MANUFACTURE AND USE OF PAPER DYES

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MANUFACTURE OF PAPER DYES

Market Profile

The dyeing of paper products is usually done with acid, basic, or direct dyes. Approximately 3000 different colorants are available commercially (over 7000 after combination) and they can take the forms of liquid, powders, press cake, pastes, or dispersions (given all industry uses), (Hobbs, 1988). All paper dyes were in powder form until the 1960's, when liquid dyes began to replace dry dyes (Pulp and Paper, 1981). Liquids are more expensive to ship, but easier to handle, and reduce exposure potential. Twenty companies (33 locations) engage in the manufacture of organic dyes (RCRA, 1992).

In most cases, the PMN chemical is likely to be the dye chemical rather than a raw material used to produce the dye. This assumption is based on the large number of commercial dyes available that are deviations on existing dyes or new combinations of the same raw materials. In some cases, new dyes may be imported for blending with other dyes to produce a new product.

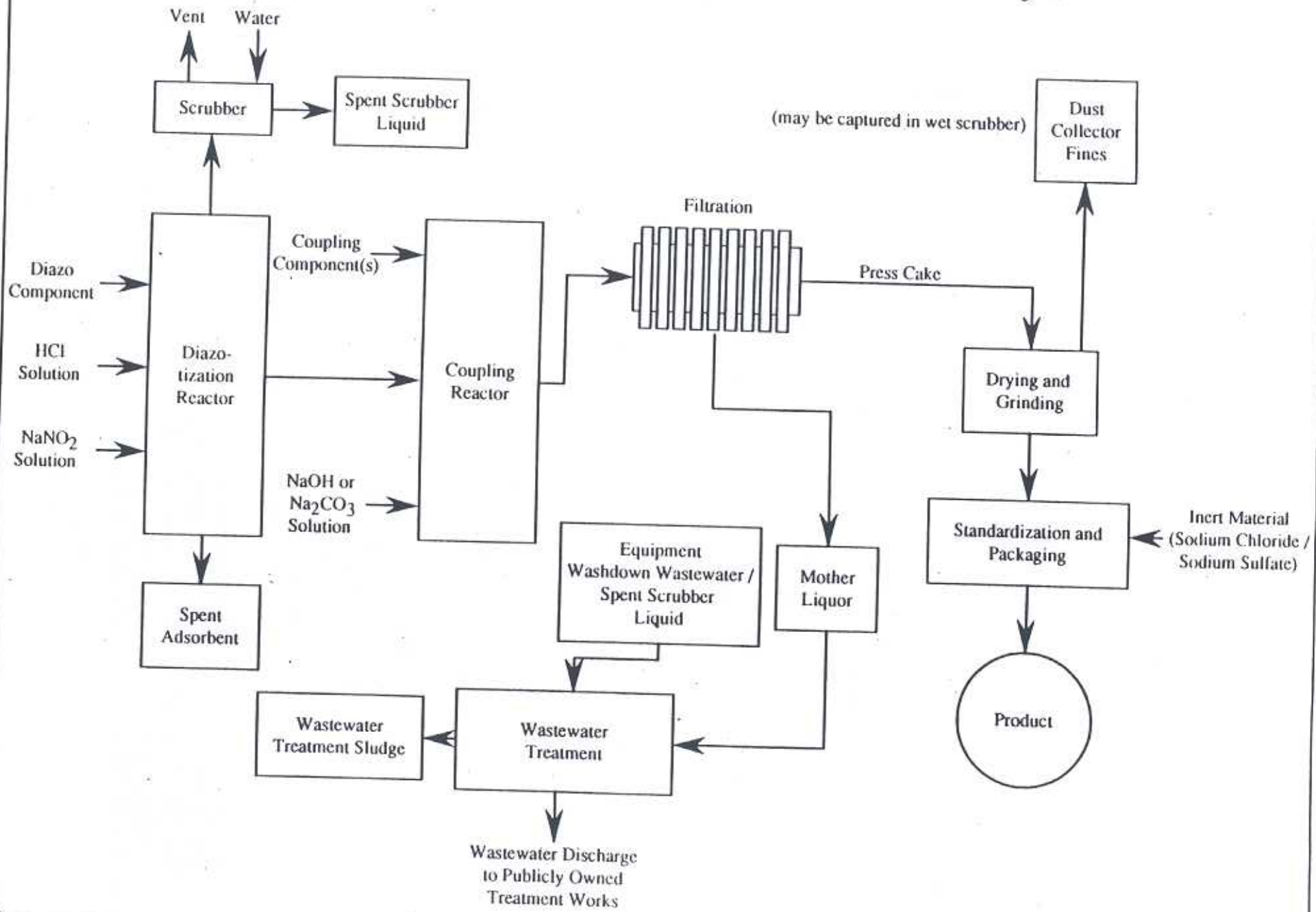
Process Description

Organic dyes are manufactured from raw materials of aromatic organic compounds using batch processes. The following steps outline the process for azo dyes which comprise the largest chemical class of organic dyes:

1. Slurry of raw materials
2. Pre-reaction of raw materials
3. Diazotization reaction
4. Clarification
5. Coupling reaction
6. Isolation (salt addition)
7. Plate and frame filter press (concentrating)
8. Drying (tray or spray)
9. Standardizing
10. Packaging and shipping

A generalized process flow diagram is attached. In some cases, additional reaction and clarification steps may be required to achieve the desired substitutions of functional groups. The first three steps, namely raw material slurrying, pre-reaction of raw materials, and the diazotization reaction, are often carried out in the same reaction vessel. Production lines may or may not be dedicated to the manufacture of one color.

Process Flow Diagram for the Manufacture of Azo Dyes



AH-2

The raw materials, water, ice (for temperature control) and other reaction components are added and the solution is agitated. Filter aids such as diatomaceous earth may be added to the diazotization reactor to remove particulate impurities from the diazonium ion intermediate. The spent filter aids are then collected in a plate and frame filter press and the press cake, called a clarification sludge, is discharged as waste.

