

THE COLORATION AND FINISHING OF NONWOVEN FABRICS

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INTRODUCTION

This review paper is intended not only to underscore the close inter-relationships between woven, knit and nonwoven fabrics but also to reflect those differences between them which necessitate individualized approaches to their coloration and finishing. A wide range of finishing chemicals, dyestuffs, and mechanical processes are used with traditional textile fabrics; relatively few are typically used on nonwovens.

Nevertheless, in the coloration and finishing of nonwovens, the factors limiting the products and processes which may be used to achieve the desired end result are precisely those which apply to the traditional knit and woven textile fabrics. A review of these factors may lead to some new possibilities for dyeing and finishing nonwoven fabrics.

COLORS AND COLORATION

Colors can be divided into two major groups, pigments and dyes. Pigments are invariably insoluble in their application media. They have no intrinsic physical attraction for the substrates to which they are applied; they are bound to the substrate surfaces only by the adhesion of the polymeric binders in which they are incorporated. By contrast, at some stage in the application process all dyes are soluble in the application medium. The medium is almost invariably aqueous, although in several important instances, dyes may sublime and be monomolecularly dispersed (dissolved) in air (1,2).

The dye property of attraction to certain polymers is known as substantivity, often incorrectly referred to as affinity. Where there is substantivity, dyeings can be carried out batch-wise. The forces of interaction between dyes and substrates are sufficient to attract dye molecules out of large volumes of dyebath and into the substrate. This effect is the basis of all batch-dyeing processes. The ratio of the weight of the dyebath to that of the fibers is known as the liquor-ratio and ranges from about 5:1 to about 40:1. In such processes the uniformity of the substrate and the uniformity of its exposure to the dye molecules in the application medium determine the overall consistency of the resultant color.

While the same forces of attraction are in operation during continuous textile dyeing processes, the dye is physically constrained to act in the immediate area to which it was mechanically applied, since there is no gross circulation of the dye liquor through the substrate. The liquor-ratio in continuous dyeing is normally less than 1:1, and substantivity plays a less conspicuous

role than in batch dyeing. In continuous textile dyeing the amount of solution applied to the substrate is referred to in terms of its percentage of the weight of the dry substrate, or percentage wet-pick-up.

Pigments, having neither solubility in the medium nor substantivity for the substrate, cannot in normal circumstances be applied batch-wise but only continuously. Consequently, the uniformity of coloration is determined to a large extent by the uniformity of the mechanical application of the pigmented binder. This placement may be modified by differential migration of the solids to the solvent evaporation boundary during drying.

Printing is not very different from either continuous dyeing or pigment bonding. It is simply the mechanical means by which dyes or pigments are applied to localized and well defined areas of the substrate (3). Printing any one color (known as a color-way) usually covers only a small fraction of the available substrate surface; but standard printing machinery could readily be used to give complete coverage. However, pigment prints suffer from limited resistance to abrasion, for their color fastness properties depend on the abrasion resistance of the binder. In the U.S. about 90% of textile printing uses pigments, for simplicity and economy. Dyes, by contrast, diffuse into the substrate fibers and away from the fiber surfaces, improving the abrasion and wet-fastness properties.

There are hybrid areas lying in between dyeing and printing in which colors are applied continuously but randomly to produce multi-colored, non-repeating effects. Examples are found primarily in the carpet industry (4).

While continuous processing permits coloration and printing using both dyes and pigments, batch processing is only suitable for dyeing. It is interesting to note that about 70% of textiles in the U.S. are dyed batch-wise (5).

The primary reason for batch dyeing is the enormous variety of colors and fastness properties the textile fashion market demands, with the consequent short yardages which need to be dyed in any one color. Considering that a continuous dye range may require 400 yards of fabric (6) for thread up, it is clearly restricted to use for dyeing longer production runs. Presently 2,000 yards is considered to be the minimum yardage that can be run satisfactorily on a textile continuous dye range. Such ranges are designed to be suitable for those fabrics containing two or more chemical polymer types, such as polyesters and cellulosics. These fibers require different application classes of dyes, one for each fiber, to be applied at different parts of the dye range. Textile dye ranges could be shortened considerably, without compromising their speed of operation, if resin bonded pigments (a single color application category) could be used since pigments do not differentially bond to fibers.

