Dye Manufacturing

Industry Description and Practices

This document discusses the synthesis of dyes and pigments used in textiles and other industries. Dyes are soluble at some stage of the application process, whereas pigments, in general, retain essentially their particulate or crystalline form during application. A dye is used to impart color to materials of which it becomes an integral part. An aromatic ring structure coupled with a side chain is usually required for resonance and thus to impart color. (Resonance structures that cause displacement or appearance of absorption bands in the visible spectrum of light are responsible for color.) Correlation of chemical structure with color has been accomplished in the synthesis of dye using a chromogen-chromophore with auxochrome. Chromogen is the aromatic structure containing benzene, naphthalene, or anthracene rings. A chromophore group is a color giver and is represented by the following radicals, which form a basis for the chemical classification of dyes when coupled with the chromogen: azo (–N=N–); carbonyl (=C=O); carbon (=C=C=); carbon-nitrogen (>C=NH or –CH=N–); nitroso (–NO or N–OH); nitro ($–NO_2$ or =NO–OH); and sulfur (>C=S, and other carbon-sulfur groups). The chromogen-chromophore structure is often not sufficient to impart solubility and cause adherence of dye to fiber. The auxochrome or bonding affinity groups are amine, hydroxyl, carboxyl, and sulfonic radicals, or their derivatives. These auxochromes are important in the use classification of dyes. A listing of dyes by use classification comprises the following:

- *Acetate rayon dyes:* developed for cellulose acetate and some synthetic fibers
- *Acid dyes:* used for coloring animal fibers via acidified solution (containing sulfuric acid, acetic acid, sodium sulfate, and surfactants) in combination with amphoteric protein
- *Azoic dyes:* contain the azo group (and formic acid, caustic soda, metallic compounds, and sodium nitrate); especially for application to cotton
- *Basic dyes:* amino derivatives (and acetic acid and softening agents); used mainly for application on paper
- *Direct dyes:* azo dyes, and sodium salts, fixing agents, and metallic (chrome and copper) compounds; used generally on cotton-wool, or cotton-silk combinations
- *Mordant or chrome dyes:* metallic salt or lake formed directly on the fiber by the use of aluminum, chromium, or iron salts that cause precipitation in situ
- *Lake or pigment dyes:* form insoluble compounds with aluminum, barium, or chromium on molybdenum salts; the precipitates are ground to form pigments used in paint and inks
- *Sulfur or sulfide dyes:* contain sulfur or are precipitated from sodium sulfide bath; furnish dull shades with good fastness to light, washing, and acids but susceptible to chlorine and light
- *Vat dyes:* impregnated into fiber under reducing conditions and reoxidized to an insoluble color.

Chemical classification is based on chromogen. For example, nitro dyes have the chromophore $–NO_2$. The *Color Index* (C.I.), published by the Society of Dyers and Colourists (United Kingdom) in cooperation with the American Association of

Textile Chemists and Colorists (AATC), provides a detailed classification of commercial dyes and pigments by generic name and chemical constitution. This sourcebook also gives useful information on technical performance, physical properties, and application areas.

Dyes are synthesized in a reactor, filtered, dried, and blended with other additives to produce the final product. The synthesis step involves reactions such as sulfonation, halogenation, amination, diazotization, and coupling, followed by separation processes that may include distillation, precipitation, and crystallization. In general, organic compounds such as naphthalene are reacted with an acid or an alkali along with an intermediate (such as a nitrating or a sulfonating compound) and a solvent to form a dye mixture. The dye is then separated from the mixture and purified. On completion of the manufacture of actual color, finishing operations, including drying, grinding, and standardization, are performed; these are important for maintaining consistent product quality.

Waste Characteristics

The principal air pollutants from dye manufacturing are volatile organic compounds (VOCs), nitrogen oxides (NO_x), hydrogen chloride (HCl), and sulfur oxides (SO_x).

Liquid effluents resulting from equipment cleaning after batch operation can contain toxic organic residues. Cooling waters are normally recirculated. Wastewater generation rates are of the order of 1–700 liters per kg (l/kg) of product except for vat dyes. The wastewater generation rate for vat dyes can be of the order of 8,000 l/kg of product. Biochemical oxygen demand (BOD) and chemical oxygen demand (COD) levels of reactive and azo dyes can be of the order of 25 kg/kg of product and 80 kg/ kg of product, respectively. Values for other dyes are, for example, BOD_5, 6 kg/kg; COD, 25 kg/kg; suspending solids, 6 kg/kg; and oil and grease, 30 kg/kg of product.

Major solid wastes of concern include filtration sludges, process and effluent treatment sludges, and container residues. Examples of wastes considered toxic include wastewater treatment sludges, spent acids, and process residues from the manufacture of chrome yellow and orange pigments, molybdate orange pigments, zinc yellow pigments, chrome and chrome oxide green pigments, iron blue pigments, and azo dyes.

Pollution Prevention and Control

Every effort should be made to substitute degradable and less toxic ingredients for highly toxic and persistent ingredients. Recommended pollution prevention measures are to:

- Avoid the manufacture of toxic azo dyes and provide alternative dyestuffs to users such as textile manufacturers.
- Meter and control the quantities of toxic ingredients to minimize wastage.
- Reuse by-products from the process as raw materials or as raw material substitutes in other processes.
- Use automated filling to minimize spillage.
- Use equipment washdown waters as makeup solutions for subsequent batches.
- Return toxic materials packaging to supplier for reuse, where feasible.
- Find productive uses for off-specification products to avoid disposal problems.
- Use high-pressure hoses for equipment cleaning to reduce the amount of wastewater generated.
- Label and store toxic and hazardous materials in secure, bunded areas.

