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2,921,831

METHOD OF TREATING SYNTHETIC FIBERS

Helen G. Sommar, Lorain, Ohio, assignor to The B. F. Goodrich Company, New York, N.Y., a corporation of New York

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The invention relates to a composition and improved process for producing fast, colorful dyeings on certain types of synthetic hydrophobic fibers, and more particularly relates to the dyeing of vinylidene cyanide interpolymer fibers using as a dye bath additive an excellent swelling agent selected from the class consisting of N,N-diphenylacetamide and N,N-diphenylformamide.

Vinylidene cyanide fiber-forming interpolymers are described in U.S. Patents Nos. 2,615,865 through 2,615,880, 2,628,954, 2,650,911, 2,654,724, 2,654,728, 2,657,197, 2,716,104 through 2,716,106 and in copending applications Serial Nos. 402,823, filed January 7, 1954, now Patent No. 2,786,046 issued March 19, 1957; 407,595, filed February 1, 1954 and now abandoned; and 526,335, filed August 3, 1955, now Patent No. 2,838,476. As described therein, synthetic fibers spun from such interpolymers possess unusually high strength and other desirable properties.

To be of value to the trade, however, any synthetic fiber produced must be readily and successfully dyeable, preferably with the dyes and techniques currently in use. Like many hydrophobic synthetic fibers and filaments, those made from vinylidene cyanide interpolymers have slick, smooth surfaces and are resistant to penetration by ordinary dyestuffs. Further, these polymeric fibers offer a minimum of points or molecular groups to which dye molecules may become affixed. Heretofore, attempts to dye vinylidene cyanide interpolymer fibers using techniques and materials known for fibers such as wool, cotton and silk have produced only weakly colored fibers lacking in attractiveness or more heavily colored fibers lacking in resistance to laundering.

One approach to the problem, used with fibers made of nitrile-containing polymers of the polyacrylonitrile type, has been copolymerization with monomers containing basic groups. This procedure fails with polymers based on vinylidene cyanide, however, for this monomer, as demonstrated in the art, homopolymerizes under polymerization conditions when basic groups or water are present, even in small amounts.

Another expedient to encourage dye penetration is to open the fiber structure by the action of a swelling agent and carrier which promotes penetration and sorption of the dye. Swelling agents may be applied to the fibers before the fibers are immersed in the dye bath, or they may be added to and mixed in the dye bath before the fibers are placed therein. The latter method is, of course, more economical and desirable. Swelling agents useful for incorporation into the dye bath include compounds such as biphenyl, nonochlorobenzene, o-dichlorobenzene, methyl salicylate, methyl phenyl carbinol, quinoline, and benzaldehyde.

Of these accepted swelling agents, only methyl salicylate performs satisfactorily when the fiber being dyed is one of the family spun from vinylidene cyanide containing interpolymers. To effectively control the dyeing of these fibers, other satisfactory carriers must be found.

Furthermore, solid swelling agents are more desirable

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than liquids as they usually have higher boiling points than their liquid counterparts and therefore show less tendency to distill out of a dye beck, condense on the overhead reel, or cover, then drip back on to the fabric below, causing non-uniformly colored spots.

I have now discovered that the presence of one of the class consisting of N,N-diphenylacetamide and N,N-diphenylformamide, which are significantly better swelling agents and carriers than those mentioned above, enables fibers spun from vinylidene cyanide interpolymers to be dyed with basic dyes, and with acetate dyes to depths and fastness of shades comparable to those obtained when dyeing hydrophylic fibers such as wool.

The swelling agents of this invention may be added to standard basic or acetate dye baths in concentrations ranging from 5 percent to 30 percent on weight of fabric (o.w.f.) and the desired improvement in dyeability of vinylidene cyanide interpolymer fabrics will be obtained. For reasons of economy and to obtain the best physical properties in the dyed fiber a preferred concentration range of these swelling agents is 5 percent to 15 percent o.w.f. with bath weight to fabric weight ratios of from 20 to 1 to 40 to 1.

An object of this invention is to provide a swelling agent for treating vinylidene cyanide interpolymer fibers to render them readily dyeable with basic and acetate dyes to deep, fast shades. Another object is to provide a treating process that will not require the use of objectionably high temperatures. A further object is to provide a carrier which will not distill out of the dye beck, condense and drip back on the articles being dyed, causing spots.