The diazonium ion is then pumped into the coupling reactor, and the premixed, dissolved coupler is added under pH control. The coupled azo product is then isolated via the addition of a salt solution which decreases the solubility of the product. The isolated product is pumped to a large plate and frame filter press where the dye is concentrated into a presscake (if solid) or filtered (if a liquid). The presscake is transferred to containers and may be either sold in this wet form or further processed. Further processing (for solid dyes) includes drying and grinding into a fine powder. Drying may be performed via tray, conveyor belt, spray, or other drying techniques.

Following these steps, the solid or liquid product is standardized to obtain the desired dye formulation. Following standardization, the PMN or dye chemical becomes less than 100 percent of the salable product. Typical values of a single PMN chemical in the salable product are 5 to 25 percent (CEB, 1991; ETAD, 1993).

The process for chemical classes other than azo dyes is similar to that described above, except that one reaction may take the place of the diazotization and coupling reactions. Isolation using a filter press and/or salt addition is generally used for all dye classes. Recently, manufacturers are trying to eliminate the generation of high volume mother liquors and salt wastes by developing processes that do not require salt addition and filtration.

Number of Manufacturing Sites: Provided by submitter (22 domestic dye manufacturing sites at 33 locations).

Days of Operation: Given or assume 250 days/year, based on batch operation.

Worker Exposure: 10-15 workers directly involved (and potentially exposed) in dye manufacturing per shift per plant. Most plants operate on three 8-hour shifts per day. Tasks associated with potential exposure are filtering, grinding, blending, standardizing, packaging, dumping, and drum filling with the powder form of the dye. Local exhaust ventilation at work stations decreases exposure potential (Rand, 1986).

In the case of moist materials (i.e., the wet dye cake), inhalation exposure is usually negligible. Cake spillage is washed down floor drains; if it drys, foot traffic will generate airborne dye dust (Rand, 1986). Inhalation exposure during handling of liquid dyes is generally negligible (Heath, 1984).

