Kirk-Othmer Encyclopedia of Chemical Technology.

DYE CARRIERS

Dye carriers are needed for complete dye penetration of polyester fibers. Carriers cause the glass-transition temperature, T_g, of the polyester polymer to become lower and allow the penetration of water-insoluble dyes into the fiber.

It is difficult for dye solutions in water to penetrate synthetic fibers such as polyester, cellulose triacetate, polyamides, and polyacrylics which are somewhat hydrophobic. The rate of water imbibition differs with each fiber as shown in Table 1 as compared to viscose (see Fibers, regenerated cellulosics), which imbibes water at the rate of 100% (1). The low imbibition rate is attributed to the high T_g obtained when the polymeric fibers are drawn. During this drawing operation the polymer chains become highly oriented and tightly packed, forming a structure practically free of voids.

Disperse dyes commonly used to dye polyester are nonionic, and dye the polyester fiber through a diffusion mechanism. Prolonged boiling of the dyebath loosens the forces binding the polymer chains to each other, causing the fiber to swell. This allows a limited penetration of the fiber surface by the dye. The rate of absorption or diffusion of disperse dyes in polyester is much lower than that on nylon (see Fibers, polyamide) or cellulose triacetate fibers (see Fibers, cellulose esters). This low dyeing rate is too costly to meet the economic requirements of industrial processing. In addition, deep shades are difficult to achieve, and the final dyeing does not meet the minimum fastness required by commercial standards (see Dyes, application and evaluation).

Deep shades and full fastness properties on polyester can be achieved using disperse dyes and carriers, or temperatures over 100°C with or without carriers.

Dye carriers, occasionally called dyeing accelerants, are used on cellulose triacetate fibers, but have found their greatest use in the dyeing of polyester. Many theories have been advanced to explain the mechanism of carrier dyeing. One of these is based on the ability of carriers to solubilize disperse dyes. However, this theory seems untenable because many organic solvents do this and yet do not exhibit carrier properties. Another theory suggests that the carrier coats the individual fibers, forming a layer through which the dye transfers to the fiber. Still another theory suggests that the carrier loosens the binding forces holding the polymer chains together, thus providing suitable spaces for the dye molecules; this is reflected in a lower T_g. An excellent discussion of these theories has been given by a research committee of the American Association of Textile Chemists and Colorists (2). No universal agreement exists on the mechanism of carrier dyeing.

1. Carrier Properties

Many substances show carrier behavior, and some have found more acceptance than others for various reasons, eg, availability, cost, environmental concerns, ease of handling, odor, etc. Most carriers are aromatic compounds, and have similar solubility parameters to the poly(ethylene terephthalate) fibers and to some disperse dyes (3).

There are many chemicals, by lowering T_g, suitable as carriers. Their bp is one of the principal criteria in selection. If bp is too low, the compound will evaporate from the dyebath at dyeing temperatures, and will be

Table 1. Rate of Water Imbibition of Fibers Comparedto Viscose[a]

Substrate, fiber	Water imbibition, %
viscose (rayon)	100
cellulose acetate	25
cellulose triacetate	10
polyamide (nylon)	11–13
polyacrylic	8–10
polyester	3
polypropylene	0

[a] Ref. 1.

lost before it is effective in its role as a carrier. It may also steam distill (condense on the cooler parts of the equipment) and cause drips that will spot the fabric. On the other hand, if the bp is too high, the compound cannot be removed from the fabric under normal plant drying conditions and will affect lightfastness of finished goods, leave residual odor, and possibly cause skin irritation to the wearer.

o-Phenylphenol was one of the earliest carrier-active compounds used industrially. Originally it was used as its water-soluble sodium salt (4). By lowering the pH of the dyebath, the free phenol was precipitated in fine form and made available to the fiber. However, proprietary liquid preparations containing the free phenol are available that afford a greater ease of handling.

Table 2 lists the four main groups of compounds most commonly used as dye carriers. In order for these compounds to act effectively as carriers, they must be homogeneously dispersed in the dyebath. Because the carrier-active compounds have little or no solubility in water, emulsifiers are needed to disperse these compounds in the dyebath (see Emulsions).

2. Emulsification

Proper emulsification is essential to the satisfactory performance of a carrier. A well-formulated carrier readily disperses when poured into water, and forms a milky emulsion upon agitation or steaming. It should not cause oil separation upon heating or crystallization and sedimentation upon cooling.