Still another object is to provide vinylidene cyanide interpolymer textiles including fibers, filaments, yarns and fabrics, which are dyeable with standard, commercially available dyes; which possess, when so dyed, light, cleaning and laundering fastness comparable to dyed woolen fibers and fabrics, and to accomplish this by utilizing a new dye bath composition.

These and other objects are attained according to this invention by the process of dyeing vinylidene cyanide interpolymer fibers in aqueous basic or acetate dye baths containing a significant proportion of a swelling agent selected from the class consisting of N,N-diphenylacetamide and N,N-diphenylformamide, which seem to act by opening up the fiber structure and rendering it receptive to the dye. It has been found helpful to use the swelling agent in the form of a dispersion.

The vinylidene cyanide interpolymer fibers may be so dyed immediately after the fibers are formed, as by spinning a solution of the polymer through a spinneret and passing the resulting filaments through a dye bath containing a swelling agent of this invention. Alternatively, the dye may be applied to the fibers, yarns, or fabrics made therefrom at any other desired time. Yarns or fabrics may be immersed in the swelling agent solution before passing them to the standard dye bath, although it is preferred to add the swelling agent to the dye bath and then immerse the textile to be dyed. Heat is not essential in the process if a long enough immersion time is allowed, the essential feature of the invention being that the treating conditions permit a significant degree of reaction between the swelling agent and the interpolymer fiber. Usually a dye bath temperature of 200° to 212° F. at atmospheric pressure is employed.

Any vinylidene cyanide interpolymer fiber may be used. Such interpolymers contain



groups in their structure, and the preferred interpolymers are bicomponent interpolymers in which the vinylidene

cyanide residue shown alternates in 1 to 1 molar ratio with the residue of the comonomers. Specific vinylidene cyanide interpolymers which may be used are disclosed in the patents set forth in the second paragraph hereof, the disclosures of which are incorporated herein by reference. The most preferred interpolymers are the 1 to 1 molar interpolymers of vinylidene cyanide with vinyl acetate.

Vinylidene cyanide interpolymers are difficult to dye, yet some weak colors can be applied to the fibers by several well-known classes of dyes including basic and acetate dyes. In general these are not commercially acceptable products, however. The use of N,N-diphenylacetamide or N,N-diphenylformamide along with the dye to act as a swelling agent or dye carrier materially improves the appearance and wearing qualities of the dye colors on fibers dyed using these materials. No special techniques are needed to apply basic and acetate dyes to the fibers when these swelling agents are used.

Advantages which may be cited for the synthetic materials dyed by the process of this invention include complete penetration of the dye into the fiber, and no change in hand or feel of the fabric.

The examples given below are intended only to illustrate the advantages of this invention and are not to be construed as a limitation upon the scope thereof, for there are, of course, numerous possible variations and modifications that will be apparent to those skilled in the art. In the examples all parts are by weight and percents are on weight of fabric (o.w.f.).

EXAMPLE 1

A supply of 100 percent vinylidene cyanide:vinyl acetate copolymer continuous filament yarn prepared as described in U.S. Patent 2,615,866 was made and formed into a knitted fabric. The fabric was scoured before dyeing for 15 minutes at 180° F. in a water solution containing 2 percent sodium N-methyl oleoyl taurate and 2 percent tetrasodium pyrophosphate to insure a clean, dirt free material. The cleaned fabric was dried and cut into test sample pieces weighing about 4.0 grams each.

Individual dye baths were prepared in large test tubes for each 4.0 gram piece of fabric to be dyed. These baths contained 160 grams of water (bath liquor to fabric ratio of 40:1). Swelling agents to be evaluated were first dissolved in methanol to form a 6 percent solution by weight. Four one hundredths gram of dioctyl ester of sodium sulphosuccinic acid (a dispersing agent) was added and hot water (temp. 130° F.) was supplied as a diluent until a milky emulsion formed. The swelling agent was then added to the warm (150° F.) dyebath in an amount equal to 10 percent o.w.f. Two percent o.w.f. of basic dyestuff Sevron Brilliant Red 4G (C.I. Basic Red 14) or acetate dyestuff Celliton Fast Blue 3BF were added and the bath was held at boil, 200–212° F., for one hour. Dyed samples were rinsed in cold water, scoured 15 minutes at 180° F. in water containing 2 percent o.w.f. sodium N-methyl oleoyl taurate and 2 percent o.w.f. sodium tetraphosphate, and dried.

