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TREATING ACRYLONITRILE COPOLYMERS
WITH SULFURIC ACID FOLLOWED BY
DYEING WITH ACETATE DYESRalph B. Baker, Springfield, Pa., assignor to
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Del., a corporation of DelawareNo Drawing. Application October 1, 1948,
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5 Claims. (Cl. 8-4)

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This invention is concerned with the art of dyeing, and relates in particular to a new method of dyeing articles composed of or comprising synthetic polymeric materials containing the nitrile group.

Articles comprising synthetic polymeric materials containing the CN group cannot be dyed satisfactorily by conventional dyeing processes such as are satisfactory for other materials. For example, the conventional method of dyeing cellulose acetate involves the use of aqueous dye baths containing the so-called "Dispersol" type dyestuffs and a swelling agent for the acetate. Level dyeings which are sufficiently deep and fast for commercial purposes are produced on cellulose acetate by that method. However, this process is not effective to produce dyeings of satisfactory depth of shade and fastness to light and washing on articles comprising synthetic polymeric materials containing the nitrile group. When the standard cellulose acetate dyeing method is applied to articles, such as filaments or yarns, comprising polyacrylonitrile or many of the acrylonitrile copolymers, and particularly those containing 40% or more by weight of acrylonitrile in the copolymer molecule, the article is either merely tinted or dyed to an extremely light shade and, in any case, the dyeing is not sufficiently fast to light and washing to meet the demands of the trade.

One object of this invention is to effect dyeing of articles comprising synthetic polymeric materials containing the nitrile group to produce deep, level dyeings of excellent fastness to light and washing. A further object is to produce deep, level, light- and wash-fast dyeings on acrylonitrile polymers. Another object is to provide a comparatively simple and inexpensive method for effecting dyeing of the acrylonitrile polymers. Other objects will appear hereinafter.

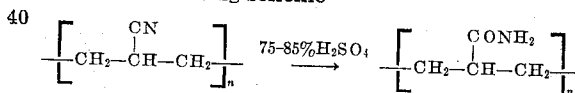
The objects of the invention are accomplished in general by treating articles comprising a synthetic polymeric material containing the group CN, such as acrylonitrile copolymers containing about 40% by weight acrylonitrile in the polymer molecule, in an aqueous solution of sulfuric acid of from 75 to 85% concentration for short periods of from 15 seconds to 5 minutes, and preferably for a period of from 15 seconds to 1 minute, the treating time varying inversely with the concentration of the sulfuric acid, at room temperature, i. e., at 20-30° C., washing the acid-treated article free of acid, drying the article, and thereafter dyeing the article in a dyebath consisting of an

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aqueous dispersion of a water-insoluble cellulose acetate type dyestuff.

The acrylonitrile copolymers show, after treatment with sulfuric acid, washing and drying thereof in accordance with this invention, an affinity for the water-insoluble cellulose acetate type dyes which is, in most instances, remarkably greater than the affinity for these dyes possessed by the acrylonitrile copolymers per se, i. e., such copolymers which are not pre-treated in accordance with the invention. Thus, when an article comprising an acrylonitrile copolymer as defined above is immersed in an aqueous dyebath containing a cellulose acetate dyestuff, a dispersing agent, and a swelling agent for the polymer, the dyestuff tends to remain with the bath, and partition of the dye between the bath and article takes place slowly and incompletely regardless of the dyeing conditions, such as dye concentration, temperature, etc. In contrast to this, when an article comprising the acrylonitrile copolymer is pre-treated with sulfuric acid solutions of from 75 to 85% concentration, washed, and dried, in accordance with this invention, and thereafter immersed in a dyebath consisting of water, a water-insoluble cellulose acetate type dye, and a dispersing agent, partition of the dye between the bath and article takes place readily and proceeds to equilibrium.

While it is not intended to restrict the invention to any theoretical explanation of the striking results obtained by the practice of the present process, it appears that when an article comprising a synthetic nitrile-containing polymeric material is treated with sulfuric acid solutions of from 75 to 85% concentration, the nitrile groups, or some of those groups, present in the polymer are converted to amido groups, in accordance with the following scheme



and that, when the article is washed free of acid, and dried, and thereafter treated with the dyebath, the cellulose acetate type dye becomes fixed to the amido groups, and to the resin through those groups. In any event, and whatever the actual explanation of the observed phenomenon may be, the dyeings obtained by the present process are deep, level, and of excellent fastness to light and washing.

Examples of synthetic nitrile-containing polymers which may be dyed in accordance with this invention are copolymers of acrylonitrile, for ex-

ample, copolymers thereof with vinyl acetate, isobutene, vinyl chloride, acrylamide, and styrene containing about 40% acrylonitrile in the polymer molecule; copolymers of fumaronitrile, for example, copolymers thereof with styrene; copolymers of acrylonitrile and butadiene, etc.

Preferably, the acrylonitrile copolymer is in the completely "set" condition when it is subjected to the sulfuric acid treatment, i. e., if the article comprises filaments or yarns of the acrylonitrile copolymer produced by the wet spinning process, the filaments or yarns are freed of absorbed coagulating liquid, stretched, and set in the stretched condition under heating, prior to being treated with the strongly concentrated aqueous sulfuric acid solution, washed, dried and dyed. However, if desired, filaments or yarns produced by the wet spinning procedure, or fabricated articles containing such filaments or yarns, may be treated with the sulfuric acid solutions while they are in the gel state, i. e., in the condition in which they exist before the gel structure has collapsed, as for example while the yarn retains a large amount of absorbed coagulating liquid, e. g. 100% or more by weight of the acrylonitrile polymer. Dyeing, however, is performed on the acid-treated article only after it has been washed free of acid and completely dried.

