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Project Summary

Wastes from Manufacture of Dyes and Pigments

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A preliminary study of the manufacture of dyes and pigments was conducted to determine if process waste streams might contain hazardous material. The study first identifies the dyes and pigments that belong to the major segments of the industry, the amounts produced, and the known U.S. producers. The chemistry of these dyes and pigments is discussed as well as the overall production process and waste treatment practices. Waste streams that could contain hazardous material are identified and companies that produce representative dyes and pigments are recommended for a sampling program to confirm the composition and amounts of these waste streams.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The Resource Conservation and Recovery Act (RCRA) requires that hazardous solid wastes produced by manufacturing operations be identified and disposed in a manner that limits the release of hazardous materials to the environment. To date, many specific waste streams from manufacturing processes have been listed in regulations as being hazardous because of their chemical composition. The objective of this preliminary study is to help determine if wastes produced by the manufacture of dyes and pigments in the United States might require listing as hazardous materials. An analysis of both the chemistry and the physical processing involved in dye and pigment manufacturing will be used to identify all wastes that may contain significant chemical hazards. An analysis of the industry will be used to determine specific manufacturers where the candidate wastes are produced. This information will help the U.S. Environmental Protection Agency, Office of Solid Wastes, to design a sampling and analysis program to confirm or disprove the presence of hazardous materials in the candidate wastes and thereby develop a basis for listing dye and pigment manufacturing wastes under RCRA. This report summarizes the content of nine reports covering the following dye and pigment classes:

- Volume I: Azo Dyes and Pigments (Benzidine and Its Congeners)
- Volume 2: Azo Dyes and Pigments (Excluding Benzidine and Its Congeners)
- Volume 3: Stilbene Dyes and Fluorescent Brightening Agents
- Volume 4: Anthraquinone Dyes and Pigments
- Volume 5: Diphenylmethane and Triarylmethane Dyes and Pigments
- Volume 6: Methine and Polymethine Dyes and Pigments
- Volume 7: Xanthene Dyes and Pigments
- Volume 8: Phthalocyanine Dyes and Pigments
- Volume 9: Sulfur Dyes

Discussion

Among the commonly recognized structural classes of dyes and pigments, the most important commercially in the United States are the azo dyes and pigments. The 1978 U.S. production of azo dyes and pigments was approximately 41,000 metric tons or about 35% of all U.S. dye and pigment production. These dyes and pigments are characterized by the presence of one or more azo groups—(-N=N-) in the molecule. Consequently, the class can be divided into subclasses (monoazo, disazo, trisazo, tetrakisazo, and polyazo). A special subclass consists of azoic compounds, namely, azoic coupling components, azoic compositions, and azoic diazo components, that are reacted on the fiber to produce azo dyes. The azo dyes and pigments class can also be divided into groups of dyes and pigments produced from one common, structurally related group of starting materials. One such group of starting materials consists of those substituted biphenyls having amine groups in both para positions (i.e., benzidine and related compounds having additional substituents in the two rings). Theoretically, this group can include a very large number of compounds, but commercially significant dyes are produced from only a limited number of compounds.

The stilbene dyes share in common the structural constituent 2,2'-stilbene disulfonic acid. However, the chromophoric system of the stilbene dyes is due to the presence of an azo or azoxy group. Even though the stilbene dyes are a subdivision of the azo class, they are treated as a separate class because they are not prepared by the classical azo coupling reaction. Many fluorescent optical brighteners are also based on stilbene derivatives and these are included in the *Colour Index* (The Society of Dyers and Colourists, 1980) with the stilbene dyes.

According to the U.S. Tariff Commission (1974), the U.S. commercial production of stilbene dyes and brighteners for 1972 was 14,000 metric tons. This represented 12% of the total reported U.S. commercial dye production of 120,000 metric tons for that year. The stilbene dyes and fluorescent brightening agents represented the third largest structural class of dyes based on U.S. commercial production volume. Approximately two-thirds of the stilbene dyes and brighteners production was attributable to the fluorescent brightening agents. Data on U.S. production of dyes by structural class have not been reported since 1972; therefore, it was not possible to determine from public sources whether the relative importance and total production of stilbene dyes and brighteners has changed.