Pigments are sometimes applied on continuous dye ranges for pale shades on polyester/cotton sheeting (7). But as previously noted, the color fastness properties are generally not very good. Their other deficiencies include: economy only at low coverage or pale shades, poor color range (notably deficient in bright reds) and resin binder interference with the application of some finishes. More important, they can affect the tactile properties of the fabric, which textile finishers refer to as the "hand".

FINISHES AND FINISHING

Unlike coloration, whose purpose is purely aesthetic, finishes can be applied to a substrate to change a broad variety of its properties such as: water repellency, soiling characteristics, crease-resistance, flammability, permeability, softness and others (8).

Conventional textile finishing may be sub-divided into mechanical (or physical) and chemical processes, although it is typical for fabrics to have been finished by a combination of the two. Sub-division of finishing processes may also be based on the nature of the end results. For example, chemical finishes frequently enhance technical performance whereas mechanical finishes, such as calendering and brushing, are primarily associated with obvious appearance changes. However, mechanical and chemical finishing are not mutually exclusive, and both processes might be applicable to particular goods.

Finishes can also be divided on the basis of their durability, termed temporary or permanent. But problems can arise with this nomenclature, since the extent to which any treatment may be called permanent or durable will depend on the treatment to which it is subjected in use.

A primary difference between chemical finishes and dyes is that few finishes show substantivity for particular polymer substrates. Consequently, with few exceptions, finishes must be applied continuously. In commission dye-houses some goods may be batch dyed and some may be continuously dyed, but virtually all goods are continuously finished. There are noteworthy exceptions. Substrate substantivity is shown by some antibacterial and antifungal finishes used on wool and nylon socks, and by several optical whiteners, which closely resemble dyes, except that they absorb ultraviolet light and re-emit some of it in the visible region.

SUBSTRATES

The usage of fibers by the textile industry is in a state of flux at the present time. Suffice it to say that it is very large (about 12 billion pounds per year) of which about 70% are dyed. Of dyed fibers, polyester and cellulosics have the lions share, about 30% each, followed by about 20% for nylon. Olefin fibers and glass fibers are major contributors to the fiber total, but are largely undyeable, although they can be printed. However, the major textile printing operations are currently fighting a rear-guard battle against Asian imported goods. All the remaining dyed fibers share 10% of the market. However, their importance should not be underestimated, since they are often blended with larger amounts of the major fibers to add desirable properties to apparel fabrics. Imagine a 60/35/5 polyester, rayon and silk blend.

The nonwovens industry is not as easy to define, but even without the contribution of the paper industry, the big three fibers with the largest usage, are cellulosics, polyesters and olefins. The high polypropylene usage is in strong contrast to the textile industry. The present difficulties in satisfactorily dyeing polypropylene provide both a research challenge and a substantial barrier to its wider use. Mass-pigmented polypropylene is widely used in a limited number of colors. Note: coloring polypropylene, or any other man-made fiber, by incorporation of pigments into the

polymer prior to extrusion, should not be referred to as “dyeing”, despite the widespread use of the term “dope-dyeing”, since no dyes are involved.

In both industries the fibers can be colored at any stage in their processing, from mass-pigmentation, to dyeing of staple and continuous filament fibers of most chemical types, through to the coloration of fabrics, webs and even individual pieces, such as fabricated garments and felt hat forms.

