0.076	0.048	1.31	4.09	12.1	1.13
Total solids	1.72	5.42	204	0.90	985	820
Total dissolved solids	1.69	5.02	204	1.80	920	820
Total suspended solids	0.026	0.39	-	-	73	3
Total volatile solids	0.92	0.0	-	-	221	7.2
Acidity	-	-	-	-	123	0.09
Alkalinity	0.69	-	3.44	0.79	0.0	-
BOD_5	0.98	-	-	-	66	5.6
COD	1.95	0.029	-	-	118	5.0
Sulfate	-	0.12	49.6	4.32	144	215
Nitrate	0.0002	-	-	-	33	112
Ammonia, as N	0.15	-	-	-	16	0.0
Phosphorus, total	0.0	-	-	-	0.5	0.0
Chloride	0.042	0.0	2.46	-	44	89
Mercury	-	-	-	-	3.6	-
Lead	-	11.2	-	-	15,000	112
Cadmium	-	0.0	-	-	625	-
Chromium	-	3.5	-	-	8,500	67
Zinc	1.27	-	3.11	-	2,100	0.0
Iron	-	3.6	105	0.007	6,700	-
Cobalt	-	0.5	-	-	-	-
Copper	-	-	-	-	1.08	-

[a] These data were taken from Corps of Engineers Discharge Permit Applications.

[b] Waste loadings for the eight metals listed are in g/metric ton of product.

Dissolved solids constitute the most significant parameter in this industry. Since one of the principal production processes is precipitation from solution, a high level of dissolved solids is to be expected because of excess reactants and by-products that are present in filtrate and washwaters. Metals of all kinds, including some of the more toxic ones, are present in significant quantities in process waters.

CONTROL AND TREATMENT TECHNOLOGY

There are three principal problems that must be dealt with in this industry. The most serious is the presence of heavy metals such as chromium and lead. These metals are present both as finely divided suspended solids from filtration and washing operations and as dissolved solids in spent mother liquor. The second problem is the high level of dissolved solids present as by-products from precipitation reactions. These are generally sodium and potassium salts, such as nitrates, chlorides, sulfates, and acetates. The third problem is the presence of suspended solids so finely divided that they pass through the filters used in the process. The varied combinations of finely divided solids and gelatinous metal hydroxides that are sometimes present result in greatly differing settling rates, which make normal sedimentation processes difficult to control.

The treatment technology employed at the five plants listed in Table 22 that treat their wastes consists of neutralization at all five plants; sedimentation at four, combined with flocculation at one; and filtration and chemical treatment at three. These methods are generally used for reduction of suspended solids, control of pH and elimination of heavy metals. The costs of treatment facilities for these five plants are summarized in Table 23.

Table 23. SUMMARY OF WASTE TREATMENT AND DISPOSAL COSTS FOR FIVE INORGANIC PIGMENT PLANTS

	Cost, millions of dollars			
	Total	Average	Low	High
Capital cost to 1973	8.1	1.6	0.1	5.6
Capital cost 1973-1977	3.4	0.68	0.25	2.0
Annual operating cost	0.91	0.18	0.012	0.5

One of the more significant heavy metals is Cr(VI). A common approach to its elimination is the segregation of Cr(VI)-containing solutions, followed by reduction to Cr(III) and precipitation as the hydroxide. Although there are a number of problems associated with this procedure, it is the best one in common use.

One plant is successfully using an ion-exchange process for the recovery of chromates (EPA Project 12020ERM). About 454 kg (1,000 lb) of chromate, formed by regenerating the ion-exchange resins at high pH, is being recovered per day. Eventually, the process is expected to pay for itself on the basis of recovered chromates. This technique should be applicable to other metals, as well.

The removal of suspended solids is accomplished by standard sedimentation processes. The problems of differential and ineffective settling must be resolved before these methods are as effective as in other industries.

At present, as in other industries, effective methods for treating dissolved solids are needed.

SECTION VII

METHODOLOGY

Sources of information used in this study included the following:

- Copies of applications to the Corps of Engineers for permits to discharge under the Refuse Act Permit Program (RAPP) were obtained for 25 paint plants, seven titanium dioxide plants, and ten plants manufacturing other inorganic pigments. These applications provided information on the characteristics of intake and effluent waters, water usage (including flow diagrams in many cases), wastewater treatment and control practices employed, products produced, daily production, and raw materials consumed.

- Data sheets were obtained during the first quarter of 1973 for 153 paint plants, seven titanium dioxide plants, and seven plants manufacturing other inorganic pigments. The nature of the information sought is indicated by the data forms in the Appendix. This information was obtained with the cooperation of the National Paint and Coatings Association and the Dry Color Manufacturers' Association.

- Visits were made to four paint plants, a titanium dioxide plant employing both the sulfate and chloride processes, and two plants manufacturing other inorganic pigments. These visits provided detailed information on water usage, waste characteristics, and control and treatment practices and costs.

- Other sources of information included Environmental Protection Agency technical reports, trade literature, personal and telephone interviews, and meetings with industry personnel and trade association committees.

