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Chapter 14: Pigments as Textile Colorants: Pigmenting or Pigmentation

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P aleolithic man discovered the use of pigments for decorative purposes some 30,000 years ago. The cave paintings of Lascaux, France, are wonderful examples, dating from 28,000-22,000 B.C. Some of the pigments used then were earth pigments including natural iron oxides and carbon black from soot. Refined versions of carbon black are still heavily used today under the generic name C.I. Pigment Black 7, as are a variety of natural and synthetic iron oxide pigments; e.g., C.I. Pigment Brown 6 types.

Despite man's early experimentation with and decorative use of pigments, the application of pigments to textiles got off to a much later and rather shaky start. This was because the natural materials available as binders, for attaching the pigments to the fiber surfaces, gave results

ABSTRACT

Pigments are used for the coloration of many different substrates, a few of which are textile. The physical and chemical nature of pigments is discussed. Fibers can be colored by pigments in one or more of four different ways-by continuous pigment padding, by batch exhaustion or deposition processes in which pigment dispersions are attracted to suitably treated fiber surfaces, by printing and by mass pigmenting molten polymer or polymer solutions prior to extrusion. In three of these cases an appropriate binder polymer is needed to entrap the pigment in a layer which adheres to the fiber surfaces. In the case of mass pigmenting, the binder is the fiber forming polymer itself.

KEY TERMS

Binders Coloration Dope Dyeing Exhaust Pigmenting Mass Pigmenting Pigment Padding Pigment Printing Producer Coloration Solubility which always had some combination of poor hand and poor durability to washing. These binders included drying oils—e.g., linseed oil, albumen and casein—all of which were perfectly satisfactory for use as artists colors, for painting canvases, but not for normal textile applications.

As might have been anticipated, the earliest serious interest in textile pigmenting went side by side with the Industrial Revolution and the resulting development of continuous engraved roller printing in the late 18th century. Here, in the coloration of small areas (blotches) and fine lines, the early deficiencies of binder hand were least apparent, and the painted feel of the fabrics was minimized.

The general application of pigments to textiles had to wait for the maturing of the polymer industry in the middle of this century before satisfactory synthetic polymer binders could be found. Excellent sources on pigments in general (1), pigmentation of textiles (2) and on the development of pigment printing between 1934 and 1984 (3) are available.

Colorants

Most would agree that any material which can be added or applied to a substrate to give it color may be referred to as a colorant and the process of addition or application can be referred to as coloration or simply coloring. The resulting product will be colored.

Most would agree that colorants may be either dyes or pigments. However, there are probably no two sets of words which are more abused in the whole area of textile coloration than those related to dyes and pigments, the products and their application.

Before the problems can be understood and resolved, it is first necessary to be quite sure what is meant by the words dyes and dyeing, pigments and pigmenting or pigmentation.

The nature of dyes and dyeing will be reviewed before the nature of pigments and pigmenting (pigmentation) are introduced.

Dyes

Dyes are highly colored, aromatic-organic molecules, anions or cations of modest

size, with relative molecular masses (rmm) ranging from as low as 200 to significantly more than 1000. If the organic materials are ionic they are accompanied by simple oppositely charged, inorganic counter-ions such as sodium ions, Na⁺, or chloride ions Cl⁻, rmm 23 and 35.5. Dyes may also include transitional metals—e.g., copper, nickel, cobalt, and chromium—incorporated in the molecules as dye-metal co-ordination complexes; e.g., premetallized dyes.

Dyes are either intrinsically soluble in water (with a wide range of solubilities) or can be made soluble in the medium in which dyeing is conducted. The medium is usually water, but in the special case of disperse dyes applied by thermofixation, the disperse dyes can sublime, become molecules of colored gas and dissolve in the surrounding air.

Dyes are used principally in the textile and paper industries, and are usually applied from water to substrates for which the water soluble colorant has some substantivity in the conditions of dyeing. Significant amounts of dyes are also used to make pigments (see later).

Dyeing

Dyeing is the collective name given to the processes whereby colors are dissolved, transported to the fiber surface and, as individual molecules or ions, diffuse into the fibers for which they have some substantivity. The soluble molecules or ions pass from an external phase, outside the fiber, and into the internal or fiber phase. This may be followed by further process steps to ensure the resistance of the soluble, diffusible ions to easy removal from the fiber by water (the solvent).

The variety of different application categories of dyes has already been discussed. Of these, acid, basic, direct and reactive dyes all dissolve quite readily in water to give aqueous solutions containing individual dye ions; i.e., the dyes can be monomolecularly dispersed. The nonionic disperse dyes are only sparingly soluble in water, but the solubility rises with temperature and the dyes do dissolve to give aqueous solutions containing individual dye molecules.