In 1972, production of 21,200 metric tons for all anthraquinone dyes was reported to the U.S. Tariff Commission (1974). This represented 18% of the total reported dye production. Anthraquinone dyes and pigments represented the second largest structural class of dyes based on U.S. production volume. An industry contact indicated that during the last few years U.S. commercial production of anthraquinone dyes has decreased significantly.

The diphenylmethane and triarylmethane dyes and pigments are among the oldest synthetic dyes. They give dyeings of extreme brightness and purity, but their fastness properties, particularly to light, are quite poor. Despite their light fugitiveness, these dyes and pigments are widely used because of their brilliant shades, their extremely high tinctorial values, and their relative low cost. In 1972, production of 4000 metric tons for all triarylmethane dyes (this figure includes diphenylmethane dyes) was reported to the U.S. Tariff Commission (1974). This represents 3.4% of the total reported U.S. dye production of 120,000 metric tons for that year. Diphenylmethane and triarylmethane dyes and pigments represented the fourth largest structural class of dyes based on U.S. production volume. Data on U.S. production by structural class have not been reported since 1972; therefore, it is not possible to determine from public sources whether the relative importance and total production of these dyes and pigments have changed.

In 1972, production of 2,500 metric tons for all methine and polymethine dyes was reported to the U.S. Tariff Commission (1974). This represents 2% of the reported U.S. dye production. Methine and polymethine dyes and pigments represented the fifth largest structural class of dyes based on U.S. production volume. Data on U.S. production by structural class has not been reported since 1972, so it is not possible to determine from public sources whether the relative importance or total production of methine and polymethine dyes and pigments has changed.

The xanthene dyes and pigments are characterized by pure, brilliant hues, by fluorescence, and by a range of colors from yellow to violet. In 1972, production of 530 metric tons for all xanthene dyes was reported to the U.S. Tariff Commission (1974). This represented 0.4% of the total reported U.S. dye production of 120, 000 metric tons for that year. The xanthene dyes and pigments represented the ninth largest structural class of dyes based on U.S. production volume. Data on U.S. production by structural class has not been reported since 1972, so it is not possible to determine from public sources whether the relative importance or total production of xanthene dyes and pigments has changed.

The phthalocyanine dyes and pigments are brilliant and greens that are stable with respect to heat and light, acid, and alkali. They are used in paints, lacquers, inks, plastics, and rubber. For fiber dyeing, the phthalocyanine pigments can be made into temporarily soluble dyes that are subsequently insolubilized on and in fibers. Soluble phthalocyanine pigments precursors can be printed on fiber and cured with heat to form the insoluble pigments. Solubilizing groups such as sulfonates can be added to make direct dyes for paper, cotton, and other textile fibers. Finally, additional chemical modification can add fiber-reactive groups for dyeing cotton.

The U.S. Tariff Commission (1974) reported a total 1972 production of 628 metric tons of phthalocyanine dyes and 6350 metric tons of phthalocyanine pigments. U.S. total production of dyes and pigments by chemical class was not reported for 1979 (U.S. International Trade Commission, 1980), but data from the Organic Dyes and Pigments Data Base prepared by SRI International (USEPA, 1984) shows a total dye production of greater than 491 metric tons and a total pigment production of greater than 8198 metric tons. Thus, pigment production grew substantially (29% minimum) in the seven-year period. If phthalocyanine dye production had grown as much, it would have been 810 metric tons, which would mean that production of phthalocyanine dyes would have increased by 182 metric tons from 1972 to 1979.