Coverage of the paint industry from data reported by 153 plants is summarized in Table 24. Indices of industry coverage in different size groups are based on number of plants, number of production workers, and production of coating products. In general, coverage was proportionally higher for plants of increasing size as characterized by number of

Table 24. COVERAGE OF THE PAINT INDUSTRY BY SOUTHERN RESEARCH INSTITUTE DATA BASE

	Size of plant (number of employees)						Total
	Fewer than 10	10 to 19	20 to 49	50 to 99	100 to 249	250 or more	
Total number of plants in size group[a]	710	311	350	171	113	46	1,701
Number of plahts covered	25	30	34	22	22	20	153
Industry coverage, %	3.5	9.6	9.7	12.9	19.9	43.5	9.0
Total number of production employees[a]	1,700	2,500	6,100	6,700	9,200	10,100	36,300
Number of production employees covered	149	433	1,018	1,580	3,371	6,962	13,513
Industry coverage, %	8.8	17.3	16.7	23.6	36.6	68.9	37.2
Production of coating products, millions of gallons per year[a]	2.8	17.0	26.4	43.4	84.8	139.7	314.1
Industry coverage, %	6.4	22.6	14.3	20.4	25.0	39.0	26.0

[a] Based on data reported in 1967 Census of Manufactures, U. S. Department of Commerce. Production reported in census adjusted to 1972.

employees. In tabulating data for the paint industry in this report, adjustments were made to take into account the differences in extent of coverage of the several size groups. The adjustments were made on the basis of the percentage of the industry's plants in each size group that supplied data. The data in Table 24 indicate that the production of coating products was approximately proportional to the percentage of plants covered in each group.

Information was obtained for ten of the eleven titanium dioxide plants to give a coverage of 90% of the plants in that industry.

Of the 35 plants manufacturing other inorganic pigments, RAPP applications were obtained for ten and data sheets for seven plants.

SECTION VIII

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SECTION IX

APPENDIX

FORMS FOR TABULATION OF DATA FROM INDIVIDUAL PLANTS

Plant Identification No.______

WASTEWATER SURVEY OF THE PAINT AND INORGANIC PIGMENTS INDUSTRIES

Data Sheet for Paint Industry

1. Number of production and supervisory employees at this plant....... ______________
2. Average production man-hours per week.............................. ______________
3. Year plant constructed... ______________
4. Year of most recent expansion or major modification of production facilities.. ______________
5. Products produced at this plant (specify lb, gal, etc.)

	Annual production
Water-based paint products....................................	
Solvent-based paint products..................................	
Clear coatings..	
Lacquers..	
Putty, caulking compounds, wood fillers, and sealers..........	
Resins and emulsions..	
Paint and varnish removers....................................	
Other (specify)______________	

6. Principal raw materials consumed at this plant (specify lb, gal, etc.)

	Annual consumption	
	Produced in plant	Purchased
Resins and oils...............		
Solvents......................		
Titanium dioxide..............		
Other inorganic pigments......		
Organic pigments..............		
Latexes.......................		
Fillers, extenders, dryers....		
Other______________ (specify)		

7. Has a Corps of Engineers' permit to discharge into navigable waters been applied for at this plant?

   ☐ Yes ☐ No

8. Have any other water-discharge permits been applied for in compliance with state or local regulations?

   ☐ Yes ☐ No

9. Are the wastewater effluents from this plant routinely analyzed?

   ☐ Yes, by plant staff
   ☐ Yes, by outside laboratory
   ☐ No, not required by disposal method
   ☐ No (specify reason)______________

10. Indicate the amount of water consumed in this plant for each major use by source.

	Amount consumed, gpd					
					Other sources	
Use	Municipal or public	Surface water body	Private well	Recycled from plant	Amount	Source
Boiler feed						
Cooling water						
Sanitary						
Cleanup						
Consumed in product						
Air pollution control						
Other ________ (specify)						
Total						

11. Indicate the amount of untreated wastewater only that is recycled to plant, lost, discharged, or otherwise disposed of for each major use. Specify methods of disposition, if not listed below, i.e., storm sewers, deep well, surface dumping, ocean barging, etc.

	Amount discharged, gpd					
					Other disposal methods	
Use	Municipal sanitary sewer	Surface water body	Evaporation	Recycled to plant	Amount	Method
Boiler feed						
Cooling water						
Sanitary						
Cleanup						
Air pollution control						
Other ________ (specify)						
Total						

12. Indicate for each major use the amount of wastewater treated in-plant prior to discharge. Also indicate amount discharged after treatment, where treated water is discharged (see headings in Question 11), and whether wastewater is analyzed before treatment or discharge.

				Wastewater analyzed	
Use	Amount treated, gpd	Amount discharged, gpd	Specify where discharged	Before treatment	Before discharge
Boiler feed				☐	☐
Cooling water				☐	☐
Sanitary				☐	☐
Cleanup				☐	☐
Air pollution control				☐	☐
Other ________ (specify)				☐	☐
				☐	☐
Total					

13 If wastewaters are not treated or not routinely analyzed, list below the major contaminants known to be present and their source (i.e., cleanup, air pollution control, etc.).

____

____

____

14. For each type of process equipment used, indicate the average size and number of batches produced per day and the total quantity of wastewater, including cleanup or other process water, that becomes contaminated and is discharged. (Do not include water consumed in product.) If different types of products are produced that vary in batch size or in quantity of water used, please use extra spaces provided.