In all these cases, it is the individual ions

Pigments

or molecules which have some level of substantivity for a particular fiber under the conditions of dyeing. Diffusion into the fiber does not end the story for reactive dyes, which must react with the fiber once they are within the fiber phase.

Of the remaining three dye application categories, some purists might say that vat and sulfur dyes are not dyes at all, because they are not intrinsically water soluble like dyes in the five categories mentioned above. If this seems to be a problem, it can be avoided by calling them vat and sulfur colors. However, they can be made to dissolve in water by alkaline reduction and once dissolved the solutions contain individual anions. And these anions are substantive to cellulose and can be transported from the external (aqueous) dyebath phase into the internal fiber phase like acid and direct dyes. Once this has happened, the original water insoluble colors are restored by acid oxidation.

There is no doubt that the sum of the processes involved in getting sulfur and vat colors into (not merely onto) the fibers can legitimately be called dyeing, which is why the colors themselves are usually referred to as dyes.

Azoic combinations are not dyes at all, and the two components may not even be highly colored. Nonetheless, the process by which the water soluble naptholate ions are encouraged to pass from the dyebath and into the fiber has the characteristics of a dyeing process.

Dyes in Solution

Just for the purpose of illustrating how small a single dye molecule (or ion) is, a one gram sample of pure C.I. Basic Green 4 (rmm 400) can produce about 15×10^{20} individual colored cations. These cations are obviously extremely small. The size of this cation is one of the factors which helps determine the rate of diffusion of dye into the fiber.

Pigments

Pigments may be white as well as colored; contrast this with dyes. There are pigments which are entirely aromatic-organic or organo-metallic co-ordination compounds. These are known as toners in the U.S. The toners are misleadingly referred to as pigment dyes in the U.K. (see later under Nomenclature).

There are other pigments which are insoluble, inorganic salts of soluble organic dyes. These types can be further extended (diluted) with insoluble inorganic substrates such as alumina or barium sulfate. Such pigments are known as lakes in the U.S.

There are still other pigments which are completely inorganic and contain no aro-

matic carbon, such as the white titanium dioxide, TiO_2 , and the yellow, brown and black iron oxides; and there is the important carbon black which is organic but not aromatic.

With a few notable exceptions, it is the toners which are used in textile coloration.

The biggest difference between dyes and pigments is that pigments are not soluble in their application medium and contain no available water solubilizing groups (see later).

The most complete working definition of a pigment known to the author is that proposed by the Colored Pigment Manufacturers Association (4). The definition particularly addresses the differences between dyes and pigments.

"Pigments are colored, black, white or fluorescent particulate organic and inorganic solids which usually are insoluble in, and essentially physically and chemically unaffected by, the vehicle or substrate in which they are incorporated. They alter appearance by selective absorption and/or by scattering of light. Pigments are usually dispersed in vehicles or substrates for application, as for instance in inks, paints, plastics or other polymeric materials. Pigments retain a crystal or particulate structure throughout the coloration process.

"As a result of the physical and chemical characteristics of pigments, pigments and dyes differ in their application; when a dye is applied, it penetrates the substrate in a soluble form after which it may or may not become insoluble. When a pigment is used to color or opacify a substrate, the finely divided insoluble solid remains throughout the coloration process."

About This Series

THIS is the twenty-third installment in this series of papers on dyes and their application. Previous installments have covered the application of anions to nonionic fibers (October 1991), direct dyes (November and December 1991), vat dyes (January and February 1992), sulfur dyes (March and April 1992), reactive dyes (May and June 1992), azoic combinations (August and September 1992), the application of nonionic dyes to fibers (October and November 1992), disperse dyes (December 1992 and January 1993), the application of ionic dyes to ionic fibers (February and March 1993), acid dyes (April 1993), continuous nylon carpet dyeing (May 1993), basic dyes (June 1993) and dyeing blends (August and September 1993). The series is intended to serve as an introductory text and source book for those who want to expand their understanding of the technology of dyeing and coloration. The author, a frequent contributor to TCC and a member of its Editorial Board, is a professor of textile chemistry at Clemson University.

Pigments for textiles have no intrinsic substantivity for fibers and are not generally found in monomolecular (solution) form but rather in the form of very finely divided water dispersible particles which have a surface negative charge. The charge is due to the attraction of the hydrophobic tails of anionic dispersant molecules for the surface of the particles. while their hydrophilic anionic (negatively charged) heads project into any water surrounding the particles. A crude schematic of this situation is shown in an earlier chapter of this series (5). This negative surface charge has been put to good use in textile coloration, for attracting the pigment particles to fiber surfaces on which cationic (positively charged) groups have been attached.

