New dyes are continuously being developed to meet the demands of new technology, new fabrics, advances in dyeing equipment, and to overcome the serious environmental concerns associated with some existing dyes. The impact of these new replacement dyes on the environment and workers can be assessed by comparing them with similar existing dyes. For this study, information was collected from the open literature, product technical brochures, trade association studies, and visits to two textile dyeing operations. The collected information was used to characterize the physical, chemical, and application properties of 14 classes of textile dyestuffs. Information collected on textile dyeing equipment was studied to describe dyeing procedures, the operation of various types of textile dyeing equipment, and to estimate both the amount of textile dyestuff released to the environment from a typical dyeing operation and the extent of worker exposure associated with each operation. These estimates were made on a weight-per-weight basis of dyestuffs to fabric dyed for typical operations. The plant visit information was used to verify data obtained from the literature and to fill data gaps. This information enabled estimates to be made of dyestuff releases from actual dyeing operations for each type of dyeing equipment described. All information was collected on an as-available basis and included data generated by site visits and discussions with other individuals familiar with this industry.

Information on air emissions to the ambient environment from textile dyeing operations was collected and reported; however, little data were available on air emissions of dyestuffs to the ambient air. For data on worker exposure to airborne dyes, four 1978 studies by the National Institute for Occupational Safety and Health were consulted. Unfortunately, these studies were of limited use since they dealt only with benzidine-based dyes which have been curtailed from widespread use by the industry. Where possible, worker exposure times were recorded during the plant visits.

A data base from EPA’s Effluent Guidelines Division was accessed: results of a brief analysis of this base are reported. Information extracted from the data base included the number and size range of wastewater treatment and pretreatment plants of various textile dyeing operations. This information, separated into direct and indirect wastewater discharges, was presented for small, medium, and large textile dyeing operations.

Since there were data gaps in the area of the emission/release of textile dyestuffs to the environment, addi-
tional areas of possible investigation are identified, including data to characterize worker exposure time and dyestuff concentration levels, quantities of dyestuffs purchased by textile dyeing operations, and updated plant size data specific to dyeing operations. This information would create a larger, more comprehensive data base from which to obtain a more realistic profile of the textile dyeing industry.

This Project Summary was developed by EPA’s Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in separate report of the same title (see Project Report ordering information at back).

Introduction
In 1980, 111 million kg (245 million lb) of synthetic organic dyestuffs were produced in the U.S. The U.S. imported another 13 million kg (29 million lb), or 12 percent of the domestically produced amount of synthetic organic dyestuffs. About two-thirds of the dyestuffs produced in the U.S. were used by the textile industry for dyeing. Until recently, azo-type acid dyes, direct dyes, and pigments based on benzidine and benzidine congeners were commercially important and very popular dyestuffs. However, recent health and environmental concerns about benzidine-based dyes have caused dyestuff manufacturers and dye users to seek less toxic and environmentally safer replacements. In addition, new technology, new fabrics, and advances in dyeing equipment provide incentive to develop new dyes.

Knowledge of the physical, chemical, and application properties of new data can provide valuable information about the dye’s environmental release and worker exposure effects. One method used to determine this information for new and replacement dyes is by comparing the properties of new dyes with similar dyes within the same dye class for which such information is already known. This report provides a basis upon which such a comparison can be made.

Summary
Three major areas of the study relate to dye class categorization, dye equipment categorization, and wastewater treatment plant size.

Dye Class Categorization
Using general dye chemistry as the basis for classification, textile dyestuffs are grouped into 14 categories or classes: (1) acid dyes, (2) direct (substantive) dyes, (3) azoic dyes, (4) disperse dyes, (5) sulfur dyes, (6) fiber reactive dyes, (7) basic dyes, (8) oxidation dyes, (9) mordant (chrome) dyes, (10) developed dyes, (11) vat dyes, (12) pigments, (13) optical/fluorescent brighteners, and (14) solvent dyes.

Six of the above dye classes (1-6), selected by EPA’s Office of Toxic Substances, were the focus of intensive data collection efforts in an attempt to describe each class, its chemistry, and chemical and physical properties as fully as possible. Information collected for the remaining eight classes (7-14) was similar, but not as detailed. Selection of these classes (1-6) was based in part on a projection of new dye development activities and concerns about the health and environmental effects of these dyes. The following paragraphs briefly identify these six classes of dyes and describe their use by the textile dyeing industry.