A. Description of products ______________________

Equipment	Typical batch size	Average no. batches/day	Wastewater, gal/batch	Ultimate disposition	Check if treated before discharge
Feed/weigh tanks					☐
Mixers					☐
Mills					☐
Tinting/thinning tanks					☐
Transfer tanks					☐
Filling machines					☐
Other ______ (specify)					☐

B. Description of products ______________________

Equipment	Typical batch size	Average no. batches/day	Wastewater, gal/batch	Ultimate disposition	Check if treated before discharge
Feed/weigh tanks					☐
Mixers					☐
Mills					☐
Tinting/thinning tanks					☐
Transfer tanks					☐
Filling machines					☐
Other ______ (specify)					☐

C. Description of products ______________________

Equipment	Typical batch size	Average no. batches/day	Wastewater, gal/batch	Ultimate disposition	Check if treated before discharge
Feed/weigh tanks					☐
Mixers					☐
Mills					☐
Tinting/thinning tanks					☐
Transfer tanks					☐
Filling machines					☐
Other ______ (specify)					☐

D. Description of products ______________________

Equipment	Typical batch size	Average no. batches/day	Wastewater, gal/batch	Ultimate disposition	Check if treated before discharge
Feed/weigh tanks					☐
Mixers					☐
Mills					☐
Tinting/thinning tanks					☐
Transfer tanks					☐
Filling machines					☐
Other ______ (specify)					☐

15. Please describe any special arrangements or agreements with waste acceptance firms, or public, municipal, or cooperative systems for the disposal or treatment of wastewaters. Describe nature and source of contaminants, and fees and other costs arising from such services.

____

____

____

16. If this plant is equipped with floor drains that receive water from cleanup, spills, leaks, etc., water goes to:

____

17. Describe the disposition of accidental spills, leaks, contaminated runoff, and off-spec batches of material.

____

____

____

18. Describe any special problems related to the treatment of waterborne wastes generated at this plant that make it difficult to comply with existing or anticipated water-effluent regulations.

____

____

____

19. Other than treatment facilities, describe any modifications of operating processes or equipment recently initiated or planned to reduce volume or extent of contamination of wastewater.

____

____

____

20. Provide the following information for any in-plant water-treatment facilities.

Date initial facility installed.. __________

Date of last major addition or modification.............................. __________

Capital cost to date... __________

Additional capital investment projected through 1977...................... __________

Annual operating costs... __________

Design volume, gpd... __________

Average volume of wastes treated, gpd.................................... __________

Method of disposal of sludge, if any____________________________

____

Adequacy of present facility in light of existing operations and regulations

☐ Adequate ☐ Not adequate ☐ Unknown

21. Describe plans for the addition or improvement of treatment facilities________________

____

____

____

____

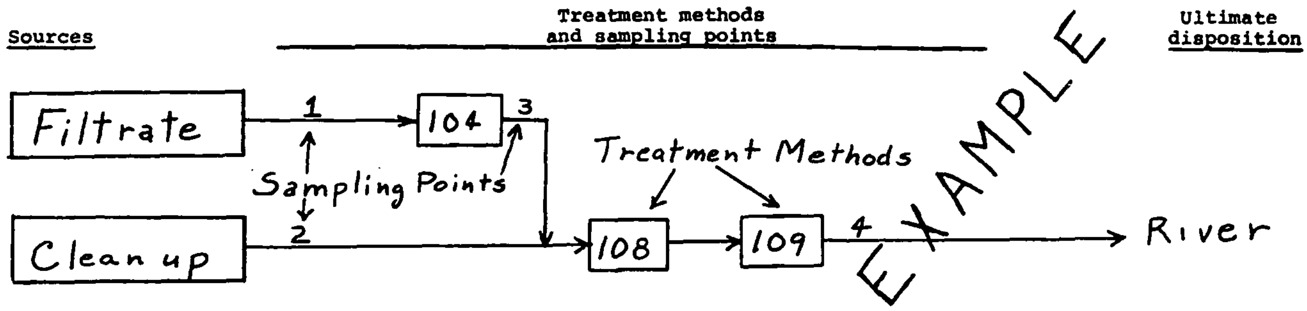
22. Describe below the waste treatment sequence for wastewaters which are treated prior to discharge by using block diagrams similar to the example.

a. Identify source from Questions 12 and 14.

b. Identify treatment with code number as given below.

c. Identify points at which samples are taken for analysis as 1, 2, 3, etc. Do not repeat number.

d. Identify ultimate disposition of treated wastewaters.



Treatment method codes

100.	Equalization	104.	Neutralization	108.	Chemical coagulation or flocculation
101.	Filtration	105.	Odor control	109.	Sedimentation or settling
102.	Flotation	106.	Trickling filter	110.	Digestion of solids
103.	Incineration	107.	Activated sludge	111.	Chemical treatment

112. Aerated lagoon (specify retention time)__________

113. Anaerobic lagoon (specify retention time)__________

114. Other (specify)__________

115. Other (specify)__________

23. For each point in the plant at which water is analyzed, provide the following information on any parameters for which data are available. If sampling point is identified in Question 22, use its identification number, otherwise please describe. Please make facsimile copies, if more are required.