Many proprietary carries are available as solids (flakes or pellets) or in preemulsified form. These present some difficulties in the dyehouse. The former require dispersion in water through steam injection and addition to a preheated dyebath. The latter suffer from short storage life owing to separation of the emultion. Currently the industry prefers clear products easily emulsified by premixing with water at the time of use.

Manufacturing of the flake and pellet forms requires melting of the various components. The mass solidifies upon cooling and can be flaked or pelletized according to need.

The preemulsified carriers contain water. These products usually require homogenization through colloidal mills or similar equipment to reduce the particle size and ultimately stabilize the product. The preemulsified as well as the clear self-emulsifying products require the use of a solvent when the carrier-active material is a solid.

3. Carrier Formulation

The formulation of a carrier depends on four considerations: (*1*) the carrier-active chemical compound; (*2*) the emulsifier; (*3*) special additives; and (*4*) environmental concerns. Additional parameters to be considered in the formulation of a carrier product with satisfactory and repeatable performance arise from the equipment in which the dyeing operation is to be carried out. The choice of equipment is usually dictated by the form in which the fiber substrate is to be processed, eg, loose fiber, staple, continuous or texturized filament, woven or knot fabric, yarn on packages or in skeins (see Textiles).

The carrier-active chemical is selected according to its effectiveness at various temperatures. Members of the phenolic group (Table 2), considered to be stronger carriers, are employed for formulations to be used in open equipment at the boil. Weaker carriers, such as the members of the aromatic ester group, are utilized generally for high temperature dyeing.

The emulsifier is seldom a single surfactant but a blend selected according to the hydrophilic–lipophilic balance (HLB) required by the chemicals employed. The performance of the final carrier preparation is limited to the effectiveness of its emulsification system. It provides the initial fine dispersion throughout the dyebath, and prevents the carrier from separating and causing spotting or uneven dyeing throughout the dyeing cycle. The system must supply effective reemulsification of the steam-distilled chemicals that drop back into the dyebath and onto the fabric. Finally, the emulsifier produces the foaming characteristics of the product that determine the suitability of the carrier for use with different types of equipment. For example, a carrier intended for use on jet dyeing equipment is formulated with low foaming nonionic surfactants (see Surfactants).

Special additives are often included in a carrier formulation to provide specific properties such as foam control, stability, and fiber lubrication during dyeing. Most important are the solvents used to solubilize the solid carrier-active chemicals. These often contribute to the general carrier activity of the finished product. For example, chlorinated benzenes and aromatic esters are good solvents for biphenyls and phenylphenols. Flammable compounds (flash point below 60°C) should be avoided.

4. Carrier Selection

A carrier is selected by the dyer according to various criteria. The type of equipment and conditions under which it is to be used have already been mentioned. Other considerations include color yield, dye migration, and product and emulsion stability.

4.1. Color Yield

The amount of dye successfully removed from the dyebath by the fiber results in a specific depth of shade or intensity of coloration (see Color). This is commonly called color yield. The color-building properties of a carrier are influenced by other factors, such as the fiber to liquor ratio (its concentration in the dyebath), the maximum temperature that can be reached on the chosen machine, and other dyebath additives. Most carriers give optimum dye utilization in atmospheric dyeing (95–100°C) at 8–12% calculated on the weight of the fiber (owf). In low pressure dyeing equipment (106–110°C), 4–6% owf is usually required. In high pressure equipment (126–132°C), the amount of carrier used can be reduced to 1–3% owf. Above these limits of optimum carrier concentrations, the equilibrium between fiber, dye, and water is switched in favor of the dyebath, and higher amounts of carriers act as shade-reducing agents, as shown in Figure 1.

4.2. Dye Migration

Dye carriers promote dye migration and transfer, thus producing level and satisfactory dyeings.

The dyestuff is exhausted out of the dyebath and into the fiber with the assistance of carriers and heat. This process can be reversed by the use of an excessive amount of carrier, the depth of shade can be greatly reduced, and the dyestuff returned to the dyebath (stripping effect). This phenomenon is utilized to level an unevenly dyed fabric. Some carriers are more effective than others in promoting dye migration and equalizing the dye distribution through the fiber substrate. Defectively dyed fabrics showing streaks or unlevelness (shade