The following examples, which illustrate but do not limit the invention and in which parts, proportions, and percentages are by weight unless otherwise specified, illustrate preferred modes of operating in accordance with the principles of the invention.

Example I

A fabric knitted from yarns of a copolymer of acrylonitrile and vinyl chloride containing about 60% vinyl chloride and 40% acrylonitrile in the copolymer molecule was immersed for one minute in 81% aqueous sulfuric acid at 25° C. The fabric was then washed free of acid, and air dried. There was no evidence of shrinking or stiffening of the fabric as a result of the acid treatment.

A dye bath was prepared by pasting 2% (based on the weight of the fabric) of Celanthrene Red 3B (Color Index No. not listed) with 0.5% (on the weight of the fabric) of a 25% aqueous solution of the sodium sulfate derivative of 7-ethyl-2-methylundecanol-4, as dispersing agent. Water was then added to provide a bath having a volume ratio of 40:1 (on the weight of the fabric). The acid-treated, washed, and dried fabric was entered into the bath at 60° C., and the temperature was raised to the boil. Dyeing was continued for 1½ hours at the elevated temperature. The dyed fabric was then rinsed in cold water, scoured in 0.25% soap solution at 60° C., rinsed, and air-dried.

By this procedure, the fabric was dyed to a strong level shade which showed excellent light and wash fastness.

Example II

The procedure of Example I was followed, with a fabric formed from the same acrylonitrile copolymer, except that prior to dyeing, the fabric was immersed in aqueous 82% sulfuric acid for 30 seconds.

Example III

The fabric and procedure were the same as in Example I, but the fabric was immersed in aqueous 83% sulfuric acid for 15 seconds, washed free of acid and dried, prior to being introduced into the dye bath.

It will be understood that the invention is not to be limited to the use of the particular water-insoluble cellulose acetate type dyestuffs shown in the specific examples. The cellulose acetate dyestuffs are a well-recognized class of dyes, and the invention is directed to the dyes as a class. Also, the dyestuffs mentioned in the examples are interchangeable.

The synthetic nitrile-containing polymeric materials may be produced by any of the known polymerization procedures, and when in the form of filaments or yarns of an acrylonitrile copolymer containing about 40% by weight of acrylonitrile in the polymer molecule, and having a molecular weight in the fiber-forming range, such filaments or yarns may be produced by either the wet, dry, or melt-spinning techniques.

The article to be dyed may be in any form such as filaments, yarns, whether in the form of skeins or wound packages such as cops, pirns, or cheeses, or it may be in the form of running lengths of the filamentary material, fabrics of all kinds, massive molded articles, tubing, rods, films, etc.

Any modification of the procedure described herein which conforms to the principles of the invention is intended to be included within the scope of the appended claims.

I claim:

1. The process of dyeing an article comprising an acrylonitrile copolymer containing about 40% by weight of acrylonitrile in the polymer molecule which comprises treating such article with an aqueous sulfuric acid solution of from 75 to 85% concentration for from 15 seconds to 5 minutes at room temperature, washing the article free of acid, completely drying the article, and then dyeing the acid-treated article in a dyebath consisting of an aqueous dispersion of a cellulose acetate type dyestuff.

2. The process of dyeing an article comprising a copolymer of acrylonitrile and vinyl chloride containing about 40% by weight of acrylonitrile in the polymer molecule, which comprises treating such article with an aqueous sulfuric acid solution of from 75 to 85% concentration for from 15 seconds to 5 minutes at room temperature, washing the article free of acid, completely drying the article, and then dyeing the acid-treated article in a dyebath consisting of an aqueous dispersion of a cellulose acetate type dyestuff.

3. The process of dyeing an article comprising a copolymer of acrylonitrile and vinyl chloride containing about 40% of acrylonitrile in the copolymer molecule which comprises treating such article with an aqueous 81% sulfuric acid solution at room temperature for one minute, washing the article free of acid, completely drying the article, and then dyeing the acid-treated article in a dyebath consisting of an aqueous dispersion of a cellulose acetate type dyestuff.

4. The process of dyeing an article comprising a copolymer of acrylonitrile and vinyl chloride containing about 40% acrylonitrile in the copolymer molecule which comprises treating such article with an aqueous 82% sulfuric acid solution for 30 seconds at room temperature, washing the article free of acid, completely drying the article, and then dyeing the dried, acid-treated article in a dyebath consisting of an aqueous dispersion of a cellulose acetate type dyestuff.

5. The process of dyeing an article comprising a copolymer of acrylonitrile and vinyl chlo-

ride containing about 40% of acrylonitrile in the copolymer molecule, which comprises treating such article with an aqueous 83% sulfuric acid solution for 15 seconds at room temperature, washing the article free of acid, completely drying the article, and dyeing the dried, acid-treated article in a dyebath consisting of an aqueous dispersion of a cellulose acetate type dyestuff.

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