Sulfur dyes have been produced commercially for more than 100 years. In spite of this long history and unlike most dyes of other classes that are clearly defined compounds of known structure, the sulfur dyes are, with few exceptions, mixtures of variable and unknown composition. There is disagreement as to what defines a sulfur dye. The early sulfur dyes formed a chemical class in that they were prepared from sulfurization or "thionation" of relatively simple intermediates with either sulfur or sodium polysulfide. They also formed a dyeing class in that, as water-insoluble substances, they were brought into soluble form for dyeing by treatment with a hot solution containing alkali and sodium sulfide. However, some newer dyes synthesized by a thionation procedure but dyed from an alkaline dithionate vat (sodium hydrosulfite vat) in the manner of vat dyes were introduced. Some argued that "sulfur dyes are best defined as those dyes which are applied in a reduced state from solutions containing sodium sulfide, hydrosulfide, or polysulfide and which are subsequently oxidized on the fiber" (Orton, 1963). This definition precluded dyes made by a thionation procedure that were applied as vat dyes. However, in the listing of dyes by classes in the *Colour Index* (1980), the "sulfurized vat dyes" are included in the sulfur dye chemical class. Therefore, we included these dyes in this study.

The total production volume of sulfur dyes is not known. In the mid-1960s, the U.S. production of sulfur dyes ranged from 8100 to 9100 metric tons per year, representing 7% to 8% of total dye production (U.S. Tariff Commission, 1965, 1967, and 1968). The importance of sulfur dyes as a commercial class has declined (Allen, 1971), although they are still in demand because of their moderately good properties and low cost.

Summary and Conclusions

In this preliminary study of dyes and pigments, several waste streams were identified that might contain hazardous materials:

- Discarded shipping containers. These would be paper bags and fiber drums used to transport dye and pigment intermediates and would contain a residual amount of intermediate when emptied.
- Solid residues from process synthesis, distillation, and filtration. These would contain unreacted dye intermediates, reagents, and reaction by-products.
- Filter cake from clarifying operations. This cake could contain dye, unreacted intermediates, solvent, by-products formed in the synthesis of intermediates, metallic catalysts, and other impurities.
- Still bottoms in the production of anthraquinone dyes and pigments from the recovery operations of many of the organic solvents—chlorobenzene, o-dichlorobenzene, acetone, xylene, nitrobenzene, isobutyl alcohol, naphthalene, phenol, and pyridine.
- Gaseous emissions that may contain nitrogen oxides (stilbene dye manufacture); phosgene, formaldehyde, nitrogen oxides and arylamines (diphenylmethane and triarylmethane dye and pigment manufacture); ethylene oxide, formamide, arylamines and chlorinated aromatic solvents (phthalocyanine dye and pigment manufacture); and hydrogen sulfide (sulfur dye manufacture).
- Process wastewater that may contain mother liquor from filtering operations. This is probably the major source of discharge of organic chemicals from most stilbene plants. In phthalocyanine dye and pigment manufacture, organic materials and heavy metals from the various synthesis steps and PCBs may be present. Brines in the manufacture of sulfur dyes contain inorganic sulfur compounds and some organic compounds. Process wastewater from the manufacture of diphenylmethane and triarylmethane dyes and pigments may contain organic materials and heavy metals.
- Wastewater treatment solids. The evidence suggests that the solids will be contaminated with low levels of all of the dye and pigment intermediates as well as the dyes and pigments themselves and some reaction by-products. If these solids are placed in a landfill, intermediates may be released as a result of reduction of the azo linkages under the anaerobic conditions prevailing in the landfill.
- Baghouse fines. The fines are generated during the drying, standardizing, and packaging of the dyes and pigments. The fines will be principally the dyes and pigments and inert salts. Anaerobic conditions in a disposal site could cause intermediates to be released from these fines.

Information on the producers of dyes and pigments and production volume information were analyzed to choose representative production facilities where a sampling program might be conducted to determine the composition of the waste emissions. The following companies are recommended by dye class:

Azo dyes and pigments (exluding benzidine)

American Color and Chemical Corp.
American Cyanamid Co.
Atlantic Chemical Corp.
E. I. Du Pont de Nemours & Co., Inc.
Harshaw Chemical Co.
Toms River Chemical Corp.