Sampling point________	Sampling point________	Sampling point________
____________________	____________________	____________________
____________________	____________________	____________________
Average flow:______gpd	Average flow:______gpd	Average flow:______gpd
Maximum flow:______gpd	Maximum flow:______gpd	Maximum flow:______gpd

Parameter	Max. concn, mg/l	Daily avg concn, mg/l	Sampling frequency	Max. concn, mg/l	Daily avg concn, mg/l	Sampling frequency	Max. concn, mg/l	Daily avg concn, mg/l	Sampling frequency
pH									
Total dissolved solids									
Total suspended solids									
Volatile suspended solids									
Acidity/Alkalinity									
BOD_5—acclimated seed									
Chemical oxygen demand									
Total organic carbon									
Total oxygen demand									
Oil and grease									
Sulfate									
Sulfide									
Organic nitrogen									
Nitrogen, as N									
Ammonia, as N									
Phosphorus, total									
Chlorides									
Mercury									
Lead									
Cadmium									
Chromium									
Zinc									
Iron									
Titanium									
Other(specify)									

Plant Identification No.______

WASTEWATER SURVEY OF THE PAINT
AND INORGANIC PIGMENTS INDUSTRIES

Data Sheet for Inorganic Pigment Manufacturers

1. Number of production and supervisory employees at this plant....... ____________

2. Average total production man-hours per week........................ ____________

3. Year plant constructed.. ____________

4. Year of most recent expansion or major modification of production facilities.. ____________

5. Products produced at this plant

	Annual production, lb		Annual production, lb
White lead pigments..	______	Cadmium-based pigments...........	______
White zinc pigments..	______	Iron oxide pigments...............	______
Other white pigments.	______	Organic pigments..................	______
Colored lead pigments	______	Other inorganic pigments (specify)	______
Colored zinc pigments	______	______	______
Chrome-based pigments	______	______	______

6. Estimated consumption of products produced at this plant

   For paint manufacturing ____% For ink manufacturing ____% For all other purposes ____%

7. Principal raw materials consumed at this plant

	Annual consumption, lb
Unrefined minerals, ores..	______
Processed minerals, pigments..	______
Acids...	______
Other (specify) ______	______
______	______
______	______
______	______

8. Has a Corps of Engineers' permit to discharge into navigable waters been applied for at this plant?

   ☐ Yes ☐ No

9. Have any other water-discharge permits been applied for in compliance with state or local regulations?

   ☐ Yes ☐ No

10. Are the wastewater effluents from this plant routinely analyzed?

   ☐ Yes, by plant staff

   ☐ Yes, by outside laboratory

   ☐ No, not required by disposal method

   ☐ No (specify reason) ____________

   ____

11. Indicate the amount of water consumed in this plant for each major use by source.

Use	Amount consumed, gpd					
	Municipal or public	Surface water body	Private well	Recycled from plant	Other sources	
					Amount	Source
Boiler feed						
Cooling water						
Process water						
Sanitary						
Cleanup						
Air pollution control						
Other ____ (specify)						
Total						

12. Indicate the amount of untreated wastewater only that is recycled to plant, lost, discharged, or otherwise disposed of for each major use. Specify methods of disposition, if not listed below, i.e., storm sewers, deep well, surface dumping, ocean barging, etc.

Use	Amount discharged, gpd					
	Municipal sanitary sewer	Surface water body	Evaporation	Recycled to plant	Other disposal methods	
					Amount	Method
Boiler feed						
Cooling water						
Process water						
Sanitary						
Cleanup						
Air pollution control						
Other ____ (specify)						
Total						

13. Indicate for each major use the amount of wastewater treated in-plant prior to discharge. Also indicate amount discharged after treatment, where treated water is discharged (see headings in Question 13), and whether wastewater is analyzed before treatment or discharge.

Use	Amount treated, gpd	Amount discharged, gpd	Specify where discharged	Wastewater analyzed	
				Before treatment	Before discharge
Boiler feed				☐	☐
Cooling water				☐	☐
Process water				☐	☐
Sanitary				☐	☐
Cleanup				☐	☐
Air pollution control				☐	☐
Other ____ (specify)				☐	☐
				☐	☐
Total					

14. For each type of process operation used, indicate the average size and number of batches produced per day and the total quantity of wastewater, including cleanup or other process water, that becomes contamined and is discharged. If different types of products are produced that vary in batch size or in quantity of water used, please use extra spaces provided. If typical batch size and average number of batches per day are not appropriate, report water usage in gal/lb of product.

