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[54] **PROCESS FOR DYEING OR PRINTING ACRYLONITRILE COPOLYMER TEXTILE MATERIALS WITH VAT DYESTUFFS**
5 Claims, No Drawings

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[50] **Field of Search** 8/34, 177, 171, 62, 70

[56] **References Cited**

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ABSTRACT: Textile materials comprising fibers of a copolymer of essentially acrylonitrile and vinylidene chloride are dyed or printed, with a dyebath or printing paste comprising a vat dyestuff reduced with thiourea dioxide, which is then oxidized in situ to regenerate the dyestuff.

PROCESS FOR DYEING OR PRINTING ACRYLONITRILE COPOLYMER TEXTILE MATERIALS WITH VAT DYESTUFFS

This invention relates to the dyeing or printing of textile materials comprising copolymers of essentially acrylonitrile and vinylidene chloride, especially such copolymers which contain 35 to 85 percent of acrylonitrile units.

It is known to dye polyacrylonitrile with cationic dyestuffs, but copolymers of acrylonitrile with vinylidene chloride, which have superior properties in some respects, e.g., resistance to ignition, to acrylonitrile homopolymers, cannot be satisfactorily dyed in this fashion. Because the copolymer has a lower affinity for the dyestuff, the latter is taken up much more slowly and prolonged processing times are required. Moreover, it is very difficult to avoid considerable amounts of surplus unfixed dyestuff becoming mechanically attached to the textile material. Such surplus is extremely difficult to remove by washing, and tends to become transferred to uncolored parts of the material.

It has now been discovered that copolymers of essentially acrylonitrile and vinylidene chloride can advantageously be dyed or printed using vat dyestuffs and thiourea dioxide as reducing agent. The present invention accordingly provides a process for dyeing or printing textile materials comprising fibers of a copolymer of essentially acrylonitrile and vinylidene chloride which comprises contacting the said material with a dye bath or printing paste (as the case may be) comprising the product of reducing a vat dyestuff with thiourea dioxide, and then oxidizing the said product of reduction to regenerate the vat dyestuff in situ on the textile material. This process is ordinarily carried out by first applying, from a dyebath or as a printing paste, a mixture of the vat dyestuff and thiourea dioxide, and heating the dyestuff mixture to a temperature in the range of 80° to 110° C. in order to convert the vat dyestuff into the free leuco derivative which is then strongly fixed on the fiber. After the heat treatment, the leuco derivative is oxidized in situ on the fiber to regenerate the vat dyestuff. This is conveniently done with a dilute solution of hydrogen peroxide made weakly alkaline with ammonia, or in any other conventional way.

The dyebath or printing paste may contain the usual additives and thickeners commonly used in such dyebaths or printing pastes respectively. It is, however, especially advantageous to include an emulsified trialkyl phosphate as it reduces the time required for the leuco dyestuff to become fixed upon the fibers. For example, when a textile material is printed with a composition comprising a vat dyestuff and thiourea dioxide and then steamed at 110° C., a 20-minute steam period is generally required, but this period can be reduced to 10 minutes only, if the steaming is carried out in the presence of a trialkyl phosphate or dialkyl phthalate. Suitable such phosphates are triethyl and triisopropyl phosphate, and they are conveniently used in the form of an emulsion in water comprising a mixture of ionic and nonionic emulsifying agents. A suitable phthalate is dibutyl phthalate.

The dyebath or printing paste, as the case may be, may also contain conventional ingredients, such as, for example, glycerol, a printing oil (pine oil), and thickeners such as British gum or gum tragacanth.

The concentration of the dyestuff in the dyebath or printing paste will ordinarily be from 1 to 10 percent, and the concentration of thiourea dioxide from 1 to 15 percent by weight, the percentages being based on the total weight of the dyebath or printing paste.

After dyeing or printing and oxidation of the leuco compounds to regenerate the vat dyestuff, the textile material is then washed and finished in the usual way. It is usually desirable, in order to obtain a good result in printing, to wash the textile material after the leuco compound has been fixed thereon but before it has been oxidized to regenerate the vat dyestuff.

The new process is applicable not only to the dyeing or printing of textile materials consisting solely of fibers of acrylonitrile/vinylidene chloride copolymers, but also may be applied to blends of such fibers with other fibers, including polyamide fibers (e.g., Nylon 66) and cotton fibers. The following Examples illustrate the invention.

EXAMPLE 1

A woven fabric consisting of a heteropolymer of 80 percent by weight of acrylonitrile and 20 percent by weight of vinylidene chloride, is printed, after a conventional precleaning, with a printing color paste of the following composition.

50 g.	Durindone Printing Red BS Paste (ICI) (Vat Red 41) C.I. 73300
50 g.	Glycerol
50 g.	Thiourea dioxide
50 g.	Tri-isopropyl phosphate emulsion (prepared as described below)
20 g.	Printing oil (pine oil)
500 g.	British gum/tragacanth
280 g.	Water
1,000 g.	

After printing, the cloth is dried ad then steamed for 10 minutes at atmospheric pressure.

The print is subsequently rinsed in cold water and then oxidized at 70° C. with an aqueous solution of 1 cc. ammonia and 1 cc. hydrogen peroxide (20 Vol) per liter of water for 20 minutes. The print is finally treated with a nonionic surfactant at 70° C., rinsed and dried. A bright red coloration of excellent fastness properties is obtained, with the nonprinted areas showing excellent preservation of their original hue.