Azo dyes and pigments (benzidine and its congeners)

Fabricolor, Inc.
Sterling Drug, Inc., Hilton Davis Chemical Co. Div.
Sun Chemical Corp.
Atlantic Chemical Corp.
Crompton & Knowles Corp.
Toms River Chemical Corp.

Stilbene dyes and fluorescent brightening agents

American Color & Chemical Corp.
American Cyanamid Co.
Ciba-Geigy Corp.
Toms River Chemical Corp.
Mobay Chemical Corp., Dyestuff Div.

Anthraquinone dyes and pigments

Toms River Chemical Corp.
American Color & Chemical Corp.
American Cyanamid Co.
BASF Wyandotte Corp.
Eastman Kodak Co., Tennessee Eastman Div.
Mobay Chemical Corp., Dyes & Chemical Div., Lowell, NC
Crompton & Knowles Corp., Dyes & Chemical Div., Lowell NC

Diphenyl methane and triarylmethane dyes and pigments

American Cyanamid Co.
Dye Specialties, Inc.
H. Kohnstamm & Co., Inc.
Max Marx Color & Chemical Co.
Sterling Drug, Inc., Hilton Davis Chemical Co. Div.

Methine and polymethine dyes and pigments

Atlantic Chemical Corp.
Mobay Chemical Corp.
BASF Wyandotte Corp.
Toms River Chemical Corp.

Xanthene dyes and pigments

Max Marx Color and Chemical Co.
Sun Chemical Corp.
Sterling Drug Inc., Hilton Davis Chemical Co. Div.

Phthalocyanine dyes and pigments

ICI Americas Inc., Chemical Specialties Co.
American Hoechst Corp., Industrial Chemicals Div.

Sun Chemical Corp.

Ciba-Geigy Corp.

American Cyanamid Co. (Marietta, OH, plant)

Toms River Chemical Corp.

Sulfur dyes

Martin-Marietta Corp., Sodyeco Div.

American Cyanamid Co.

Process Chemistry

A discussion of the process steps required to synthesize dyes and pigments will aid in formulating the emission estimates and is found in the reports on each major dye class.

Sources of Waste Discharges During Dye and Pigment Manufacturing

The wide range of dye and pigment production processes and the specific plant characteristics and process control capabilities make estimating material losses during dye manufacture a difficult task. In general, the most significant material losses are intermediates that do not react and by-products such as incomplete dye or pigment molecules. The intermediates and by-products from the dye manufacture are present either in the product or in the solid waste streams regulated under RCRA, which include wastewater, solid residue, and the vapor and dust emissions. The material in the wastewater is discharged in the plant effluent and some is discharged on any wastewater treatment solids.

The sources of wastes from dye manufacture identified in Figure 1 are summarized below:

- Material handling—Air emissions from raw material dusting and volatilization, solid residue on shipping containers, and process wastewaters from equipment washdown.
- Dye syntheses—Air emissions from the volatlization of intermediates and by-products from reaction vessels, solid residuals from distillation residues and spills, and process wastewaters from equipment washdown.
- Product and intermediate filtration—Air emissions from unreacted intermediate and by-product volatilization during material handling, solid residues from spills, and process wastewater from equipment washdown. A significant additional source of process wastewater is the mother liquor when aqueous processes are used.
- Drying—Air emissions from volatilization of by-products and unreacted intermediates in the drying oven, and solid residues from spills and dusting of the product dye.
- Grinding, blending, standardization, and packaging—Solid residues from dusts produced by the grinding operations that may be either in the air streams from vent systems designed to prevent the material from entering the workplace environment or as a solid residue from spills.
- Air pollution control—Solid residues from baghouses or scrubbers collecting fine dusts and process wastewaters from scrubbers.

Each dye producer may have a different wastewater treatment system. Some process wastewaters are discharged directly to sewers and thus to publicly owned treatment works. Some wastewaters are sealed in drums, which are placed in a landfill. Some producers have on-site wastewater treatment plants. All these treatment plants will be site-specific designs with site-specific behavior. Several examples of on-site treatment facilities at dye production sites are discussed to indicate the type of treatment often used and its effectiveness.