Acid dyes are typically used to dye acrylics, wool, nylon, and nylon/cotton blends. They are called acid dyes because they are normally applied to the nitrogenous fibers of fabrics in organic or inorganic acid solutions. Chemical reactions between the dye and fiber form an insoluble color molecule on the fiber. In 1980, acid dyes accounted for 10 percent of total U.S. dye production. The three most commercially important acid dyes are azo, anthraquinone, and triarylmethane. These dyes are generally applied as a liquid at elevated temperatures of greater than 39°C (102°F). Although acid dyes may be used for transfer printing, this use is not commercially important. In general, these dyes have poor wet fastness. Molecular weights range from 200 to 900, and the higher the molecular weight, the poorer the leveling (uniformity of dye uptake) property.

Direct dyes are applied in an aqueous bath containing ionic salts and electrolytes. These dyes are normally used to dye cotton and other cellulosic fibers; they bond to fibers by electrostatic forces. In 1980, 13 percent of the dyes produced in the U.S. were direct dyes. These dyes are highly soluble even in cold water; most have solubilities in water from 8 to 40 g/l. A few have solubilities up to 80 g/l.

Azoic dyes are applied by combining two soluble components impregnated in the fiber to form an insoluble color molecule. These dye components, sold as paste-like dispersions and powders, are used chiefly for cellulosics, especially cotton. Dyebath temperatures of 16-27°C (60-80°F) are generally used to the shade.

Disperse dyes are colloidal and have very low water solubilities. Most of these dyes are used for polyester, nylon, acetate, and triacetate fibers. They are usually applied from a dye bath as dispersions by direct colloidal absorption. Dye bath conditions (temperature, use of carrier) are varied based on the degree of difficulty encountered by the dyes in penetrating the fiber being dyed. They are sometimes applied dry at high temperatures by means of a sublimation process followed by colloidal absorption. High temperature sublimates the dye and, once it is inside the fiber, the dye condenses to a solid colloidal state and is absorbed on the fiber.

Sulfur dyes are used primarily for cotton and rayon. The application of sulfur dyes requires carefully planned transformations between the water-soluble reduced state of the dye and the insoluble oxidized form. Sulfur dyes can be applied in both batch and continuous processes; continuous applications are preferred because of the lower volume of dye required. These dyes generally have a poor resistance to chlorine. In general, sulfur blacks are the most commercially important colors and are used where good color fastness is more important than shade brightness. Sulfur dyes are not applicable to wool or silk because the fibers are chemically damaged by the dyeing process.

Fiber reactive dyes derive their name from the fact that they form covalent bonds with the fiber molecules to be dyed. Molecules of fiber reactive dyes are much smaller than the complex molecules of direct dyes. Fiber reactive dyes are unique in that they become an integral part of the textile fiber that is dyed. Although more expensive than direct dyes, advantages of reactive dyes are excellent shade reproducibility and good leveling properties. These dyes also have outstanding wet fastness. In 1980, about 2 percent of the total dyestuffs produced in the U.S. were fiber reactive dyes. These dyes can be subdivided into either "hot" or "cold" dyeing groups, based on the temperature of application. Although silk and nylon can be dyed with fiber reactive dyes, the chief fibers dyed are cellulosics and wool. These dyes are also popular for printing textiles, since even the brightest colors are wet fast.
Fiber reactive dye products were first introduced in 1956; by 1980 there were 66 on the market. Of these, 59 represent about equal numbers of yellow, orange, red, and blue dyestuffs. The remaining include black, brown, green, and violet shades. By 1982, the number of fiber reactive dyestuffs listed for sale had increased to 139, more than twice the number available in 1980. This increase, along with the fact that the dye shades are very reproducible and wash fast, indicates a continued increase in importance of fiber reactive dyes in the future.

Based on a linear regression projection of the past 10 years' production volumes of fiber reactive dyestuffs, this class of dye is expected to show a 56 percent increase in production volume by 1990 to a level of approximately 19.7 million kg (49.3 million Ib). The fiber reactive dye class is expected to experience the largest percentage increase in production of any of the 14 dye classes by 1990.

Dye Equipment Categorization

Ten major types of dyeing equipment are now in use by the textile dyeing industry. Some of these machines required minor operational modifications to accommodate the newer dyes and to take advantage of recent advances in dyeing equipment technology. The 10 general types of dyeing equipment are: (1) beams, (2) becks, (3) jigs, (4) jets, (5) package units, (6) vats, (7) semicontinuous (pad-batch dye machines), (8) continuous dyeing (TAK dyeing, space dyeing, thermosol dyeing, and pad-steam dyeing), (9) transfer printers, and (10) direct textile printers.

