United States Patent Office 2,743,231 Patented Apr. 24, 1956

2,743,231

PROCESS FOR THE DYEING OF NYLON FIBERS AND FABRICS WITH 5-CHLOROSALICYLIC ACID

David X. Klein, Montclair, N. J., and James Falcon, Rumford, R. I., assignors to Heyden Chemical Corporation, New York, N. Y., a corporation of Delaware

No Drawing. Application December 8, 1951, Serial No. 260,766

3 Claims. (Cl. 8—55)

This invention relates to the dyeing of fibers, and more specifically, to a new and improved method for dyeing fibers and fabrics of nylon, a synthetic linear polyamide.

Conventional methods employed in the dyeing of nylon fibers or fabrics involve the use of various organic acids such as benzoic acid, salicyclic acid, tannic acid, etc. as carriers or dye assistants. The actual mechanism by which these acids improve the dyeing characteristics of the fiber or fabric is not known but it is believed that a swelling of the material is induced which allows the dye to disperse into the fiber where it is held until the carrier is removed at a later step in the dyeing operation. In the dyeing process, quantities as high as 10% of the organic acids are used as dye assistants. The use of such high concentrations of swelling agents is undesirable in that a resulting shrinkage or plasticization of the nylon fiber is effected. Various attempts to reduce the concentration of the acid carrier invariably have resulted in a corresponding reduction of the color yield obtained in the subsequent dyeing step. In other words, deeper coloration of the nylon material to be dyed could only be obtained hitherto by increasing the concentration of the swelling agent used.

It has now been found that substantially high color yields are obtained in the dyeing of nylon fibers and fabrics when the material is exposed to a pretreatment with aqueous solutions containing relatively small amounts, i. e. as low as about 0.5% by weight, of either 5-chlorosalicylic acid or cresotinic acid (hydroxytoluic acid) prior to the dyeing operation. Surprisingly, the nylon fibers and fabrics pretreated with either of these organic acids are dyed to a deeper shade by various types of dyes as compared with untreated nylon fabric or nylon fiber treated with conventional carriers such as benzoic or salicylic acid or tannic acid, the latter acid being used in a concentration as high as 10%. Because of their greater ability to increase the receptivity of nylon to various dyes, 5-chlorosalicyclic acid or cresotinic acid may be used in a concentration as low as 0.5% to obtain maximum color depth as distinguished from the organic acids used hitherto which required a concentration ranging from at least 2% to as high as 10% to achieve results considered to be far less satisfactory in nature.

In a more specific embodiment of this invention, nylon fabric samples were treated in a relaxed state for three minutes at the boil in baths containing from 0.5% to 3% by weight of either cresotinic acid or 5-chlorosalicylic acid in aqueous solutions thereof. The samples were thoroughly washed in warm water followed by cold water to remove the acid carrier and then dyed for about thirty minutes at a temperature of 190° F. in a bath containing the appropriate dye. Untreated samples of the same material were exposed in the same manner to a dyeing treatment in order to provide a control or basis for comparisons between samples exposed to pretreatment and those which had not. In a separate procedure, the fabrics were also treated with aqueous solutions containing from 0.5% to 3% salicylic acid by weight and the results obtained by the use of this acid were compared with those obtained by the use of the lower concentrations of 5-chlorosalicylic acid or cresotinic acid. All of the nylon fabric samples subjected to these treatments were exposed to various dyes such as acid dyes, direct dyes, and acetate dyes. In each instance, the samples pretreated with 5-chlorosalicylic acid and cresotinic acid were considerably darker in color than either the samples pretreated with salicylic acid or the samples that were not exposed to any pretreatment.

Additional advantages and features of this new and highly improved process are set forth in the following examples which disclose the principle of the invention and the preferred embodiment of applying that principle. It is understood, however, that these examples are merely illustrative and not limitative in nature, being capable of various other modifications.

EXAMPLE I

Acid dyes

Acid dyes are ordinarily employed in the dyeing of wool. These dyes are azo dyes of lower molecular weight.

Nylon fabric samples were treated in a relaxed state for three minutes at the boil in baths containing from 0.5% to 3% by weight of salicylic acid, cresotinic acid and 5-chlorosalicylic acid. The samples were thoroughly washed in warm water followed by cold water and then dyed together with an untreated sample of the same material for 30 minutes at 190° F. in a dyebath containing

1% acid dye (on weight of the fabric)
2% H_2SO_4 (on weight of the fabric)
10% NaCl (on weight of the fabric)

The water-fabric ratio was 30:1.

Pontacyl green N. V. Ex. Conc.[1] (Colour Index No. 735) (manufactured by E. I. du Pont de Nemours and Co.) and Wool Violet 4BN (Colour Index No. 698) (which is manufactured by National Aniline Div., Allied Chemical and Dye Corp.) were the acid dyes used in this test. The dyed samples were thoroughly washed in cold water and dried. In each case the samples pretreated with 5-chlorosalicylic acid and cresotinic acid were considerably darker than either the samples pretreated with salicylic acid or the sample that was not exposed to the pretreatment step.

EXAMPLE II

Direct dyes

Direct dyes are used ordinarily in dyeing cotton material. They are water soluble azo dyes containing sulphonic acid groups.