The tri-isopropyl phosphate emulsion was prepared by dispersing 10 g. or tri-isopropyl phosphate in 988 g. of water containing 1 g. of lauryl sulphate and 1 g. of a condensation product of nonylphenol and ethylene oxide in a molar ratio of 1:10–15.

EXAMPLE 2

A fiber consisting of a heteropolymer from 80 percent acrylonitrile and 20 percent vinylidene chloride in the tow form is impregnated continuously by passing first through an impregnating bath at 50° C. and then directly into a steaming chamber where it is subjected to the action of saturated steam at 100 ° C. for 10 minutes.

The impregnating bath has the following composition:

10 g.	FD Caledon Olive R Powder fine (ICI) (Black 27) C.I. 69005
50 g.	Thiourea dioxide
50 g.	Glycerol
50 g.	Tragacanth thickener
840 g.	Water
1,000 g.	

On passing the tow material through the steamer, the vat dyestuff is taken up by the fiber as the leuco derivative. It is subsequently reoxidized in the usual way, rinsed and soaped. An olive-green shade of excellent light fastness is obtained.

EXAMPLE 3

A woven fabric produced from a heteropolymer of 80 percent acrylonitrile and 20 percent vinylidene chloride is padded at 50°–60° C. on a padding mangle with the following composition:

50 g.	Indanthrene Brilliant Blue BR conc. Paste (Cassella) (Vat Blue)
50 g.	Glycerol
50 g.	Thiourea dioxide
50 g.	Tragacanth thickener
800 g.	Water
1,000 g.	

After padding, the cloth is dried by hot air and then steamed for 20 minutes with saturated steam at 100° C. After the usual rinsing, oxidation and soaping, a navy blue shade of excellent fastness results.

EXAMPLE 4

A woven fabric produced from a 50:50 blend of polyamide and 80:20 acrylonitrile/vinylidene chloride fiber is printed with the following composition:

50 g.	QF Caledon Printing Jade Green XBN Paste (Vat Green 1) C.I. 59825
50 g.	Glycerol
50 g.	Thiourea dioxide
45 g.	Triethyl phosphate emulsion (prepared as described in Example 1 replacing the tri-isopropyl phosphate by triethyl phosphate).
20 g.	Pine oil
500 g.	British gum/tragacanth thickener
285 g.	Water
1,000 g.	

After printing, the cloth is steamed for 20 minutes at 100° C. with saturated steam, rinsed, oxidized and soaped. A bright green shade is obtained with good coverage of both fibers.

EXAMPLE 5

A fiber consisting of a heteropolymer of 80 percent by weight of acrylonitrile and 20 percent by weight of vinylidene chloride is dyed in yarn form in a goods:liquor ratio of 1:20 from a dyebath of the following composition.

10%	Disodium hydrogen phosphate
5%	Disodium methylene dinaphthalene sulphonic acid
5%	Sodium lauryl sulfate
3%	Thiourea dioxide
10–20%	Dibutyl phthalate emulsion Yorkshire (Yorkshire Dyeware Co. Ltd.)
2.5 %	Indanthrene Brilliant Green FFB S/F Paste (Color Index No. 59825)
2.5%	Indanthrene Printing Blue GF S/F Paste
62–52%	Water

The procedure employed is to mix together all the constituents of the dyebath except the thiourea dioxide and raise their temperature to 50° C. The thiourea dioxide is added and the bath maintained at the same temperature for a further 5 minutes. The fiber is then introduced and the bath raised to 95°–100 C. over 15 minutes and maintained at this temperature for 45 minutes. The yarn is subsequently rinsed and then oxidized at 70°–80° C. with an aqueous solution containing 1 cc. 0.880 aqueous ammonia and 1 cc. hydrogen peroxide (20 vols.) per liter of water for 20 minutes. The yarn is finally treated with a nonionic surfactant at 70° C., rinsed, and immediately dried at 130° C. in order to reluster the fiber and develop the proper hue. A blue-green shade of excellent light fastness is obtained.

I claim:

1. A process for dyeing or printing a textile material comprising fibers of a copolymer consisting essentially of acrylonitrile and vinylidene chloride, which comprises the successive steps of:
   a. contacting said textile material with a dyebath or printing paste comprising a vat dyestuff and thiourea dioxide as the sole agent for reducing said dyestuff to a stable leuco form:
   b. effecting reduction of said dyestuff to its free leuco form; and
   c. oxidizing the resultant product of step (b) to regenerate the vat dyestuff in situ on said textile material.

2. The process of claim 1, wherein step (b) is conducted by heating to a temperature of 80° to 110° C.

3. The process of claim 1, wherein the oxidation step (c) is conducted with alkaline hydrogen peroxide.

4. The process of claim 1, wherein said dyebath or printing paste includes an emulsified trialkyl phosphate or dialkyl phthalate.

5. The process of claim 1, wherein said vat dyestuff is present in step (a) in an amount of from 1 to 10 percent and said thiourea dioxide is present in step (a) in an amount of from 1 to 15 percent, each amount being a concentration expressed in terms of said dyebath or printing paste.

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