A dye and pigment manufacturing plant should prepare and implement an emergency plan that takes into account neighboring land uses and the potential consequences of an emergency. Measures to avoid the release of harmful substances should be incorporated in the design, operation, maintenance, and management of the plant.

Target Pollution Loads

Implementation of cleaner production processes and pollution prevention measures can yield both economic and environmental benefits.

Specific reduction targets for the different processes have not been determined. In the absence of specific pollution reduction targets, new plants should always achieve better than the industry averages cited in "Waste Characteristics," above.

Treatment Technologies

Air Emissions

Stack gas scrubbing and/or carbon adsorption (for toxic organics) are applicable and effective technologies for minimizing the release of significant pollutants to air. Combustion is used to destroy toxic organics. Combustion devices should be operated at temperatures above 1,100° C (when required for the effective destruction of toxic organics), with a residence time of at least 0.5 second.

Liquid Effluents

Effluent treatment normally includes neutralization, flocculation, coagulation, settling, carbon adsorption, detoxification of organics by oxidation (using ultraviolet systems or peroxide solutions), and biological treatment. Exhausted carbon from adsorption processes may be sent for regeneration or combustion. Reverse osmosis, ultrafiltration, and other filtration techniques are used to recover and concentrate process intermediates.

Solid Hazardous Wastes

Contaminated solid wastes are generally incinerated, and the flue gases, when acidic, are scrubbed.

Emissions Guidelines

Emissions levels for the design and operation of each project must be established through the environmental assessment (EA) process on the basis of country legislation and the *Pollution Prevention and Abatement Handbook*, as applied to local conditions. The emissions levels selected must be justified in the EA and acceptable to the World Bank Group.

The guidelines given below present emissions levels normally acceptable to the World Bank Group in making decisions regarding provision of World Bank Group assistance. Any deviations from these levels must be described in the World Bank Group project documentation. The emissions levels given here can be consistently achieved by well-designed, well-operated, and well-maintained pollution control systems.

The guidelines are expressed as concentrations to facilitate monitoring. Dilution of air emissions or effluents to achieve these guidelines is unacceptable.

All of the maximum levels should be achieved for at least 95% of the time that the plant or unit is operating, to be calculated as a proportion of annual operating hours.

Air Emissions

The emissions levels presented in Table 1 should be achieved.

Liquid Effluents

The effluent levels presented in Table 2 should be achieved.

Table 1. Emissions from Dye Manufacturing
(milligrams per normal cubic meter)

Parameter	*Maximum value*
Chlorine (or chloride)	10
VOCs	20

Table 2. Effluents from Dye Manufacturing
(milligrams per liter, except for pH)

Parameter	*Maximum value*
pH	6–9
BOD	30
COD	150
TSS	50
Oil and grease	10
Phenol	0.5
Chromium (hexavalent)	0.1
Copper	0.5
Zinc	2
AOX	1
Toxic organics such as benzidine (each)	0.05

Note: Effluent requirements are for direct discharge to surface waters.

Solid Wastes

Contaminated solid wastes should be incinerated under controlled conditions to reduce toxic organics to nondetectable levels, in no case exceeding 0.05 mg / kg or the health-based level.

Ambient Noise

Noise abatement measures should achieve either the levels given below or a maximum increase in background levels of 3 decibels (measured on the A scale) [dB(A)]. Measurements are to be taken at noise receptors located outside the project property boundary.

Receptor	*Maximum allowable log equivalent (hourly measurements), in dB(A)* Day (07:00–22:00)	Night (22:00–07:00)
Residential, institutional, educational	55	45
Industrial, commercial	70	70

Monitoring and Reporting

Frequent sampling may be required during start-up and upset conditions. Once a record of consistent performance has been established, sampling for the parameters listed in this document should be as described below.

Monitoring of air emissions should be done on a continuous basis. Liquid effluents should be monitored for toxic ingredients at least once every shift. The remaining parameters should be monitored at least daily.

Monitoring data should be analyzed and reviewed at regular intervals and compared with the operating standards so that any necessary corrective actions can be taken. Records of monitoring results should be kept in an acceptable format. The results should be reported to the responsible authorities and relevant parties, as required.

Key Issues

The key production and control practices that will lead to compliance with emissions guidelines can be summarized as follows:

- Avoid the manufacture of toxic azo dyes and provide alternative dyestuffs to users such as textile manufacturers.
- Replace highly toxic and persistent ingredients with less toxic and degradable ones.
- Control loss and wastage of toxic ingredients.
- Return packaging for refilling.
- Use equipment washdown waters as makeup solutions for subsequent batches.
- Minimize wastage by inventory control and find uses for off-specification products.

Sources

Kirk, Raymond E., and Donald F. Othmer. 1980. *Kirk-Othmer Encyclopedia of Chemical Technology.* 3d ed. New York: John Wiley and Sons.

Austen, George T., R. N. Shreve, and Joseph A. Brink. 1984. *Shreve's Chemical Process Industries.* New York: McGraw-Hill.