Pigments are used for a much greater diversity of end use applications than dyes, and can be used to color concrete, cosmetics, ceramics, elastomers, food, magnetic tapes, paints, paper, plastics, printing inks and, of course, textile fibers. Major chemical companies separate their pigment and dye divisions because both the products and the markets are quite distinct. Pigment application to textiles represents a modest but significant overlap.

Pigmenting (Pigmentation)

Any pigments applied to textile fibers from an external medium-e.g., pad liquor, color bath, print paste-will require the additional use of polymeric materials, known as binders, to encapsulate the particles deposited on the fiber surfaces and hold them on the surface by virtue of the adhesion between the fiber and the binder. This adhesion has nothing to do with the pigment but depends on the characteristics of the binder. The same is true of the hand of the finished fabrics. Clearly the binder is an addition which is a necessary complement to the pigment. The binder has no parallel in dyeing technology.

Without the binder, the particles deposited on the fiber surfaces will wash off, crock and abrade from the fibers without difficulty and will reveal the unpigmented base color of the fibers beneath. The pigment particles will have been too large to penetrate into the fibers.

In mass pigmenting, the polymer in the spinning dope can act as its own binder and, after extrusion of the dope, the pigment particles are trapped within the fiber.

In summary, binder films should be chemically and physically inert with respect to acids, alkalis, chlorine bleaches, nitrogen oxides, ozone, UV and visible light and, under hot pressing conditions, should neither discolor nor be thermoplastic.

Pigment Dispersions

Pigment dispersions, like those of vat

colors and disperse dyes, contain particles which have a distribution of different sizes (all small). The particle sizes and their distribution can depend on both the nature of the pigment and the intended end use. However, it is safe to say that the majority of properly dispersed organic pigment particles have diameters of one micron $(1 \times 10^{-6} \text{ meters})$ or less.

A particle of diameter 0.5 microns $(0.5 \times 10^{-6} \text{ meters})$ could contain in the order of 100 million (10^8) molecules even though the particle diameter is only of the same order of magnitude as the wavelengths of visible light $(0.4-0.7 \times 10^{-6} \text{ meters or } 400-700 \text{ nanometers})$. Compared to the size of a single pigment or dye molecule, a minute pigment particle suddenly looks very large.

It is not surprising that pigment particles cannot diffuse into fibers as dye molecules can by slipping between the fiber molecules.

Pigment Physical Properties

There are two physical properties of pigments which materially influence the appearance of substrates in which the pigments have been dispersed. Neither of these properties is important when dealing with dyes. The properties are the differential refractive index—i.e., the difference between the refractive index of the pigment and the refractive index of the binder medium—and the particle size and particle size distribution.

Without examining either of the properties rigorously, the description of a simple experiment can show how both of them affect the color appearance of a pigment-binder combination.

Prepare three different samples of pyrex (borosilicate) glass from glass tubing such that one sample is short pieces of broken tubing, the second is crushed granular glass and the third is very finely divided (milled) glass power. These represent insoluble pigment in three stages of particle size reduction.

The first sample should be essentially transparent, the second glittering crystalline particles, the third a fine white powder.

Place an amount of each glass sample into a test tube and just cover with water, to represent a binder. The glass-water combinations in each of the three test tubes will look slightly different from the three original samples in air—one virtually transparent, one less so and one an opaque white.

Place a further amount of each sample into one of three more test tubes and just cover with a 14:86 methanol:benzene mixture. The glass-solvent combinations in each of the test tubes will all appear essentially transparent with little or no visual evidence of the glass. The glass will seem to have disappeared.

The reasons for the two sets of observa-

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tions are as follows. In the first set of observations, the refractive indexes of water and borosilicate glass are about 1.33 and 1.46 respectively. Therefore, light passing from water-glass-water will be refracted, reflected and scattered rather than transmitted. The smaller the particle size the more light is scattered and less light is transmitted. The refractive index difference between the glass (pigment) and the water (medium, vehicle or binder) accentuates the effect. But in the second set of observations, the refractive indexes of the borosilicate glass and the methanol: benzene mixture are both 1.46. Therefore, in the second set of observations the light passes unrefracted and unscattered through both the solvent and the glass and the combinations all look transparent regardless of the particle size of the glass.

The conclusion is that to get the greatest degree of opacity out of a pigment-binder combination, the pigment should have a much higher refractive index (R.I.) than the binder and its particle size should be very fine.