A. Solids and Dust

Scenario: Transferring powder dyes during dryer loading, grinding, standardizing, and packaging.

1. Inhalation (mg/day) (CEB, 1991, eq. 4-11)

$$I = C_{m,s}bh$$

where: I = Daily inhalation exposure, mg/day
$C_{m,s}$ = Airborne concentration of PMN, mg/m^3
b = Inhalation rate, m/hr
h = duration, hr/day

$C_{m,s}$ can be calculated as follows:

$$C_{m,s} = KC_t Y_s$$

KC_t = 15 mg/m^3 (OSHA PEL for total dust)
Y_s = Weight fraction of PMN chemical in dye formulation (provided by submitter) or 5 to 25% (CEB, 1991, pg 4-10; ETAD, 1993).

2. Dermal

Gloves, coveralls, and short task duration minimize exposure. The CEB estimates dermal exposure to powder dyes during dye weighing at end-use operations such as textile dyeing. This does not account for glove use, frequency of handling or skin perspiration, all of which will affect dermal exposure (CEB, 1991).

D = (1300 to 3900 mg/day) x (% of PMN)
where % of PMN = 5 to 25% or as provided by submitter.

B. Liquids

Dye manufacturers typically utilize direct piping of liquids between reaction vessels during dye synthesis. Therefore, potential exposure to liquid dye exists only at the end of the finishing step, when prepared for packaging and sale.

Inhalation: Negligible based on low vapor pressure.

Dermal Scenario: Filling drums with liquid dye.

Assume 650 to 1,950 mg/day from routine, one hand contact with the pure PMN substance; for other activities assume:

650 to 1950 mg/day x (% of PMN substance in formulation)

Environmental Release:

Sources of environmental releases during dye manufacturing include filtration liquors (called mother liquors), equipment washdown, and other process waters, spent filter cloths and wastewater treatment solids. The latter two wastes are not generated at all sites. Dye dust and fines are generated during drying, grinding, standardization, blending, and packaging operations. They may be captured in a baghouse and recycled to the process or disposed in a landfill, or they may be released to the atmosphere, allowed to settle on the floor, and washed into floor drains. TRI data on environmental release of dyes is scarce due to the low number of dyes on the TRI reporting list. Estimated releases, based on percentages of production volumes, were obtained from an SRI study (SRI, 1981).

Air: Negligible due to low vapor pressure.

Land: Assume 2% of production volume solid waste loss (i.e., dust/fines) from product finishing (SRI, 1981).

Water: Assume 2.7% of production volume lost to water (SRI, 1981).

(%PMN[1])(PV provided by submitter/# PMN sites/# days operating)(0.027) = Loss to water in kg/site/day.

[1]% PMN = Multiply by percent PMN in final dye formulation if production volume provided by submitter is for final dye formulation instead of 100 percent dye chemical.

USE OF PAPER DYES IN PAPER MANUFACTURING INDUSTRY

Market Profile:

Dyes and other chemicals may be added during the paper-making process to give the paper product its desired color and preferred properties.

In 1990, 549 paper mills were operating in the U.S. Over 175,000 people were employed at paper mills (DOL, 1991).

Acid, base, and direct dyes make up the great majority of dyes used in the paper industry. The following is the U.S. consumption of dyes by the paper industry for 1971 (SRI, 1984):

Acid Dye	18.3
Direct Dye	12.5
Basic Dye	3.0
Total	33.8 million pounds

Paper Manufacture:

Batch systems have been replaced largely with continuous, pump-through equipment. The following steps summarize manufacturing steps:

1. Stock (Pulp) preparation - several operations undertaken to form the pulp into an aqueous slurry

   a. Beating and refining - Mechanical action on pulp
   b. Filling and loading - Materials are added to stock to improve brightness, opacity, smoothness, and softness
   c. Sizing - Material are added to stock to make the paper resistance to penetration by liquids
   d. Coloring - Addition of dye

2. Sheet Forming, Pressing, and Drying

Two types of continuous sheet forming and drying machines are used: the cylinder machine and the Fourdrinier machine.