The dyed fabrics were visually examined for depth of shade, fastness of color, dyebath exhaustion, fabric shrinkage and uniformity of color. Ratings of excellent (E), good (G), and poor (P) were given as indicated in the table below:

Table 1

	carrier at 10% o.w.f.			
	methyl salicylate	N,N-diphenylacetamide	N,N-diphenylformamide	methanol
2% basic dye Sevron Brilliant Red 4G.	G	G	E	P
2% acetate dye Celliton Fast Blue 3BF.	E	E	E	P

EXAMPLE 2

The procedure of Example 1 was followed employing fabrics made from vinylidene cyanide:vinyl chloride copolymer, U.S. Patent 2,615,870, vinylidene cyanide:isobutylene copolymer, U.S. Patent 2,615,865 and vinylidene cyanide:butadiene:styrene terpolymer, U.S. Patent 2,716,105. In all cases good to excellent ratings were applied to the fabrics dyed in either the basic or acetate dyebaths.

The carriers of this invention have been shown to be as effective when used with vinylidene cyanide interpolymers in encouraging good dyeing results as methyl salicylate—one of the best such agents known in the art. Further advantages of these materials lie with their higher melting and boiling points; they show less tendency to distill out of the dye beck, condense, and fall back on the materials being dyed.

The foregoing examples are merely illustrative, and not limiting, of the scope of this invention. Variations and modifications of the invention will be apparent to those skilled in the art. The invention is intended to be limited only by the scope and spirit of the appended claims.

I claim:

1. The process of dyeing vinylidene cyanide interpolymers textiles which comprises treating said textiles at the equivalent of 200–212° F. and atmospheric pressure with a dye selected from the class consisting of acetate and basic dyes in the presence of a member of the class consisting of N,N-diphenylacetamide and N,N-diphenylformamide as an additive.

2. The process of dyeing vinylidene cyanide:vinyl acetate copolymer textiles which comprises treating said textiles at the equivalent of 200–212° F. and atmospheric pressure with a dye selected from the class consisting of acetate and basic dyes in the presence of from 5 to 20 percent on weight of fabric of one of the class consisting of N,N-diphenylacetamide and N,N-diphenylformamide which has been added to the dye bath in the form of an emulsion.

3. The process of dyeing vinylidene cyanide:vinyl acetate copolymer textiles which comprises treating said textiles at the equivalent of 200–212° F. and atmospheric pressure with an acetate dye in an aqueous dye bath containing 5–20 percent on weight of fabric of an emulsion of one of the class consisting of N,N-diphenylacetamide and N,N-diphenylformamide.

4. The process of dyeing vinylidene cyanide:vinyl acetate copolymer textiles which comprises treating said textiles at the equivalent of 200–212° F. and atmospheric pressure with a basic dye in an aqueous dye bath containing 5–20 percent on weight of fabric of an emulsion of one of the class consisting of N,N-diphenylacetamide and N,N-diphenylformamide.

5. The process of dyeing vinylidene cyanide:vinyl chloride copolymer textiles which comprises treating said textiles at the equivalent of 200–212° F. and atmospheric pressure with a dye selected from the class consisting of acetate and basic dyes in the presence of from 5 to 20 percent on weight of fabric of one of the class consisting of N,N-diphenylacetamide and N,N-diphenylformamide which has been added to the dye bath in the form of an emulsion.

6. The process of dyeing vinylidene cyanide:isobutylene copolymer textiles which comprises treating said textiles at the equivalent of 200–212° F. and atmospheric pressure with a dye selected from the class consisting of acetate and basic dyes in the presence of from 5 to 20 percent on weight of fabric of one of the class consisting of N,N-diphenylacetamide and N,N-diphenylformamide which has been added to the dye bath in the form of an emulsion.

7. The process of dyeing vinylidene cyanide:vinyl acetate terpolymer textiles which comprises treating said textiles at the equivalent of 200–212° F. and atmospheric

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pressure with a dye selected from the class consisting of acetate and basic dyes in the presence of from 5 to 20 percent on weight of fabric of one of the class consisting of N,N-diphenylacetamide and N,N-diphenylformamide which has been added to the dye bath in the form of an emulsion. 5

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