Herein lies the importance of titanium dioxide. Depending on which of the two principle crystalline forms is chosen, the refractive index is about 2.8 for the rutile form and 2.5 for the anatase form. No polymeric binder comes close! These pigments can be very finely ground and are used in countless applications—e.g., oil and latex paints, man-made fibers—where opacity and an ability to hide the background surface (hiding power) are required.

Some inorganic pigments can have high refractive indexes called hiding or prime pigments. Others have low refractive indexes-e.g., silicas, R.I. 1.46, called filler or extender pigments. By contrast the organic aromatic and premetallized pigments (toners) have refractive indexes close to those of the binders, which render the pigment-binder combinations transparent. Note that the reason only approximate refractive indexes are given is that they depend not only on the wavelength of incident light but also on the direction in which the light passes through the crystal lattice of the pigment. Some pigments are colored because they selectively absorb some wavelengths of visible light more than others. It is the specificity and intensity of this light absorption which gives many organic pigments their intense and brilliant colors.

Binders

As has been noted already, binders are an essential component of the padding, printing and batch exhaustion or deposition methods of textile pigmentation. The development of binders has been discussed (3,6) particularly in reference to printing.

Most binders in use today are applicable in completely aqueous systems. They are in the form of dispersions of water insoluble droplets of compositions containing low molecular weight prepolymers (macromolecules) often based on acrylates, styrene acrylates, styrene butadienes or vinylacrylates. The droplets are of comparable sizes with those of the pigment particles, usually less than 0.5 microns in diameter.

In the drying and curing phases of pigmentation, the droplets coalesce (fuse) to form a film only a few microns thick in which the pigment particles become embedded and trapped on the fiber surfaces. The resistance to removal of a particular binder film may be enhanced by including reactive groups in the macromolecules which under curing conditions cause the binder polymer molecules to crosslink with others to form a much more intractable polymer network.

The crosslinked polymer will swell less readily and this will enhance the durability of the film to wet treatments. However, too much crosslinking can result in the film's becoming too rigid and the desired hand can be lost.

This small section is not the place to examine the details of binder manufacture, as it requires a considerable amount of formulating experience. Suffice it to say, the detailed physical properties of the binder film are responsible for all of the apparent washfastness, crocking and rubbing fastness and abrasion resistance of the entrapped pigment, as well as the hand characteristics of the resultant pigmented fabrics. Not only this, but the binder dispersions should have good stability to electrolytes, and must be easily cleaned up afterwards.

It is noteworthy but not surprising that the same binder chemistry will not be equally suitable for all the fibers and fabrics to which pigments might be applied. Different binders will be needed for cotton, as opposed to fibers such as glass or polypropylene.

Nomenclature

There is no reasonable justification for using the word dye when the correct word is pigment, or dyeing to describe the processes of applying pigments to fibrous substrates such as textile goods. The words pigmenting and pigmentation are easily understood and are the correct words for the purpose. It has been shown that the terms dyeing and pigmenting, or dyes and pigments, have little besides color in common and in the case of inorganic white pigments they do not even have that.

The nomenclature trap is easy to fall into! Even the AATCC Buyer's Guide (7), in the section listing Dyes and Pigments by Colour Index Generic Names, has a subheading Pigment Dyes. Since the words pigment and dye are contradictory in most circumstances (a typical oxymoron), what is a pigment dye? On the other hand, why bother looking for an explanation when in this particular case Pigment is the correct subheading?

Some Europeans have favored the term pigment dye for special purposes. However in the U.S. the term is unnecessary, generally confusing, frequently misused and should be avoided.

Unfortunately, further consideration of nomenclature cannot be avoided. The next sections, which deal with four methods of pigmenting textiles, will be littered with terms which are deliberately chosen to avoid ambiguities and which may not be the ones to which the reader has been exposed. It is because pigment and dye technologies have grown up separately that their terminologies are not always compatible. The same is true of the textile coating and finishing businesses.

Pigment Padding

There is no purpose served by padding a pigment onto a textile fabric if it is not accompanied by a binder, unless it is destined to be chemically transformed into a soluble substantive anion—e.g., the pigmentary vat colors. The section could be headed Pigment/Binder Padding but since the binder is essential its presence may be assumed. This process should not be referred to as Pigment Pad Dyeing since neither dyes nor dyeing processes are involved.

Like any other color application category, pigments have their advantages:

• Pigments are not generally considered substantive (see later) and as a result can be applied continuously to each and every single fiber and blended fiber fabric for which a suitable binder system can be found.