Paper dyeing is often done with dyes in liquid form, which is metered into the paper-making equipment. This can be done with automatic equipment. Dye can be added at almost any point during the paper-making process.

Stock dyeing dyes the paper fiber before the sheet is formed. Dry dye is added or liquid is metered into the pulper. Most paper is stock dyed.

Continuous dyeing constantly feeds dye solution at the fan pump or head box so the dye pulp goes immediately to the paper making machine. Most manufacturers combine the two methods (Pulp and Paper, 1981).

Number of Paper Manufacturing Sites:

(549 U.S. Paper Mills, DOL, 1991).
Provided by PMN submitter, or use following algorithm:

sites = Use volume / (Use rate x # days/yr)

Use rate = 180 kg/site-day:

U.S. Paper Production = 38.1 million short tons/yr
(U.S. DOC, 1991)

$\frac{\text{0.5 lb commercial dye (light)}}{\text{short ton paper}}$ or $\frac{\text{7.0 lb commercial dye (heavy)}}{\text{short ton paper}}$

Average annual dye consumption = 2 lbs dye/ton paper
(EPA, 1981, and Georgia-Pacific, 1993)

$$\frac{(\text{38.1 million short tons/yr})(\text{2 lbs dye/ton paper})(\text{0.454 kg/1 lb})}{(\text{549 sites})(\text{350 days/yr})}$$

= 180 kg/site-day

Days of Operation: Given or assume 350 days/year, based on continuous operation.

Days of Potential Exposure: Assume 250 days/year.

Worker Exposure: Use of liquid dye and automated equipment greatly reduces the exposure potential. Up to four percent of the production workers at paper manufacturers hold positions associated with potential dye exposure (Soklow, 1984). Assuming a plant work force of 300 workers (DOL, 1991), up to 12 employees are potentially exposed to dye. Job categories in paper mills with potential dye exposures include: machine operators, engineering technicians, plumbers and pipe fitters, laborers and mixing operators (Soklow, 1984).

A. Solids and Dust

Scenario: Weighing and transferring dry dyes into blend tanks. Based on textile dye activities, continuous operation (page 4-10 of CEB, 1991).

1. Inhalation exposure (mg/day)

   Typical case: I = 0.0314 x % conc. of PMN x 3-4 dye weighings/day

   Worst case: I = 0.170 x % conc. of PMN x 3-4 dye weighings/day

   % conc. of PMN is given or estimated to be 5-25%
   (CEB, 1991; ETAD, 1993)

2. Dermal

   Gloves, coveralls, and short task duration make dermal exposure potential low. Assume 2-hand incidental contact:

   D = (1300 to 3900 mg/day) x (% PMN in dye formulation).

B. Liquids

1. Inhalation exposure is assumed to be negligible based on the fact that the dyes are in solution and have low vapor pressures.

2. Dermal

   Assume 2-hand incidental contact:

   D = (1300 to 3900 mg/day) x (% PMN in dye formulation).

<u>Environmental Release</u>:

Assume: 90% exhaustion of dye onto paper
10% is released to environment.
(ref: EPA, 1981)

Major sources of waste include trimmings, plant dust, wastewater treatment sludges, and other process residues. An estimated 99.8% of the waste is released as solid waste, 0.1% as air release, and 0.1% as water release (ref: EPA, 1981).

Use rate (kg/site-day)= use volume/(# sites x # days)= 180 (default). The default value should be used only if the submitter did not provide the number of sites nor the number of days.

Waste release rate (kg/site-day) = Use rate x 10% = 18 (default)

Air: 0.1% of total released = 0.001 x waste rate = 0.02 kg/site/day (default)

Solid: 99.8% of total released = 0.998 x 0.1 x use volume

Water: 0.1% of total released = 0.001 x waste rate = 0.02 kg/site/day (default)

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$.02 + 17 + .02$

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