Using the procedure described in Example I, samples of nylon pretreated with aqueous solutions containing from 0.5% to 3% by weight of 5-chlorosalicylic acid, cresotinic acid and salicyclic acid were dyed along with an untreated sample in a dyebath containing 1% of Pontamine Blue 3R (Colour Index No. 464) or Pontamine Brilliant Violet (Prototype Number 35) (both of which are manufactured by E. I. du Pont de Nemours and Co.) and 20% of sodium chloride based on the weight of the fabric. The water to fabric ratio was 25:1. In this case also, the samples pretreated with

[1] The Colour Index Numbers and Prototype Numbers mentioned here and throughout the specification are a standard of identification for commercially important organic dyes listed in the "Technical Manual and Year Book of American Assn. of Textile Chemists and Colorists," volume XXVI, 1950, page 150. Also referred to in "Library Guide for Chemists," Soule, McGraw Hill Publishing Company, 1938.

5-chlorosalicylic acid and cresotinic acid were dyed to a much deeper shade than were the untreated sample and the samples treated with salicylic acid.

EXAMPLE III

Acetate dyes

These dyes are water insoluble and are normally employed in the form of aqueous dispersions.

The procedure described in Example I was repeated using a dyebath containing:

1% acetate dye—on weight of fabric
10% triton X100—on weight of fabric (alkylarylpolyethylene oxide) (JACS 69, 334, 1947—Rohm and Haas Co.)

The water to fabric ratio was 30:1.

Acetamine Violet 2R (du Pont de Nemours and Co.) and Eastone Rubine C (Tennessee Eastman Corporation) were the acetate dyes used.

The samples pretreated with 5-chlorosalicylic acid or with cresotinic acid were noticeably darker than those which were not pretreated or which were pretreated with salicylic acid.

EXAMPLE IV

Comparison of activity of the acid carriers

The relative activity of the various acid carriers in different concentrations and their effectiveness in increasing the affinity of nylon for various types of dyes is shown in the following table. The activity was determined by dyeing tests similar to those described in the preceding examples. Samples pretreated with cresotinic acid, 5-chlorosalicylic acid and salicylic acid were dyed with Eastone Yellow GNS and SRA Red V11 (acetate dyes—manufactured by Tennessee Eastman Corp.), Pontamine Blue 3R and Pontamine Brown NCR Conc. 150% (Colour Index No. 596) (direct dyes), Pontacyl Light Red BL Conc. and Pontacyl Brilliant Blue A Conc. (acid dyes—manufactured by E. I. du Pont de Nemours and Co.), and Ponsol Brilliant Green 4G and Ponsol Dark Blue BRD Bbl. Pdr. (Colour Index No. 1099) (vat dyes). In the following table the lightest shade produced has been indicated by the number 1.

	5-Chlorosalicylic Acid					Cresotinic Acid					Salicylic Acid					Control
	0.5%	1.0%	1.5%	2.0%	3.0%	0.5%	1.0%	1.5%	2.0%	3.0%	0.5%	1.0%	1.5%	2.0%	3.0%	
Direct Dyes	6	6	6	5	6	5	5	6	5	6	1	1	2	2	3	1
Acid Dyes	5	6	5	6	6	6	6	5	6	5	1	1	1	2	3	1
Acetate Dyes	5	5	6	5	6	5	5	5	5	6	1	1	2	2	2	1
Vat Dyes	6	5	5	6	5	4	5	6	5	5	1	1	1	2	3	1

The data listed in the chart above indicates that far superior results are obtained when an acid carrier such as 5-chlorosalicylic or cresotinic acid is used in the pretreatment of nylon fabrics in minor amounts, that is, as low as 0.5%, as compared with a conventional acid carrier of the same concentration. It is likewise indicated that similar results are obtained when the amount of the acid carrier used is increased to 2% and higher. Since color depth is not materially improved when the concentration of either 5-chlorosalicylic acid or cresotinic acid is raised beyond about 1% and up to about 10%, for practical reasons, the acid is used in a concentration of about 1%.

While the color values of the dyed nylon samples pretreated with 5-chlorosalicylic acid, cresotinic acid at 120°, 150°, and 175° F. are higher than those of the salicylic acid pretreated sample and the sample that was not pretreated, there is a marked increase in the color value of samples pretreated with 5-chlorosalicylic acid or cresotinic acid at a temperature between about 180° F. and the boiling point of the bath.

Maximum color values are obtained when the pretreating solutions containing as little as 0.5% of 5-chlorosalicylic acid or cresotinic acid are used and when the pretreatment process is carried out at a temperature varying between 180° F. to 200° F. for a period of three minutes and preferably, at a temperature of about 190° F.

It is apparent from the foregoing that the invention is capable of various modifications and that, therefore, it is intended and desired to embrace within the scope of this invention such modifications and changes that are necessary to adapt it to varying conditions and uses, as defined by the scope of the appended claims.

We claim:

1. In a process for coloring nylon fibers and fabrics, the improvement which comprises pretreating the nylon material in an aqueous solution containing from 0.5% to 1.5% by weight of 5-chlorosalicylic acid and while the aqueous solution is at a temperature between 180° F. and the boiling point of the aqueous solution, washing the material thus treated and subsequently dyeing said material.

2. In a process for coloring nylon fibers and fabrics, the improvement which comprises pretreating the nylon material in an aqueous solution containing from 0.5% to 1.5% by weight of 5-chlorosalicylic acid, said pretreatment being effected at a temperature ranging between about 180°–200° F., washing the material thus treated and subsequently dyeing said material.

3. In a process for coloring nylon fibers and fabrics, the improvement which comprises pretreating the nylon material in an aqueous solution containing from 0.5% to 1.5% by weight of 5-chlorosalicylic acid, said pretreatment being effected at a temperature of about 190° F., washing the material thus treated and subsequently dyeing said material.

References Cited in the file of this patent

FOREIGN PATENTS

614,009 Great Britain ---------- Dec. 8, 1948

OTHER REFERENCES

American Dyestuff Reporter for February 4, 1952, p. P78.

American Dyestuff Reporter for May 14, 1951, p. 312.