• Pigmenting procedures are simple and involve equipment which is readily available in a dyeing and finishing plant. This can be as extensive as a good padder; a vacuum extractor to remove much of the unbound pad liquor, to lower wet pickup, to decrease migration, and as a result to allow increased fabric speeds and give improved appearance; a predryer, also to e. minimize migration; dry cans, and finally, a tenter frame with very well controlled temperature and temperature uniformity for curing the goods at an acceptable width. However, with the correct choice of pigments, binders and antimigrants, a padder and a tenter frame may sometimes suffice.

• Pigments are economical at depths of shade up to about 1% owg but this value is

only a general rule of thumb. Pigmenting and resin finishing can often be combined, which eliminates one process step in the production of finished goods and lowers the costs.

• Pigments have a fairly good color gamut, and with selection, high color fastness to light, drycleaning, gas fumes, chlorine (as aqueous hypochlorites) and perspiration can all be achieved.

But pigments also have their disadvantages.

• The abrasion resistance and hand of the goods are very dependent on the correct choices of a softener and the binder, and with heavy depths, particularly on lightweight or heavy weight fabrics, the results may be unsatisfactory.

• Very heavy or very bright shades may require selection of an appropriate, alternative dye application category. Carbon black is no match for sulfur blacks; navies are better dyed with vats, sulfurs or azoics, and reactive dyeings can be considerably brighter than most pigmented goods although there are some brilliant specialty fluorescent pigments of generally poor lightfastness.

Incidentally, it was these same brilliant fluorescent pigments which were widely used in all kinds of pop fashion wear and beachwear two or three years ago, either as single colors or as pigment prints. Undoubtedly they will return at some future time.

Pigment Padding Procedure

It should go without saying that a very well prepared fabric is one of the principal requirements for ensuring a first quality finished product.

There are only a few ingredients in a conventional pigment pad bath—the pigment dispersion, the binder dispersion (emulsion), the antimigrant, the wetting agent and, for some acrylic binders, ammonia. Occasionally a little defoamer may be needed.

It is essential to ascertain the compatibility of all of these components, particularly when evaluating a new binder or when changing a finishing mix.

The wetters are normally nonionic and low foaming (ca. 1 g/L), and the antimigrants (ca. 10 g/L) are the same soluble polymeric materials used in continuous dyeing of polyester/cotton blends—i.e., colorless synthetic and natural products which rapidly increase the viscosity of the pad mix as water is driven off (8) and cause particle agglomeration, thus lowering the ability of particulate materials to migrate to the drying surface.



The concentration of binder in the mix should increase with the increasing concentration of pigment but it usually falls in the 20-60 g/L of pad mix range.

The padding (with or without the vacuum extractor) should leave the fabrics with from 30-70% wpu depending on the chemical and physical nature of the fabric.

Curing at 175C (350F) for about 90 seconds is usually sufficient.

Pigment Padding and Finishing

The one-bath application of pigment and durable press (DP) or crease resistant finish (crf) reactants or resins on polyester/cotton goods is obviously desirable but is generally limited to lighter shades where there may be not more than about 10 g/L pigment in the pad mix. The reactant-resin can be used at ca. 50-100 g/L and the catalyst at 12-25 g/L.

It is conventional to add the pigment to the pad mix last, immediately after the catalyst. However, it is safer to reverse the order of these last two adds. The problem is the possibility of interaction between the anionic dispersant for the pigment and the cationic metal ions of many catalysts (Mg⁺⁺, Al⁺⁺⁺, Zn⁺⁺; magnesium, aluminum and zinc). The same situation holds if a cationic softener is added. But unlike the catalyst, a different ionic type of softener can be chosen.

Most problems in pigment padding can be attributed to just a few causes—the fabric preparation, the mix (mixing procedure, agitation/stirring, straining, incompatibility), the binder (amount, type, buildup), the pigment (amount, type, buildup), migration on drying (antimigrant and equipment), the auxiliary chemicals and the curing conditions.

All of these can be overcome by attention to procedural details and the recommendations of the pigment/binder manufacturers.

A properly equipped laboratory to evaluate the effects of changing process and product variables is always worthwhile.

Pigment Printing

The subject of pigment printing is in some ways anomalous in a series devoted to dyes and their applications. Printing has not been considered in previous chapters, although almost all of the dye application categories are printed routinely, with the possible exception of sulfur colors. There was some mention of heat transfer printing (HTP) in the section devoted to disperse dyes, but it was only to draw the parallel between HTP and thermofixation, both of which depend on the ability of disperse dyes to sublime. In any case there is a convenient textbook devoted to printing (9).