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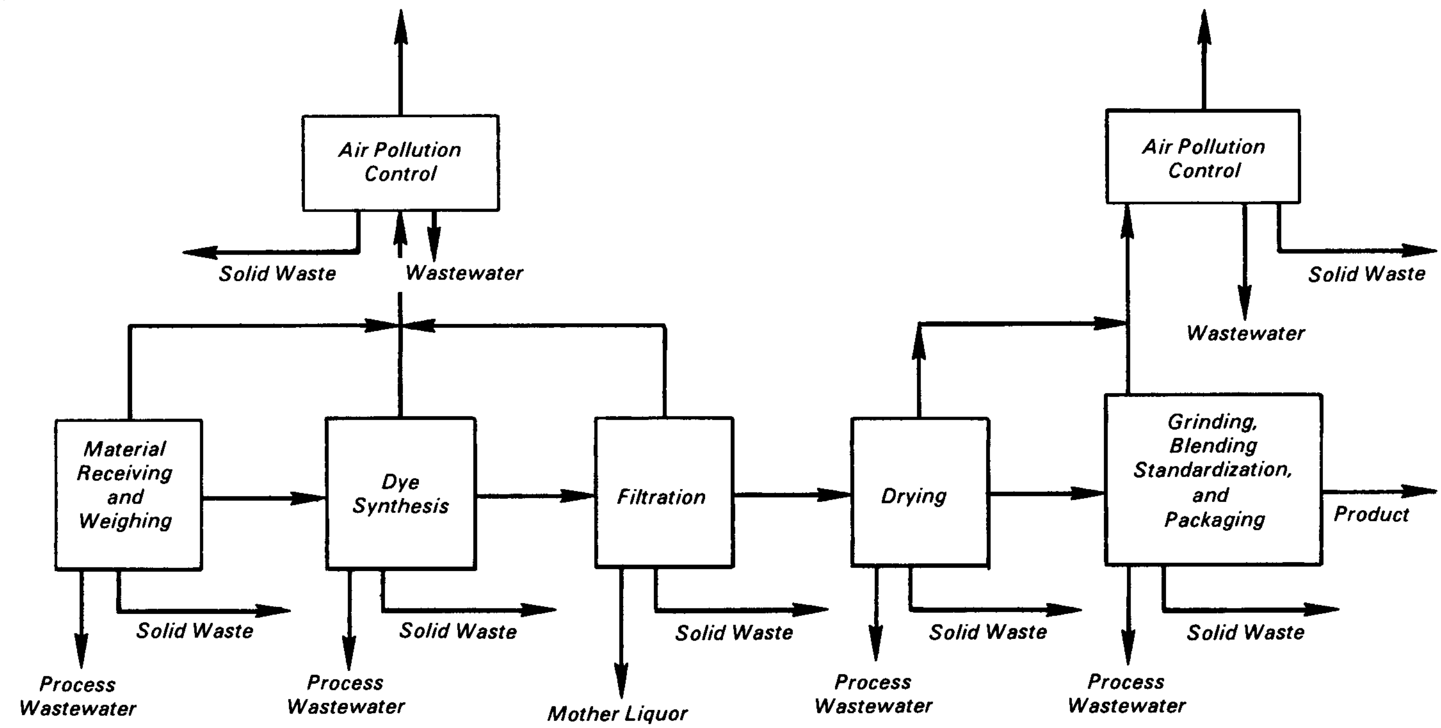

Figure 1. *Production operations that are sources of waste emissions in dye and pigment manufacture.*

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The complete report consists of nine volumes, entitled "Wastes from Manufacture of Dyes and Pigments:" (Set Order No. PB 84-200 864; Cost: $79.50)

"Volume 1. Azo Dyes and Pigments (Benzidine and Its Congeners Subsector," (Order No. PB 84-200 872; Cost: $11.50)

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