Four of the 10 classes (2, 7, 9, and 10) were selected by EPA’s Office of Toxic Substances for detailed study. Selection was based on the predicted continued and predominant use of the equipment in the textile dyeing industry.

The four types of dyeing equipment are fully described with respect to operation methods and procedures, physical features, and the dyeing processes for which they are suitable. Machine types also are categorized by the fabric which can be dyed and then related to the dye classes that typically would be used with the various machine/fabric combinations. Detailed time/temperature dyeing profiles also were developed for numerous fabric/machine/dyestuff combinations.

The important advantages and features of these classes of dyeing equipment were identified along with their limitations and disadvantages in dyeing different types of fabric. The equipment specifications are presented for the currently available dyeing equipment, and dyestuff use requirements were estimated for each machine, based on typical fabric/dye combinations. These estimates were verified with information collected during two plant visits.

Two textile dyeing operations were visited to verify information collected in the literature search and to verify actual dyeing procedures, attainable dye exhaustion rates, and drug room procedures, and to determine the typical quantities of dye and fabric used in dyeing operations. The two plants visited were selected because: (1) small and large dyeing operations were represented; (2) four types of dyeing equipment of interest were in use; (3) a commission dyeing operation involving several dye products was represented; and (4) the distance from Research Triangle Park, NC, was less than a day’s drive. Information obtained from these two plant visits was used to develop a mass balance for typical dye equipment/fabric/dyestuff combinations.

The mass balance estimates indicate the amount and manner in which a dye substance is released to the environment from specific types of dye equipment. The dyestuff release from the fabric and rinse water was found to vary widely for the different types of dyeing equipment and the fabric dyed. The total amount of dyestuff can be accounted for in the fabric, in the rinse water, and in the atmospheric environmental release. Therefore, rinse time, rinse volume, and dye exhaustion rates are important parameters for estimating environmental release. The following descriptions of each type of dyeing equipment and its typical mass balance illustrate the variability of dyeing equipment.

Beck dyeing takes place in a U-shaped box or trough with a gradually curved bottom. The fabric to be dyed is placed on a driven reel above the box and is allowed to slide down the back of the box, travel through the dye liquor in the box, and then continually return to the reel. This procedure is continued until dyeing is completed. Beck dyeing is best suited to woven knit and woven goods as well as heavyweight fabrics such as carpets, twills, and satins.

Beck dyeing utilizes the exhaustion dyeing method which is aided by heating the dye liquor with steam. In order to decrease the dyeing time, beck dyeing machines are pressurized to accelerate the exhaustion process. These high temperature and high pressure becks (jets) are best suited to elastized fabrics where machine tension on the fabric could cause damage. Pressure becks typically use 3,300 (889 gal.), or 3,246 kg (7,153 lb), of water per 454 kg (1,000 lb) of fabric dyed; an atmospheric beck uses twice this volume of water to dye the same quantity of fabric. The typical fabric dyed in an atmospheric beck is cotton; polyesters generally are dyed in a pressure beck. Dye exhaustion rates of 90 to 100 percent were achieved depending on the dye class used and the shade of color desired. For example, a medium to light color was found to exhaust 100 percent; whereas, a dark color would only achieve 90 percent exhaustion.

A typical atmospheric beck using sulfur dyes on cotton fabric releases about 0.5 kg (1.2 lb) of dye solids per 454 kg (1,000 lb) of fabric dyed in its rinse water effluent. This amount depends on the exhaustion and dye shade desired. An additional 4.8 kg (11 lb) of dye per 454 kg (1,000 lb) of fabric dyed leaves the dye operation with the fabric, depending on the exhaustion and dye shade desired. Pressure becks (or jet machines) typically apply disperse dyes on polyester. This operation releases 1.2 kg (2.7 lb) of disperse dyes per 454 kg (1,000 lb) of fabric dyed in water effluent, depending on the exhaustion and shade desired. The dyed fabric typically contains 11.2 kg (24.5 lb) of disperse dye solids per 454 kg (1,000 lb) of polyester fabric, but this can vary depending on exhaustion and desired shades.