To the fibrous raw materials of the textile industry, the nonwovens industry can add a variety of materials used as binders, including low melting fibers. These may be of the same chemical polymer types as textile fibers but do not have the same degree of crystallinity or polymer orientation as do textile fibers. Differences of crystallinity (often referred to as fiber morphology) is of critical importance when considering the possibility of dyeing nonwoven materials, for the binders may absorb dye much more readily than the more crystalline fibers they bind. This is a serious bar to achieving color uniformity by dyeing. Even minute differences in the morphology of conventional textile fibers of the same chemical type, manufacturer and even the same production lot, which are undetectable by normal analytical methods, can greatly influence the rate and extent of dyeing (9). Furthermore, those nonwovens which incorporate binders must cause concern to colorists because of the potential for irregularities in the distribution of the binders throughout the fabric. If a fabric woven from intimately blended polyester and viscose staple yarns is cross-dyed using a disperse dye, which will only dye the polyester, the result will be a fabric with a 'heathery' appearance but generally good overall uniformity. By contrast, if a nonwoven fabric is similarly dyed, in which polyester and viscose fibers are bound together with a more accessible and less crystalline polyester binder fiber, the resulting fabric could have a distinctly mottled or blotchy appearance. The binder fiber would expropriate the largest part of the dye due to its much more rapid rate of dyeing. In fact, the dyeing technique is useful for checking the uniformity of the web and effectiveness of the blending process on the nonwoven line, when a binder or binder fiber is used along with normal textile fibers (10).

DYE/FINISH SUBSTRATE INTERACTIONS

All possible types of physical interaction between applied chemicals and fibrous substrates have been exploited in the century since the birth of the synthetic dyestuff industry, in 1856 (1). Although the initial attractions between the applied chemicals and the substrate can be subdivided into only two primary types, there are two additional means by which the chemicals can be retained by the substrate once they have been attracted. The four methods of attraction and retention are:

i) Electrostatic Interactions

If a polymeric substrate has the possibility of carrying a charged ion on the polymer chain, then it can be induced to interact with a dye chromophore bearing the opposite charge. For example: nylon, silk and wool contain amino groups which, in the presence of water containing different amounts of acids, are readily dyed with a group of anionic dyes known as acid dyes (11). These dyes are attracted to the acid-induced quaternary ammonium ions on the polymer chains. The dye molecules continue bound to the

substrate after the acid is removed. This can be attributed to more subtle non-ionic attractive forces which give rise to substantivity. In the same way, acrylics with anionic or negative charges on their polymer backbones interact with cationic (basic) dyes (12).

ii) Non-Ionic Interactions

Cotton cellulose (in contrast to wood pulp and other partially degraded cellulosic fibers) contains anionic carboxylate ions) has virtually no ionic groups on its polymer chains and yet there are numbers of colored anionic compounds which have strong substantivity for the cellulose. Many of these are known as direct dyes. They resemble acid dyes except that they are normally of about twice the molecular weight and are frequently linear, planar molecules. Their substantivity has been variously attributed to van der Waal's forces, Heitler-London dispersion forces, hydrogen-bonding, pi-bonding and other means. A combination of these forces seems probable (13). The overall effect is that the cellulose behaves as if it were a solvent for the dye, and the partitioning of the dye between the aqueous solution (dyebath) and the cellulose can be made to greatly favor the cellulose by salt addition. The partition of the non-ionic disperse dyes, which are sparingly soluble in water, between the aqueous dyebath and hydrophobic fibers is clearly similar, but because of the hydrophobic nature of both dye and fiber this is referred to as hydrophobic bonding. Disperse dyes are used for dyeing acetates, nylons, acrylics, urethanes, and many polyesters.

Most textile fibers can be readily batch dyed in water at the atmospheric boil. But with polyester fibers, the combination of their hydrophobicity and high second-order glass transition temperature made dyeing difficult in the early days (14). There are now three alternative methods. Either i) there is a "carrier" or co-solvent present in the dyebath, capable of swelling the polyester sufficiently to allow access to the dilute aqueous solution of dye at the atmospheric boil, or ii) high-temperature, pressurized dyebaths up to 140 degrees C can be used with the same effect, or, iii) gaseous disperse dye can be generated by heating the solid dye in close proximity to the fiber, causing sublimation, followed by diffusion of monomolecular gaseous dye into the polymer (15, 16). In all cases the driving force of the dyeing is the non-ionic attraction between dye and fiber molecules.