A. Description of products ____________________

Operation	Typical batch size	Average no. batches/day	Wastewater, gal/batch	Ultimate disposition	Check if treated before discharge
Precipitation					☐
Filtration and washing					☐
Calcining					☐
Quenching					☐
Wet grinding					☐
Milling					☐
Other ________ (specify)					☐

B. Description of products ____________________

Operation	Typical batch size	Average no. batches/day	Wastewater, gal/batch	Ultimate disposition	Check if treated before discharge
Precipitation					☐
Filtration and washing					☐
Calcining					☐
Quenching					☐
Wet grinding					☐
Milling					☐
Other ________ (specify)					☐

C. Description of products ____________________

Operation	Typical batch size	Average no. batches/day	Wastewater, gal/batch	Ultimate disposition	Check if treated before discharge
Precipitation					☐
Filtration and washing					☐
Calcining					☐
Quenching					☐
Wet grinding					☐
Milling					☐
Other ________ (specify)					☐

D. Description of products ____________________

Operation	Typical batch size	Average no. batches/day	Wastewater, gal/batch	Ultimate disposition	Check if treated before discharge
Precipitation					☐
Filtration and washing					☐
Calcining					☐
Quenching					☐
Wet grinding					☐
Milling					☐
Other ________ (specify)					☐

15. Please describe any special arrangements or agreements with waste acceptance firms, or public, municipal, or cooperative systems for the disposal or treatment of wastewaters. Describe nature and source of contaminants, and fees and other costs arising from such services.

____

____

____

16. If this plant is equipped with floor drains that receive water from cleanup, spills, leaks, etc., water goes to:

____

17. If wastewaters are not treated or not routinely analyzed, list below the major contaminants known to be present and their source (i.e., cleanup, air pollution control, etc.).

____

____

____

18. Describe any special problems related to the treatment of waterborne wastes generated at this plant that make it difficult to comply with existing or anticipated water-effluent regulations.

____

____

____

19. Other than treatment facilities, describe any modifications of operating processes or equipment recently initiated or planned to reduce volume or extent of contamination of wastewater.

____

____

____

20. Provide the following information for any in-plant water-treatment facilities.

Date initial facility installed.. __________

Date of last major addition or modification................................ __________

Capital cost to date.. __________

Additional capital investment projected through 1977....................... __________

Annual operating costs.. __________

Design volume, gpd.. __________

Average volume of wastes treated, gpd....................................... __________

Method of disposal of sludge, if any____________________

21. Indicate adequacy of present wastewater management practices in light of existing operations and regulations.

☐ Adequate ☐ Not adequate ☐ Unknown

22. Describe plans for the addition or improvement of treatment facilities__________

____

____

____

____

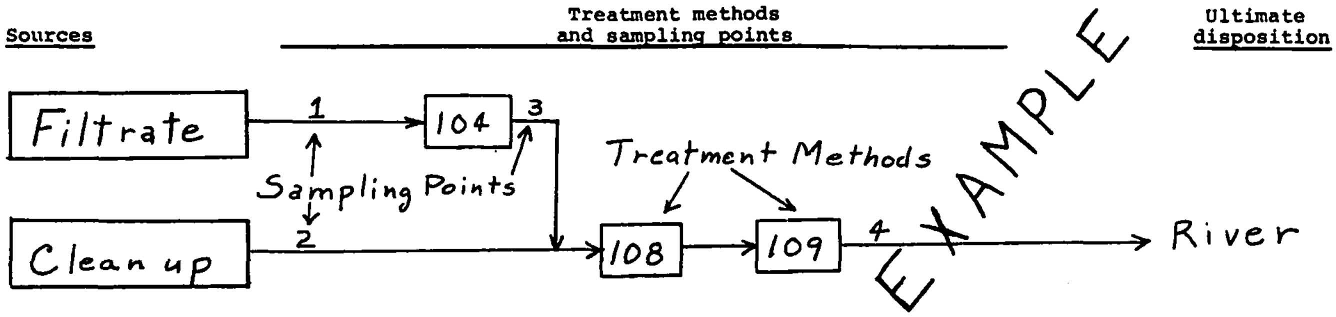
23. Describe below the waste treatment sequence for wastewaters which are treated prior to discharge by using block diagrams similar to the example.

a. Identify source from Questions 13 and 14.

b. Identify treatment with code number as given below.

c. Identify points at which samples are taken for analysis as 1, 2, 3, etc. Do not repeat number.

d. Identify ultimate disposition of treated wastewaters.



Treatment method codes

100. Equalization	104. Neutralization	108. Chemical coagulation or flocculation
101. Filtration	105. Odor control	109. Sedimentation or settling
102. Flotation	106. Trickling filter	110. Digestion of solids
103. Incineration	107. Activated sludge	111. Chemical treatment

112. Aerated lagoon (specify retention time)________

113. Anaerobic lagoon (specify retention time)________

114. Other (specify)________

115. Other (specify)________

24. For each point in the plant at which water is analyzed, provide the following information on any parameters for which data are available. If sampling point is identified in Question 23, use its identification number, otherwise please describe. Please make facsimile copies, if more are required.