Pad-batch dyeing is accomplished with a padding machine that is equipped with a set of wringers which forces the dyestuff through the fabric. Once the fabric has been saturated with dye, the fabric is developed in a batch immersion operation to exhaust the dye onto the fabric. This process can be used for vat, sulfur, azoic, solubilized vat, and diazotized, and developed direct dyes. Exhaustion rates for this type of equipment range from 60 to 95 percent, and depend on the amount of process time and the fabric/dye class. Rinse time for this process ranges from 1 hour to 4 or 5 hours. Because of the numerous steps required, this process is a large user of water compared with other wet dyeing operations. Water use ranges from 6,240 to 9,120 (1,648 to 2,409 gal.), or 6,232 to 9,110 kg (13,739 to 20,084 lb), per 3,175 kg (7,000 lb) of fabric dyed in a batch.

The third type of dyeing equipment investigated in detail was a transfer printer. The method most commonly used in the transfer printing process involves the
direct transfer of a pattern or color from a printed paper to the fabric. This is a dry process and achieves almost complete color exhaustion onto the fabric. A typical transfer printing operation purchases its supply of transfer paper and therefore does not generate any dye waste at the textile printing facility. The expended transfer paper minus its dyestuff coating is discarded with the plant's refuse.

Transfer printing is accomplished by a sublimation process in which the solid (dye) is vaporized by heat and condenses into a solid on the fabric when cooled. Disperse dyestuffs are the dye class most typically used for transfer printing onto a polyester fabric. Transfer printing uses about 0.5 kg (1.1 lb) of disperse dyestuff per 45 kg (100 lb) of fabric. Some other methods of transfer printing use a wet or semiliquid process, but the dry process described above is becoming predominant because it is unique, uncomplicated, and requires less skill to operate than other types of dyeing equipment. In addition, the dry process is suitable for polyester fabric, which has traditionally been one of the most difficult fibers to dye. This process also can be used on acetate, triacetate, and nylon; its use with disperse dyes and because of cylinder head temperatures as high as 230°C (446°F) that will scorch these delicate fibers.

The fourth type of textile dyeing equipment that was investigated in detail was direct textile printing. This method uses a combination of mechanical and chemical means to dye the fabric substrate. The two primary methods of direct printing are roller and screen: in both, the dyestuff is applied as a print paste or printing ink. The paste or ink is dispersed and either rolled directly onto the fabric (roller printing) or extended (screen printing) from a circular or flat perforated screen onto the fabric. Acid dyes are typically used in this process and are applied to nylon knit fabrics; pigments and reactive dyes are used for cottons. In actual printing operations, 100 percent of the dye is applied to the fabric; consequently, the only environmental dyestuff release is via the printed fabric. However, some of the dyestuff on the printed fabric will be released during rinsing. Since this printing method results in high quality designs, it is becoming the most appealing method for coloring designer and fashion apparel.

### Wastewater Treatment

#### Plant Size

Data from EPA's Effluent Guidelines Division were analyzed to characterize the volume of wastewater effluents from textile dyeing operations and the general methods of treatment. Although this is the most current data available, it does not reflect any changes since it was compiled in 1977. The data are based on information provided by textile operations from two standard industrial classifications (SIC): 223 and 226. These classifications, covering wool weaving and finishing mills and textile finishing (excluding wool) plants, were selected for analysis because most dyeing operations fall into one or the other.

The data provided by 434 plants performing textile dyeing were analyzed. Of these, about 30 percent (only 147 plants) discharge their wastewater effluent after on-site wastewater treatment. The rest pretreat their wastewater and discharge it to publicly owned treatment works (POTW).

Both the indirect and direct discharges were separated into three plant size categories (small, medium, and large) based on their daily fabric production rates. These categories were determined by selecting the medium-sized plant production rate range to be between 0.75 and 1.25 times the overall average daily production rate. Plants with higher production rates were considered to be large; those with lower production rates were considered to be small. From this distribution, typical average plant production rates and wastewater volumes were determined for each plant size.

A typical small plant, directly discharging to the surface waters after on-site waste treatment, produces 14,000 kg (31,000 lb) of fabric per day and generates 0.02 m³/s (0.04 million gpd) of wastewater. The typical medium-sized plant produces 44,000 kg (97,000 lb) of fabric per day with a resultant wastewater discharge of 0.04 m³/s (0.90 million gpd). The typical large direct discharging plant produces 107,000 kg (236,000 lb) of fabric per day and discharges an average of 0.08 m³/s (1.90 million gpd) of wastewater.