iii) Insolubilization

One of the oldest dyes known to man, Indigo, is an insoluble pigment when on the fabric. During application it is a pale-yellow, water-soluble anionic material formed by the alkaline reduction of the pigment. The colorless material behaves like a direct dye and is attracted to the cotton fiber due to its substantivity. The insoluble form of the dye is regenerated by oxidation once the reduced form has dyed the fiber by non-ionic interaction. Colors with these redox properties are known as vats (17) or sulfurs (18) and they are primarily utilized on cellulosic fibers. But, since they can show the behavior of both dyes and pigments, it is safest to call them "colors". Another example of color insolubilization is with azoic combinations. Azoic combinations comprise pairs of water soluble dye intermediates with some substantivity for cellulose, which react with one

another on the substrate to give highly colored, water insoluble pigments, in situ (19). They are practically obsolete because of fears about their potential carcinogenicity

iv) Fiber Reactivity

In 1956, a line of dyes which could react with cellulose ions in the presence of alkali (20) was introduced by I. C. I. (UK), and other dye manufacturers have since followed suit. Because the linkage between the dye and the fiber is chemical rather than physical, the durability to subsequent washing is outstanding. This durability is a direct function of the stability of the linkage to hydrolytic attack.

Five application categories of colors were developed to improve the water resistance or wet fastness of dyeings on cellulose (direct, sulfur, vat , reactive, azoic combinations).By contrast, only one dye category (disperse) is needed for many hydrophobic fibers. The cause is the hydrophilic nature of cellulose, which leaves water-soluble dyes in the substrate vulnerable to removal by wet treatments.

Finishes could also be categorized in a similar manner to colors (8). There are anionic and cationic softeners, for example, which could have substantivity for polymers capable of bearing positive and negative charges respectively. There are also non-ionic softeners, but unlike the non-ionic disperse dyes, they have very low substantivity. The durable-press and crease-resistant chemical finishes are, like fiber reactive dyes, reactants for cellulose. To cross-link cellulose they require reaction conditions which include catalysis with Lewis acid catalysts at 150-180 degrees C. Some water-soluble acrylic polymers are insolubilized at high temperatures leaving water insoluble residues on the fabrics (c.f. vat colors). So, it can be shown that all four substrate-dye interaction types have their parallels in finishing chemicals.

However, few finishes have the intermediate molecular weight or necessary carbocyclic, conjugated structures of dyes; consequently, they do not generally have substantivity. Polymeric or high molecular weight finishes cannot readily diffuse into other polymers, fibrous or otherwise, and must be content with surface property modification by adhesion to the substrate surface. This surface absorption is, of course, exactly what you would want of a water repellant finish.

Low substantivity is the reason almost all chemical textile finishing is carried out continuously, in strong contrast to dyeing.

MECHANICAL HANDLING OF FABRICS

Those textile fabrics having robust structures, can withstand repeated creasing and re-creasing when saturated with water and can be dragged about wet without distortion or structural alteration, are suitable for processing in rope-form. Such fabrics can be dyed batch-wise on becks and jet dyeing machines (21).

If the fabric structures are not sufficiently robust, then the fabrics have to be handled in the open width to avoid creasing and crack marks. This processing may be done batch-wise, e.g. on jig dyeing machines, but handling continuously on a suitable dye range would be more appropriate.

Knit goods, elasticated and stretch woven goods, and thermoplastic fibers all are capable of causing problems during continuous processing due to their deformability. How to ensure that these goods retain the desired physical dimensions, and consequently their weight per unit area, through processing has been a major problem with the manufacturers of tenter frames, curing ovens and steamers for many years. It should be appreciated that the problems involved are sometimes too difficult to overcome without compromising the physical properties desired of the resultant goods.

COLORATION AND FINISHING OF NONWOVENS

General

Troesch (22) reviewed the different stages at which fibers going into nonwoven fabrics can be colored. The different coloration methods which could be used are called: the "classical" continuous dyeing methods of the textile industry, mass pigmentation prior to extrusion (23), raw-stock dyeing of staple fibers, simultaneous coloration and wet-laying (as in paper-making) and the application of pigments along with binders. The relative merits of the different methods were assessed using the following criteria: color fastness achievable; ease with which different shades can be obtained; width of webs possible; technical problems in the processes; effluent quality; fiber inventory; fiber loss in changing shades; economics; the types of web for which the particular coloring process is most suitable.