Sampling point________	Sampling point________	Sampling point________
____________________	____________________	____________________
____________________	____________________	____________________
Average flow:______gpd	Average flow:______gpd	Average flow:______gpd
Maximum flow:______gpd	Maximum flow:______gpd	Maximum flow:______gpd

Parameter	Max. concn, mg/l	Daily avg concn, mg/l	Sampling frequency	Max. concn, mg/l	Daily avg concn, mg/l	Sampling frequency	Max. concn, mg/l	Daily avg concn, mg/l	Sampling frequency
pH									
Total dissolved solids									
Total suspended solids									
Volatile suspended solids									
Acidity/Alkalinity									
BOD_5—acclimated seed									
Chemical oxygen demand									
Total organic carbon									
Total oxygen demand									
Oil and grease									
Sulfate									
Sulfide									
Organic nitrogen									
Nitrogen, as N									
Ammonia, as N									
Phosphorus, total									
Chlorides									
Mercury									
Lead									
Cadmium									
Chromium									
Zinc									
Iron									
Titanium									
Other (specify)									

Plant Identification No.______

WASTEWATER SURVEY OF THE PAINT
AND INORGANIC PIGMENTS INDUSTRIES

Data Sheet for Titanium Dioxide Manufacturers

1. Number of production and supervisory employees at this plant....... ______
2. Average production man-hours per week.............................. ______
3. Year plant constructed.. ______
4. Year of most recent expansion or major modification of production facilities.. ______
5. Products produced at this plant

	Annual production, tons
Titanium dioxide..	______
Other (specify) ______	______

6. Estimated consumption of products produced at this plant

   For paint manufacturing ____% For paper manufacturing ____% For all other purposes ____%

7. Principal raw materials consumed at this plant

	Annual consumption, tons	
	Produced in plant	Purchased
Ore..........................	______	______
Acids (specify type) ______	______	______
______	______	______
Chlorine.....................	______	______
Mineral additives............	______	______
Other (specify) ______	______	______

8. Type of ore and typical assay (if more convenient, attach ore specification or analysis sheet)

______
______
______

9. Has a Corps of Engineers' permit to discharge into navigable waters been applied for at this plant?

   ☐ Yes ☐ No

10. Have any other water-discharge permits been applied for in compliance with state or local regulations?

   ☐ Yes ☐ No

11. Are the wastewater effluents from this plant routinely analyzed?

   ☐ Yes, by plant staff
   ☐ Yes, by outside laboratory
   ☐ No, not required by disposal method
   ☐ No (specify reason) ______
   ______

12. Indicate the amount of water consumed in this plant for each major use by source.

Use	Amount consumed, gpd: Municipal or public	Surface water body	Private well	Recycled from plant	Other sources: Amount	Other sources: Source
Boiler feed						
Cooling water						
Process water						
Sanitary						
Cleanup						
Air pollution control						
Other ______ (specify)						
______						
Total						

13. Indicate the amount of untreated wastewater only that is recycled to plant, lost, discharged, or otherwise disposed of for each major use. Specify methods of disposition, if not listed below, i.e., *storm sewers, deep well, surface dumping, ocean barging, etc.*

Use	Amount discharged, gpd: Municipal sanitary sewer	Surface water body	Evaporation	Recycled to plant	Other disposal methods: Amount	Other disposal methods: Method
Boiler feed						
Cooling water						
Process water						
Sanitary						
Cleanup						
Air pollution control						
Other ______ (specify)						
______						
Total						

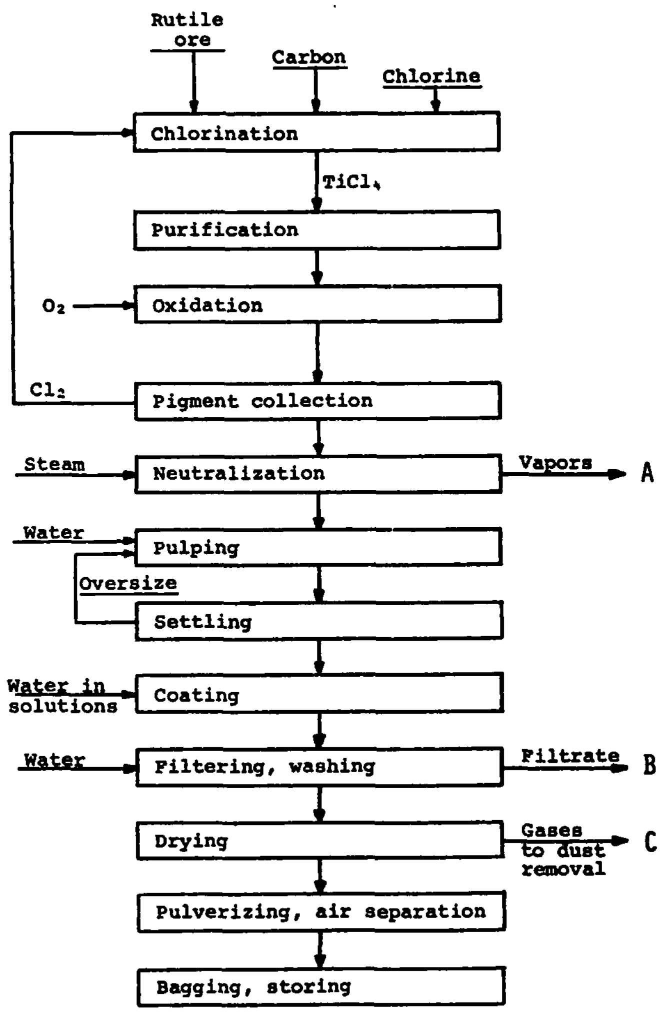
14. Indicate for each major use the amount of wastewater treated in-plant prior to discharge. Also indicate amount discharged after treatment, where treated water is discharged (see headings in Question 13), and whether wastewater is analyzed before treatment or discharge.