Typical daily production rates for the small, medium, and large plants discharging their wastewater to a POTW were 6,000 kg (14,000 lb), 23,000 kg (50,000 lb), and 86,000 kg (195,000 lb), respectively. Pretreatment facilities for these three plants were found to have the following design capacities: small, 0.01 m³/s (0.26 million gpd); medium, 0.02 m³/s (0.52 million gpd); and large, 0.05 m³/s (1.1 million gpd). The design flow of the respective POTWs that received the typical dyeing plant effluent averaged: small, 0.73 m³/s (16.70 million gpd); medium, 0.83 m³/s (18.90 million gpd); and large, 1.20 m³/s (28.40 million gpd).

### Conclusions

Based on the information collected for this study, new dyestuffs will continue to replace older dyes. In the textile industry, the two dye classes that will experience the most growth are fiber-reactive and disperse (sublimable) dyes. A concurrent increase in the use of new dyeing equipment (e.g., the pressure beck jet and transfer and direct printers) is expected because of their high dyeing efficiency and exhaustion rates. For these reasons and since this type of equipment uses little or no water with other equipment (e.g., the beam, pad-batch operation, and atmospheric beck), many dyers will reduce the quantity of wastewater and dye solids discharged to the environment. However, because the new dry printing method (transfer printing) uses dyes that sublime, use of this method may transfer dye emissions from a water medium to the atmosphere surrounding the machine. Use of this method could have a greater impact on worker exposure than wet dyeing methods. In addition, both plant visits conducted for this study revealed that dye operations can, with proper machine operation, achieve a very high degree of dye exhaustion onto the fabrics. Based on observations at the two plants visited, this effort is already being made to maximize the effective use of dyestuffs and minimize the cost of dye purchases.

### Recommendations

Several areas were identified where information was incomplete or unavailable on textile dyeing operations. In most instances, the unavailable information was nonexistent; obtaining it would require detailed research efforts. In other instances, the information was available, but the database was incomplete or insufficient to establish reliable emission/release estimates and trends. The areas of textile dyeing operations requiring additional study are:

- Developing Information on Properties of Dyestuffs-Most information available on physical/chemical dyestuff properties is general and does not describe the properties of specific large volume dyestuffs now
in use. The use of chemical property estimation techniques and/or actual testing of specific dye substances could develop detailed information in this area. This effort could also be enhanced by preparation of environmental fate and accumulation estimates for the dyestuffs, using recently published estimation methods.

- Characterizing the Size, Capacity, and Dye Use of Textile Dyeing Operations—The most recent data available was from EPA's Effluent Guidelines Division and was about 6 to 10 years old. Since that time, new dyes and fabric combinations have replaced older dyestuffs, fabrics, and machines. This currently available information primarily focuses on textile finishing operations, rather than dyeing operations. Additional data collection efforts could focus on textile dyeing operations, rather than on textile finishing operations as past data collection efforts did.

- Developing Data on Worker Exposure to Dyestuffs—Little information was available in the literature on worker exposure to dyestuffs, except for benzidine-based dyes which have been largely dropped from use by the industry. Parameters to be considered include: frequency, duration, and exposure concentrations for workers. No data were found to characterize the type and concentrations of volatilized dye or solvent emissions from dry transfer printing operations to the atmosphere or dyestuff releases via the expended transfer paper. This, as well as other batch and continuous dyeing methods, could be investigated with respect to worker exposure.

- Studying Advanced Wastewater Treatment of Dyes—Much information was available in the open literature on wastewater treatment of textile effluents. However, these data did not focus on removing specific dyestuffs by these technologies, nor did they address the removal efficiency of advanced technologies; e.g., reverse osmosis and hyperfiltration for specific dyestuffs.

- Investigating Multimedia Transfer of Dyestuffs—Both existing and advanced candidate wastewater treatment technologies produce wastewater sludge or other liquid concentrates that must be disposed of. Virtually no data were available for the quantity of dyestuffs transferred to the residual wastes from treatment of textile dyeing wastewater.

- Compiling Information on Dyeing of Leather and Non-woven Textile Products—Data on these topics were available, but were not a major focus of this study.

- Additional Plant Visits to Textile Dyeing Operations—Additional plant visits to collect similar information would broaden the data base for plant operations and dyestuff release estimates. This study investigated only two plants; more such visits would be useful in obtaining a realistic profile of the textile dyeing industry.


J. S. Ruppersberger is the EPA Project Officer (see below).

The complete report, entitled "Textile Dyes and Dyeing Equipment: Classification, Properties, and Environmental Aspects," (Order No. PB 85-173 771/AS; Cost: $31.00, subject to change) will be available only from:

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