Table 2. Compounds Most Commonly Used as Dye Carriers

Compounds	CAS Registry Number	Mol wt	Bp, °C
phenolics			
o-phenylphenol	[90-43-7]	170.2	280–284
p-phenylphenol	[92-69-3]	170.2	305–308
methyl cresotinate	[23287-26-5]	166.0	240
chlorinated aromatics			
o-dichlorobenzene	[95-50-1]	147.0	172–178
1,3,5-trichlorobenzene	[108-70-3]	181.45	214–219
aromatic hydrocarbons and ethers			
biphenyl	[92-52-4]	154.2	255.9
methylbiphenyl	[28652-72-4]	168.24	255.3
diphenyl oxide	[101-84-8]	170.0	259.0
1-methylnaphthalene	[90-12-0]	142.2	244.6
2-methylnaphthalene	[91-57-6]	142.2	241
aromatic esters			
methyl benzoate	[93-58-3]	136.14	198–200
butyl benzoate	[136-60-7]	178.22	250
benzyl benzoate	[120-51-4]	212.24	323–324
phthalates			
dimethyl phthalate	[131-11-3]	194.18	298
diethyl phthalate	[84-66-2]	212.18	298
diallyl phthalate	[131-17-9]	246.25	290
dimethyl terephthalate	[120-61-6]	194.18	284

variations from side to center or from one end of a length of fabric to the other) are usually repaired by treating them with two or three times the amount of carrier normally required in dyeing.

Barré is caused by uneven tension in knitting, defective yarn, improper needle action, or other similar factors that are not recognized until the fabric is dyed. It appears as a repetitive characteristic pattern of varying intensity that is easily recognizable.

Its causes may be mechanical or chemical: variations in knitting tension cause lack of uniformity of fabric density that in dyeing produce the barré effect, and different degrees of crystallinity of the polymeric fiber owing to uneven drawing or subsequent heat treatments of the filament are also responsible for barré. Dye carriers in combination with selected dyes are instrumental in overcoming this condition.

4.3. Product Stability and Emulsion Stability

These properties are not necessarily related, but are both highly prized in the selection of a carrier. The first refers to the storage or shelf stability of the product. Many carrier preparations are not properly balanced, or unsuitable emulsifiers have been used. Upon storing, these products separate in layers, particularly when exposed to temperature changes.

Emulsion stability refers to the stability of the emulsion in water. It must withstand various dyebath conditions.

4.3.1. The Dilution Factor of the Dyebath

The amount of water in a dyebath may vary from 5–25 times the weight of fiber to be dyed, according to the capacity and type of equipment employed. The larger water-to-fiber ratio dilutes the emulsifier, thus reducing its effect.

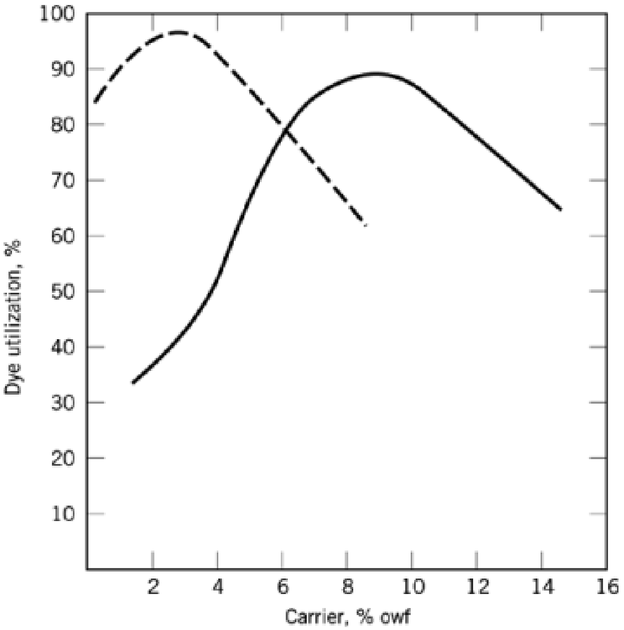

Fig. 1. Dyestuff utilization as a function of carrier concentration. (—), 98°C; (— — —), 120°C.

4.3.2. Elevated Temperatures of the Dyebath

Emulsions that are stable in cold or warm water lose their stability at higher temperatures. The carrier-emulsifier equilibrium undergoes stress, particularly when the time at high temperature is prolonged.

4.3.3. Agitation and Shear Action of the Dyebath

In some equipment fabrics are rotated through the dyebath, thus keeping it in constant agitation. In other equipment the dyebath is circulated through the fabric or yarn. In jet equipment the high speed circulation of the liquid is responsible for the rotation of the fabric. Although agitation contributes to the stability of certain emulsions, the high shear of the pumps used in the equipment with forced circulation is often detrimental.