Troesch found the application of pigments along with binders to be the most versatile and generally acceptable coloration method, but his primary emphasis was on the problems of color migration and the consequent color non-uniformities. Whenever solvents are evaporated from solutions or dispersions which are associated with an entanglement of fibers, there is always a migration of the dispersed or dissolved materials towards the source of heat and the evaporation front. Unfortunately, such systems are so varied and physically complex, that it is not yet possible to predict where in the web a particular material will end-up after the solvent has been driven off during drying or curing (24). Despite this, the worst problems of migration can be largely overcome (6) with careful selection of chemicals, including antimigrants, and control of the drying conditions.

The preceding sections have pointed with increasing inevitability to the fact that both the coloration and finishing of nonwoven fabrics should generally be carried out continuously, in open width (24).

Except in certain special cases, the selection of a pigment and binder for coloration of nonwovens is the obvious choice over dyes. This choice is particularly safe when dealing with those nonwovens which contain mixtures of fibers and binders of very different chemical types or morphology. The potential disadvantage of poor color fastness to abrasion might be more imaginary than real where resistance of the substrate itself to abrasion is not usually so critical as

in textile sheeting and apparel fabrics, for example. Pigments have the great advantage that they can give the same shade regardless of the nature of the polymers present in the nonwoven fabric. The possibility of shade and depth non-uniformities when using dyes is very great, unless there is primarily only one fibrous polymer present in the product; as in papers and some cellulosic and polyester needled or spunlaced nonwovens.

Specific

In a technological breakthrough, Groebke and Martin (26) describe the use of new types of dyes for dyeing paper. Slight modifications of known cellulose substantive direct dye structures, by introducing cationic charges onto the chromophore, have resulted in cationic, substantive, paper dyes. When these new dyes are used on wood pulp (which, unlike cotton cellulose, has large numbers of anionic end-groups capable of electrostatic interactions with cations) markedly better color-retention, less color in the effluent and better water resistance for the product are all achieved.

The sublimation of disperse dyes has been widely exploited by the textile industry for both the continuous dyeing of polyester/cellulosic blended fabrics and for the process known as heat transfer printing (15, 16) and more recently the literature is filled with reports on digital ink-jet printing, e.g. (34). Besides disperse dye inks, digital inks are now available for most application categories of colors.

In dyeing polyester/cellulosic fabrics, the disperse dye, which is applied in the form of an aqueous dispersion, is first dried onto the substrate and then heated in a thermosol oven for about 1-2 minutes at 200-220 degrees C. In the oven, monomolecular dye diffuses from the surface and into the polyester fibers. Fabrics of 100% polyester are rarely treated in this way because, in the absence of a hydrophilic fiber to strongly absorb the dispersion, the problem of dye migration on drying is severe. However, Burlington Industries holds a patent for continuously dyeing spunlaced, nonwoven polyester textiles (27).

Heat transfer printing has been frequently reviewed since its inception in the late fifties, e.g. (28, 29). In this process a design is first printed on an inert substrate (paper) with inks containing subliming (disperse) dyes. The inert printed substrate is then held against a new substrate (often polyester or nylon) for which the dyes have substantivity. Transfer is accomplished by heating the two substrates together. Under these conditions the dyes sublime to the new substrate. There is no reason why many thin non-woven synthetic fiber webs could not be heat transfer printed from such papers. Polypropylene is unsuitable, however, since it has poor substantivity for disperse dyes and has too low a softening point.

A primary problem with transfer printing has been the short distances that the dye molecules move during transfer. They do not penetrate through to the back of most fabric substrates, or even to the bottom of the rib of many knit goods. However, this problem can be overcome by first printing an air permeable fabric as the inert substrate. Then, during heat transfer, a flow of hot air can be forced to pass through the printed, inert fabric and out through the back of the web to which the dye is to be transferred. Apparently, this procedure enables even low-pile nylon carpet to be printed with satisfactory penetration (30).