There are three reasons why a short section on pigment printing is included here. First, the technology was developed and brought to its present status largely as a result of work carried out in the U.S. This is detailed in a paper entitled The Development of Pigment Printing Over the Last 50 Years (3), with 87 references. Second, in the world at large only about 50% of printed goods are pigment printed but in the U.S. the figure is over 70% and over 90% for polyester/cotton blends. Third, it completes the list of four methods for pigmenting fibers.

The beauty of pigment printing is the same as that of pigment padding—it is a simple economical process which is applicable to all types of fibers to produce a fairly good range of colors with high lightfastness. Conversely, the highest levels of fastness to abrasion and drycleaning (solvent) cannot be achieved, and the effect of unsuitable binder on hand, and the possibility of buildup on rolls, in engravings or in screens should be self evident.

A comprehensive paper on printing would have to include sections on printing methods, print paste thickeners, viscosity, discharge, resist and random printing styles and techniques as well as mentioning the flatbed screen, rotary screen and engraved roller printing equipment and means of screen patterning and roller engraving. All these are covered elsewhere (9).

Exhaust Pigmenting

The word exhaust implies a batch process and although the pigment in the following process cannot diffuse into the fiber, it does leave the bath for the fiber surfaces.

This section outlines a small area of color application technology developed as a result of the recent surge of interest in garment dyeing. This interest, in turn, results from the added flexibility in inventory control which retailers would stand to gain if apparel items could be dyed on demand, to meet the dictates of (color) fashion. The buzz words quick response and just-in-time reflect a real need which is easy to articulate but hard to fulfill.

It is true to say that there are serious inherent difficulties associated with dyeing madeup garments. These include the tightness of seams, with associated poor penetration of dye liquors; the presence of foreign objects such as buttons, zippers, sequins etc.; the differences between the dyeability of sewing threads and the garment itself, compounded by the problems of dyeing garments which were durable press (DP) or crease resist finished (crf) in the piece, or alternatively of DP or crf finishing the garments after dyeing.

Consequently, it is probably also true to say that for the foreseeable future garment dyeing will be more concerned with the ephemeral concepts of style and fashion rather than those of quality or luxury. Here then, in a nutshell, is the market niche into which the exhaust pigmenting of garments fits rather conveniently. The elements of exhaust pigmenting (a recent process) appear to be as follows:

• A colorless (polymeric) material with multiple cationic groups is applied to the fibers. With or without substantivity for the internal fiber phase, it will be attracted to the surface negative potential which all fibers show when immersed in water. This parallels the superficial staining of many basic (cationic) dyes on a variety of fibers. The result will be a fiber whose surface is covered with an excess of positive (cationic) charges. The excess pretreatment chemical is rinsed off.

• The pigment dispersion is added to the bath and by virtue of the anionic charge (-) from the anionic dispersing agent which is surrounding and suspending the disperse particles, the particles exhaust from the bath and onto the cationic (+) charges on the fiber surface by means of the same ionic (or coulombic) attraction which dye anions have for cationic fibers, cf. acid dyes on wool.

• The process is completed by means of an aftertreatment that deposits a substantive binder material at the fiber surfaces which binder is cured by the subsequent drying of the goods (garment).

The overall result is very similar to that achieved when pigment padding fabrics, but the mechanism of arriving there is substantially different. Since the pretreatment and aftertreatment chemicals (the particle fixative and the binder) are proprietary, the precise mechanism of the process is uncertain; but there is little doubt that it works quite satisfactorily.

However, the gradual buildup of the somewhat intractable pigment particles on the equipment requires the timely use of a reductive clearing treatment, comprising caustic soda and thiourea dioxide, or an oxidative treatment, with calcium hypochlorite followed by a sodium bisulfite antichlor.

Depending on the liquor-to-goods ratio and the severity of a rinse cycle inserted between exhaustion of the pigment and its treatment with the binder, a number of effects may be achieved which mimic the fashionable stone washing, tie dyeing, acid washing and other visual effects, without the abrasive wear and effluent problems associated with tumbling goods with pumice stones.

Mass Pigmenting

The process whereby pigments are incorporated into synthetic fibers before spinning is absolutely routine. All but the bright grades of man-made fibers contain some amount of the white pigment titanium dioxide as a delustrant, opacifier or a dulling agent. The quantities are usually not more than ca. 0.5% owg.

Routine or not, the following nine terms have all been used to name the process of incorporating pigments into fibers—dope dyeing, extrusion dyeing, mass dyeing, melt dyeing, solution dyeing, spin dyeing, producer coloration, solution coloration and mass pigmenting. There may be more!

Let us agree that several of the words (mass, dope, melt or solution) might apply to man-made polymeric material prior to its extrusion (spinning) by the fiber producer. But if the chemical addition made at this stage (colored or noncolored) is not a dye, the process terms which include the word dyeing are at best misleading and at worst meaningless.