4.3.4. pH and Electrolyte Content of the Dyebath

A pH of 4–5 provides the best conditions for dyeing polyester with disperse dyes. A carrier emulsion must be stable under this condition. In addition, when cellulose is present in a fiber blend with polyester and it is to be dyed in the same dyebath with direct or fiber-reactive dyes, the carrier emulsion needs to have considerable stability to large amounts of inorganic salts. Sodium chloride or anhydrous sodium sulfate are employed for this purpose in 10–50% owf.

4.4. Other Considerations

Some carrier-active products, especially *o*-phenylphenol and methylnaphthalenes, have an adverse effect on the lightfastness of the finished dyeing. The reason for this is not clear, but the effect is readily established. This problem is overcome by submitting the dyed material to temperatures higher than those normally required in drying. Under the conditions (150–175°C) that are usually required to heat-set dyed fabrics or to cure resins applied in finishing operations, the residual carrier is volatilized.

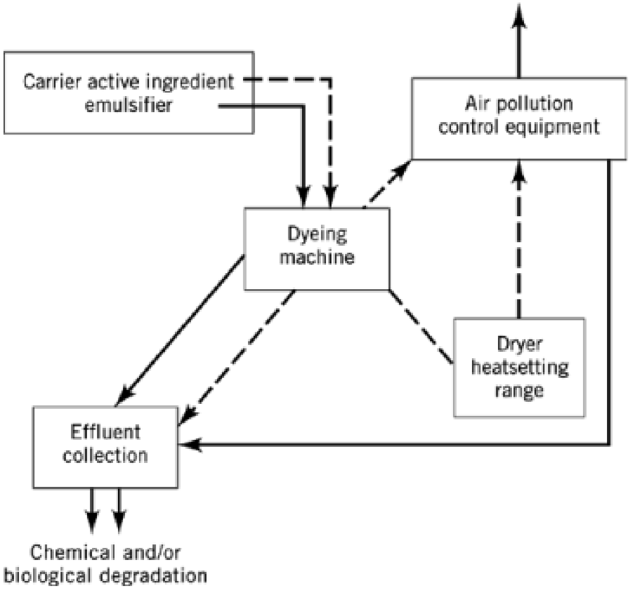

Fig. 2. Air and water pollution controls for dye carriers.

The cost of a carrier, in addition to its satisfactory performance in dyeing, is often a considerable factor in selection. The rising cost of petroleum-derived chemicals is a factor in the price structure of carrier-active chemicals and most carriers, unfortunately, fall in this category.

5. Dyeing Procedures

Dyeing procedures vary according to the fiber content of the textile material and the equipment to be used. Examples of basic carrier dyeing proceduresare as follows.

5.1. 100% Polyester Fabric Dyed Atmospherically

The dyebath is prepared with water conditioning chemicals as needed to control the hardness of the water being used. Dispersion of the dyes is done by pasting them with cold water and diluting them with warm water (70°C). The dye dispersion is added to the bath and the equipment run for 10 minutes. Addition of 5–10 g/L of carrier is done following the dilution procedures recommended by the manufacturer. Acetic acid is used to adjust pH to ca 5. The system is brought to a boil in 30–45 min, and held at the boil for at least 1 h before checking the shade. After slow cooling and rinsing completely, the bath is dropped and an afterscour is done as required to remove residual carrier and unfixed dye.

5.2. 100% Polyester (Textured or Filament) Dyed Under Pressure

The dyebath (50°C) is set with water conditioning chemicals as required, acetic acid to ca 5 pH, properly prepared disperse dyes, and 1–3 g carrier/L. The bath is run for 10 minutes, then the temperature is raised at 2°C/min to 88°C and the equipment is sealed. Temperature is raised at 1°C/min to 130°C, and the maximum temperature held for 1/2–1 h according to the fabric and depth of shade required. Cooling to 82°C is done at

1–2°C/min, the machine is depressurized, and the color sampled. The shade is corrected if needed. Slow cooling avoids shocking and setting creases into the fabric. Afterscour is done as needed.