Use	Amount treated, gpd	Amount discharged, gpd	Specify where discharged	Wastewater analyzed: Before treatment	Wastewater analyzed: Before discharge
Boiler feed				☐	☐
Cooling water				☐	☐
Process water				☐	☐
Sanitary				☐	☐
Cleanup				☐	☐
Air pollution control				☐	☐
Other ______ (specify)				☐	☐
______				☐	☐
Total					

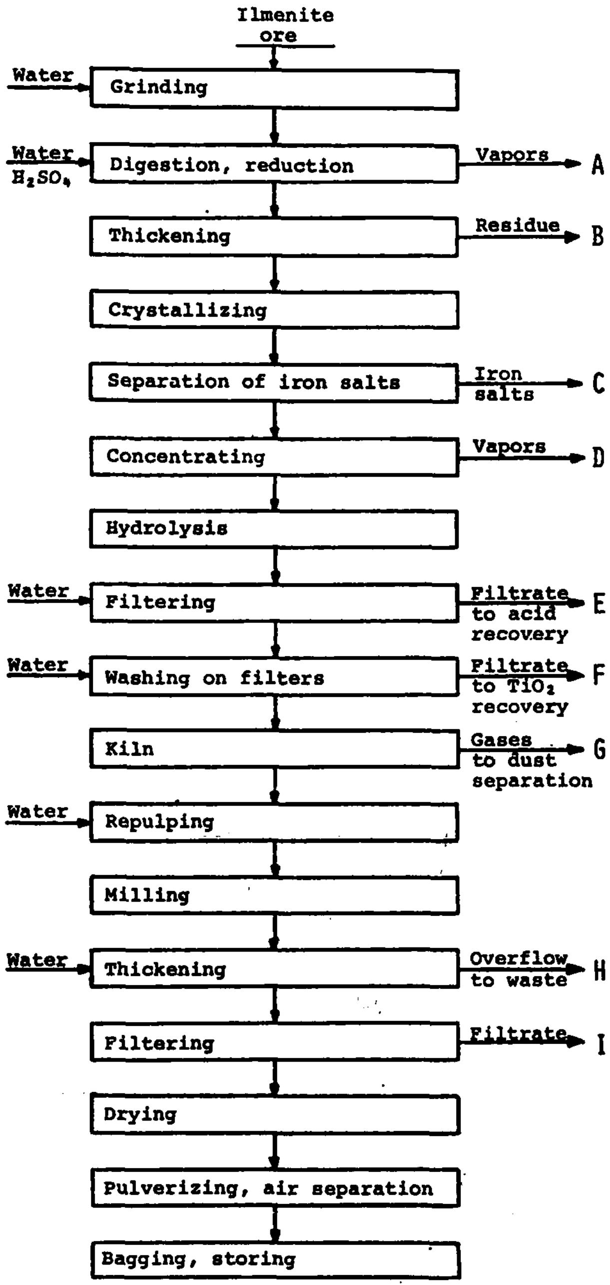
15. Refer to the appropriate diagram below and indicate the quantity, composition, and ultimate disposition of process wastewater at Points A through C for chloride process or Points A through I for sulfate process. Please modify diagram, if necessary.

Point	Flow, gal/ton of product	Major contaminants	Ultimate disposition	Check if treated before discharge
A				☐
B				☐
C				☐
D				☐
E				☐
F				☐
G				☐
H				☐
I				☐

CHLORIDE PROCESS



SULFATE PROCESS



16. Please describe any special arrangements or agreements with waste acceptance firms, or public, municipal, or cooperative systems for the disposal or treatment of wastewaters. Describe nature and source of contaminants, and fees and other costs arising from such services.

____

____

____

17. If this plant is equipped with floor drains that receive water from cleanup, spills, leaks, etc., water goes to:

____

18. Describe the disposition of accidental spills, leaks, contaminated runoff, and off-spec batches of material.

____

____

____

19. Describe any special problems related to the treatment of waterborne wastes generated at this plant that make it difficult to comply with existing or anticipated water-effluent regulations.

____

____

____

20. Other than treatment facilities, describe any modifications of operating processes or equipment recently initiated or planned to reduce volume or extent of contamination of wastewater.

____

____

____

21. Provide the following information for any in-plant water-treatment facilities.

Date initial facility installed.. ____________

Date of last major addition or modification.............................. ____________

Capital cost to date... ____________

Additional capital investment projected through 1977..................... ____________

Annual operating costs... ____________

Design volume, gpd... ____________

Average volume of wastes treated, gpd.................................... ____________

Method of disposal of sludge, if any______________________________

____

Adequacy of present facility in light of existing operations and regulations

☐ Adequate ☐ Not adequate ☐ Unknown

22. Describe plans for the addition or improvement of treatment facilities____________

____

____

____

____

23. Describe below the waste treatment sequence for wastewaters which are treated prior to discharge by using block diagrams similar to the example.