The problem is compounded by the fact that some polymer solutions are in fact colored by dyes (which are soluble in the same solvent as the polymer) prior to extrusion. This is still true of some acetate fibers produced outside the U.S. These polymers are truly solution dyed.

The word coloration is an acceptable hedge to use in avoiding a decision whether the additive is a dye or a pigment. Therefore producer coloration is always correct provided the additive is colored. Solution coloration is always correct provided the polymer is in solution prior to extrusion.

The author leans towards either of the phrases mass pigmenting or producer pigmenting, both of which describe the process quite well. More descriptive, more precise, but also more cumbersome, would be polymer mass pigmenting or fiber producer pigmenting.

Amid this flurry of semantics it should be remembered that, on the rare occasion when all the parties to a communication understand one another, the actual words may not be so important after all, for

"What's in a name? That which we call a rose By any other name would

smell as sweet." (10)

But, too many of us base our communications on the model set up by Humpty Dumpty

"When I use a word ... it

means just what I choose it to

mean-neither more nor less."

"The question is," said Alice,

"whether you can make words

mean so many different things." (11).

The Mass Pigmenting Process

The technology of the mass pigmenting process is built around the means whereby pigments can be uniformly dispersed in a polymer mass (generally a melt) without thermal degradation and prior to extruding (spinning) the pigmented polymer mass into fibers. Most inorganic pigments are relatively inert to thermal degradation but with organic aromatic pigments color changes can occur at temperatures considerably lower than those used to spin nylons or polyester, ca. 280-300C (535-570F).

To facilitate uniform pigment dispersion and at the same time minimize the thermal decomposition of some pigments, the pigments can first be incorporated into a much lower melting carrier polymer,



Color concentrate pellets are injected into the hot mass as shortly as possible prior to extrusion (spinning). The carrier polymer melts rapidly and the polymer mass is homogenized along with the pigment particles. Molten polypropylene is dispersible in molten polyester, but with nylon there are technical limitations to using polypropylene as a carrier polymer.

Benefits of mass pigmenting include the following:

• Polypropylene cannot be satisfactorily colored by any other method. Despite considerable efforts, few dyes and fewer dyeing processes have been developed which give dyeings of satisfactory fastness on polypropylene. Consequently, mass pigmented polypropylene has a good share of the vast commercial carpet fiber market.

• Lightfastness levels which are quite unobtainable with dyes and UV absorbers or other lightfastness enhancing chemicals can be achieved on nylon and polyester (12). This possibility is very interesting to automotive fabric manufacturers.

• The presence of insoluble pigment particles, entrapped within the fiber phase, ensures excellent fastness to wet treatments.

The following drawbacks to mass pigmenting are worth noting:

• In the case of polyester fibers mass pigmented with a polypropylene carrier, there is a tendency for fibers to fibrillate (subdivide into fibrous shards) at the surface boundaries between the polyester and the incorporated polypropylene.

• Large runs and colored waste have been characteristic features of mass pigmenting. Because of the former, ingenious threadline blending techniques have been developed to produce a wide range of yarns of different apparent overall colors from a relatively few basic mass pigmented shades. However, the color flexibility of dyeing processes is nowhere near paralleled by mass pigmenting.

• Batch to batch color variability is a problem which is hard to correct.

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There is no likelihood that mass pig-



Fig. 1. Typical structure of monoazo metallized pigment reds.

menting will replace topical dyeing or pigmentation techniques any time soon, although the automotive and carpet industries can put mass pigmenting to considerably more use than they do at the present time.

Pigments: General and Chemistry

The AATCC Buyer's Guide lists 550 pigment products under 120 different Colour Index names. Of these about 25% are yellows, 40% are reds, 12% are blues and there are lesser percentages of oranges, violets, greens, browns and blacks. The surprising apparent lack of a large number of different blues is easy to explain. The blue copper phthalocyanine chromophore is so dominant, has such outstanding fastness characteristics, is so easy to synthesize, has such a range of chemically substituted and physically different forms that little room is left for other blue or green chromophores.

For textile purposes most pigments are characterized by their inertness and insolubility in water. The products usually are supplied in the form of water dispersible powders, pastes and in a variety of forms in which the surface characteristics of the pigment particle has been modified (resin bonded pigments) or the pigment has been preblended with an appropriate binder. Other pigment forms are available for different markets-e.g., color concentrates for fiber producers. The pigment manufacturers often provide the pigment (dry, as presscake or as flushes) to compounders whose business is to render them into suitable physical forms for a particular user industry.