There is little doubt that digital ink jet printing offers many promises and challenges. However, it is relatively slow, and its precise definition would be lost on a thick web.

There are several useful reports on the finishing of nonwovens e.g. (31), and there are several articles in the patent literature and trade press describing particular manufacturers' equipment for handling nonwovens, e.g. (32, 33).

SUMMARY

For many purposes it is simpler to color nonwoven webs by the continuous application of resin-bonded pigments, even though there are some problems of uniformity and fastness associated with them.

But, the number of stages at which the components of the webs might be colored, the multi-variety of webs and their end-use requirements all suggest the following: a basic knowledge of the factors governing dyeing, pigmenting and printing could prove valuable to any company wishing to determine the best combination of conditions for coloring a particular web for a particular application.

Some will note that the literature cited is not particularly recent. This reflects reality: there is very little new in the principles of polymer coloration. However, coloration of the variety of products poised to enter the nonwovens field should still prove challenging to those involved with their development.

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The What, When, How & Why of Coloration

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Basic Elements of a Polymer Coloration System

- Colorants (Pigments / Dyes)
- Transfer Vehicle (Application medium)
- Polymers (Fibers / Films / Binders)



Expanded Elements

- Colorants
- Fibers
- Transfer Vehicle
- Chemicals
- Machinery
- Economics
- Performance Criteria
- Customer Satisfaction



Colorants: Dyes

- Soluble (Water / Air)
- Molecules or Molecular Ions
- Organic or Organometallic (FBA's)
- Substantivity for Particular Polymers
- Very Selective Between Polymers & Between Same Polymers with Different Morphology
- Diffuse into Polymers





Colorants: Pigments

- Particles, Insoluble but Dispersible in Transfer Medium
- Some Inorganic some White
- No Substantivity for Polymers
- Cannot Diffuse into Polymers
- Require Binders
- Mass Pigmentation
- Refractive Index (Hiding Power)



A General Comparison

Conventional Textiles vs Nonwovens

- Colorants
- Polymers
- Application Medium
- Coloration Method
- Physical Properties of Goods
- Fastness of Colorants



Summary I

Worst Case Scenario for Nonwovens

- Thick, Weak Goods
- Multiple Polymers
- Thermal Sensitivity
- Batch-Dyeing to Union Shades
- Good Color Uniformity
- High Fastness
- Finicky Customer



Summary II

Best Case Scenario for Non-wovens

- Thin, Strong Goods
- Thermally Stable Single Polymer
- Low Coverage Print
- Single Color
- Pigment / Binders
- Forgiving Customer



Reality Check

- Infinite Variety of Possibilities
- Rarely an Ideal Situation
- Use of Pre-Colored Fibers & Films



Points to Ponder I

- 8 Application Categories of Colorants
- Specificity of Dye / Polymer Interactions
- Non-specificity of Pigments



Points to Ponder II

- 9 Chemical Categories of Fibrous Polymers
- Dyeing Rate / Extent Morphology Dependent
- Dyeing Rate / Extent Denier and X-Section Dependent
- Non-diffusion of Pigments



Points to Ponder III

Batch-Dyeing / Continuous-Dyeing

- Uniformity
- Wet strength
- Chemical Additives
- Color Migration During Dyeing / Washing



Points to Ponder IV

- Printing with Most Dyes
 - Penetration
 - Wicking
 - Migration
 - Removal of Additives

Continued..



Points to Ponder IV...Continued

- Printing with Disperse Dyes
 - Man-made Fibers only
 - Dry Fixation at 350°F +
- Printing with Pigments
 - Heat Curing of Binders
- Thermal Stability to Color Fixation





Summary and Conclusions

- Polymer Coloration Principles: Old, Well Established
- Migration of Liquids Within Webs: Unique
- Web Coloration Problems: No General Solutions
- Good Luck