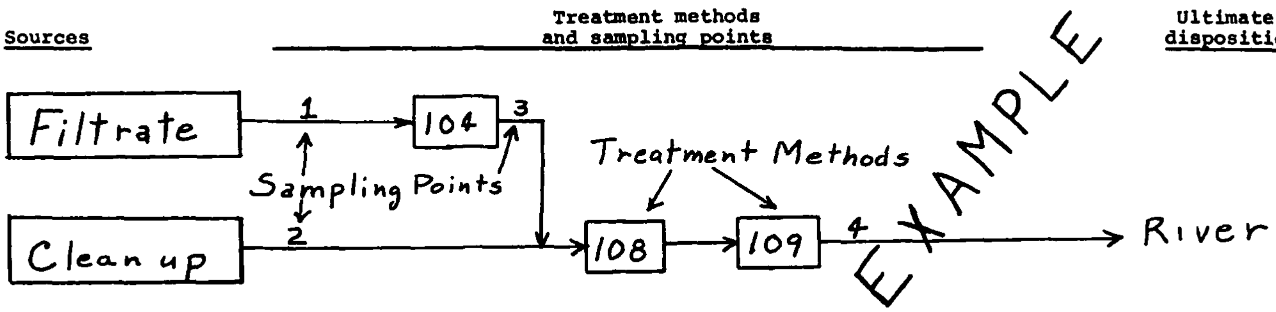
   a. Identify source from Questions 14 and 15.

   b. Identify treatment with code number as given below.

   c. Identify points at which samples are taken for analysis as 1, 2, 3, etc. Do not repeat number.

   d. Identify ultimate disposition of treated wastewaters.

Sources	Treatment methods and sampling points	Ultimate disposition



Treatment method codes

100.	Equalization	104.	Neutralization	108.	Chemical coagulation or flocculation
101.	Filtration	105.	Odor control	109.	Sedimentation or settling
102.	Flotation	106.	Trickling filter	110.	Digestion of solids
103.	Incineration	107.	Activated sludge	111.	Chemical treatment

112. Aerated lagoon (specify retention time)__________

113. Anaerobic lagoon (specify retention time)__________

114. Other (specify)__________

115. Other (specify)__________

24. For each point in the plant at which water is analyzed, provide the following information on any parameters for which data are available. If sampling point is identified in Question 23, use its identification number, otherwise please describe. Please make facsimile copies, if more are required.

	Sampling point________	Sampling point________	Sampling point________
	________________	________________	________________
	________________	________________	________________
	Average flow:_______gpd	Average flow:_______gpd	Average flow:_______gpd
	Maximum flow:_______gpd	Maximum flow:_______gpd	Maximum flow:_______gpd

Parameter	Max. concn, mg/l	Daily avg concn, mg/l	Sampling frequency	Max. concn, mg/l	Daily avg concn, mg/l	Sampling frequency	Max. concn, mg/l	Daily avg concn, mg/l	Sampling frequency
pH									
Total dissolved solids									
Total suspended solids									
Volatile suspended solids									
Acidity/Alkalinity									
BOD_5—acclimated seed									
Chemical oxygen demand									
Total organic carbon									
Total oxygen demand									
Oil and grease									
Sulfate									
Sulfide									
Organic nitrogen									
Nitrogen, as N									
Ammonia, as N									
Phosphorus, total									
Chlorides									
Mercury									
Lead									
Cadmium									
Chromium									
Zinc									
Iron									
Titanium									
Other (specify)									

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

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EPA-670/2-74-030		

4. TITLE AND SUBTITLE	5. REPORT DATE / 6. PERFORMING ORGANIZATION CODE
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7. AUTHOR(S) William J. Barrett, George A. Morneau, and John J. Roden, III	**8. PERFORMING ORGANIZATION REPORT NO.**
9. PERFORMING ORGANIZATION NAME AND ADDRESS Southern Research Institute 2000 Ninth Avenue South Birmingham, Alabama 35205	**10. PROGRAM ELEMENT NO.** 1BB036;ROAP21AZQ;TASK01 **11. CONTRACT/GRANT NO.** R-800602
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15. SUPPLEMENTARY NOTES

16. ABSTRACT

This report describes a study of the wastewater management practices in the paint and inorganic pigments industries. Information was obtained from 153 plants manufacturing paints, 10 titanium dioxide plants, and 10 plants that produce other inorganic pigments. The data were analyzed to identify the sources and characteristics of wastewater from the manufacturing processes of these plants, to determine the practices for wastewater control and treatment that are presently employed, and to identify deficiencies in technology that may require research and development to improve control and treatment methods. The major findings of the study indicate that although the paint industry uses approximately 300 million liters (80 million gal.) of water per day, only a small portion of this, less than 5%, is necessarily contaminated by virtue of its use. Suspended solids, consisting of pigments and resin particles, are the major wastewater contaminants of the paint industry. The wastewaters from plants that produce titanium dioxide or other inorganic pigments generally contain a high level of dissolved solids and acids for which no entirely satisfactory control and treatment methods exist.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Paints, *Pigments, *Titanium dioxide, *Industrial wastes, Waste water, *Waste treatment, Titanium	*Water pollution sources, Waste water disposal, Chemical wastes, Waste water treatment, *Heavy metals, *Colored pigments, *Inorganic pigments, Water pollution control	13B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)* / 20. SECURITY CLASS *(This page)*	21. NO. OF PAGES / 22. PRICE
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