Like dyes, the potential organic pigment chromophores are legion, but of these only a few will be illustrated by way of examples. They include metallized azo, unmetallized azo, quinacridones, perylenes, phthalocyanines, disazodiarylides and tetrachlorisoindolinones. If organic colors are in question it is hard to escape the azo group (-N=N-).

• Metallized Azo: A series of these pigment products have as their parent organic component the water soluble, sul-



Fig. 3. Quinacridone, the parent compound of quinacridone reds (C.I. Pigment Violet 19).



Fig. 2. Typical structure of monoazo (nonmetallized) pigments reds.

fonated acid dyes of general structure shown in Fig. 1. The substituents may be relatively simple ones: R_1 can be methyl or chloro (-CH₃, -Cl); R_2 can be methyl, chloro, hydrogen or ethyl (-C₂H₅); R_3 can be hydrogen or carboxylic acid (-COOH).

When the sulfonic and carboxylic acid groups are in the form of their sodium salts, the products are typical acid dyes. But the colored salts of metal ions with two or more positive charges—e.g., barium and calcium, Ba^{++} and Ca^{++} —are water insoluble and are referred to as being metallized pigments. This is not to be confused with the premetallized dyemetal co-ordination complexes.

Since several differently metallized pigments are possible from the same acid dye structure, the Colour Index names for the pigments can be given an additional number (see also later). For example, the soluble product C.I. Pigment Red 48 (another nomenclature problem) is the parent dye from which several metallized pigments are derived-e.g., C.I. Pigment Reds 48:1 (the insoluble calcium salt) and 48:4 (the insoluble manganese salt). Here $R_1 = -H, R_2 = Cl and R_3 = COOH.$ Other families of differently metallized pigments include those based on C.I. Pigment Reds 52, 53 and 57 (also water soluble acid dyes prior to metallization).

• Unmetallized Azo: A number of red pigments are derived from the general structure shown in Fig. 2, where R_1 can be a methyl, chloro or nitro group, and R_2 can be a nitro, chloro or hydrogen group. There is no need to metallize such products and they have no intrinsically water soluble salt forming groups. Examples include C.I. Pigment Reds 1, 3 and 4 where R_1 and R_2 are -NO₂ and -H; -CH₃ and NO₂; -NO₂ and -Cl, respectively.

• Quinacridone: Fig. 3 shows the parent compound, C.I. Pigment Violet 19, of a series of high performance pigments (primarily reds) where hues can range from orange to violet, depending on the number and position of simple substituents. Family members include C.I. Pigment Reds 122 and 202, which have two chloro and two methyl substituents respectively.



Fig. 4. General formula of perylene reds.





Fig. 6. Parent structure of disazo diarylide yellows.

Fig. 5. Copper phthalocyanine, C.I. Pigment Blue 15

• Perylene: Fig. 4 shows the general formula of a family of reds which include C.I. Pigment Reds 123, 149, 178 and 179.

• Copper Phthalocyanine: The most famous pigment blue of all, C.I. Pigment Blue 15, is shown in Fig. 5. It has two different crystalline forms, one of which is designated alpha, and is a bright, red shade of blue, and the other more stable beta form is a turquoise blue shade. This pigment is sold under at least six C.I. Pigment Blue 15 categories, from 15:1 to 15:6, all with different performance characteristics. For many more details, see Ref. 1.

This remarkable compound is the parent chromophore of many acid, direct, reactive and sulfur bright blue and green dyes and shows up wherever turquoise shades are required.

More importantly for pigment technology, the substitution of any of the hydrogen atoms on the four benzene rings (Fig. 5), with chloro groups then bromo groups,

-Br, takes the hue to progressively yel-> lower and yellower shades of green. C.I. Pigment Green 7 has 13-15 of the 16 available hydrogen atoms replaced by chlorine. The yellower C.I. Pigment Green 36 may contain as many as 13 bromo groups and two chloro groups.

• Miscellaneous Structures: Figs. 6 and 7 show the general structures of disazodiarylide pigment yellows and tetrachloroisoindolinone pigments-not so much in the belief that they will prove valuable in isolation, but simply to illustrate that besides reds, blues and greens there are pigment yellows and oranges, and that the structural diversity of pigments is enormous.

Review

This article represents a short dash through the application methods and appropriate terminology for the pigmenting of textile fibers and fabrics, as well as a brief look at the diversity of pigment chemistry.

Pigments can be inorganic or organic. white or colored, opaque or transparent in polymer binders, but they are not water soluble and they do not dye anything. The



Fig. 7. Tetrachloroisoindolinone pigments; e.g., C.I. Pigment Orange 61.

importance of binder polymers has been discussed m

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