6. Economic Aspects

Manufacturing capacities and sales volumes of dye carriers are difficult to assess because the materials used are made by many companies for use in a variety of applications. Companies manufacturing dye carriers include:

Apollo Chemical Corp.z
Applied Textile Technologies Inc.
BASF, Fibers Division, Dispersions & Textile Chemicals Group
Burlington Chemical Co.
Chemonic Industries Inc.
Ciba-Geigy Corp., Dyestuff & Chemicals Division
CNC International LP
Crompton & Knowles Corp., Dyes & Chemicals Division
Dexter Chemical Corp.
Eastern Color & Chemical Co., Pigment Division
Emkay Chemical Co.
Finetex Inc.
Glo-Tex Chemicals Inc.
Grant Industries Inc.
Gresco Mfg. Co.
A. Harrison & Co.
High Point Chemical Corp.
Hoechst-Celanese Corp., Colorants & Surfactants Division
Hydro Labs Inc.
ICI Americans Inc.
IVAX Industries Inc., Textile Products Division
Leatex Chemical Co.
Lenmar Chemical Corp.
Marlowe-Van Loan Corp.
MFG's Chemical & Supply Co.
Mobay Corp., Dyes, Pigments & Organics Division
Novachem Corp.
Organic Dyestuffs Corp.
Piedmont Chemical Industries Inc.
Reilly-Whiteman Inc.
Rhône-Poulenc Inc.
RPM American Emulsions Co.
Sandoz Chemicals Corp.
Specialty Chemicals Co.
Stockhausen Inc.
Surpass Chemical Co.
Sybron Chemicals Inc.
Troy Chemical Corp.
Union Carbide Chemicals & Plastics Co.
Unitex Chemical Corp.
The Virkler Co.
Witco Corp., Organics Division

7. Health and Safety Factors

Most carrier-active compounds are based on aromatic chemicals with characteristic odor. An exception is the phthalate esters, which are often preferred when ambient odor is objectionable or residual odor on the fabric cannot be tolerated. The toxicity of carrier-active compounds and of their ultimate compositions varies with the chemical or chemicals involved. The environment surrounding the dyeing equipment where carriers are used should always be well-ventilated, and operators should wear protective clothing (eg, rubber gloves, aprons, and safety glasses or face shields, and possibly an appropriate respirator). Specific handling information can be obtained from the supplier or manufacturer.

OSHA and EPA have established exposure limits that must be carefully considered in relation to the waste disposal method available and the environment in which dye carriers are to be used. Some are only skin irritants, whereas others can contribute to air and water pollution. Atmospheric dyeing equipment should be exhausted to scrubbers that wash the vapors into the general plant effluent for chemical or biological degradation. The same system applies to drying and heat-setting equipment where residual carriers are

Table 3. LD_{50} and Threshold Limit Values for Compounds Most Commonly Used as Dye Carriers[a]

Compound	TLV (in air)[b]	LD_{50} mg/kg[c]	Title III Sara[d]	Clean air[d]
phenolics				
o-phenylphenol		2700	yes	
p-phenylphenol				
methyl cresotinate				
chlorinated aromatics				
o-dichlorobenzene	50 ppm	500	yes	
trichlorobenzene	5 ppm	756	yes	yes
aromatic hydrocarbons and ether				
biphenyl	0.2 ppm	3280	yes	yes
methylbiphenyl				
diphenyl oxide	1 ppm	3370		
methylnaphthalene		4360		
aromatic esters				
methyl benzoate		2170		
butyl benzoate		5140		
benzyl benzoate		1700		
phthalates				
dimethyl phthalate	5 mg/m^3	6900	yes	yes
diethyl phthalate	5 mg/m^3	5058	yes	
diallyl phthalate		770		
dimethyl terephthalate		4390		

[a] Data extracted from Ref. 5.

[b] TLV indicates the upper limit to which workers can be exposed without adverse effect in an 8-h day.

[c] LD_{50} values are for rat-oral (ingestion) except for diethyl phthalate which is rat-intraperitoneal.

[d] Yes indicates that compound is listed in act.

completely volatilized out of the dyed fibers. A schematic illustration for the control of air and water pollution is shown in Figure 2 (see Air pollution control methods).

Sara title III, section 313, Clean Air Act 1990, threshold limit values, and LD_{50}s are given in Table 3 for the substances for which data are available. Additional information is continuously being developed to provide guidelines for the safe handling of dye carriers and carrier-active chemicals.

The increasingly stringent government regulations and the introduction of carrierless–dyeable polyester have not substantially affected the use of carriers. The factor with the greatest impact on their use has been provided by the spectacular technological advances in dyeing equipment that have taken place since the early 1980s. High temperature dying has greatly reduced the time element (dyeing cycle) and the need for carriers.

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