

[54] TREATMENT OF DYED POLYAMIDES

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[51] Int. Cl..... **D06p 1/84**

[58] Field of Search..... **8/74, 165**

[56] References Cited

UNITED STATES PATENTS

2,315,951 /1943 Fox 8/94.21 UX
2,716,655 8/1955 Boyd 260/38
2,922,690 1/1960 Mueller 8/21

2,972,508 2/1961 Kruckenkerag et al. 8/41 X
3,389,549 6/1968 David 57/140
3,475,111 10/1969 Meyer 8/15 X
3,504,997 4/1970 Clapham et al. 8/21 A

FOREIGN PATENTS OR APPLICATIONS

699,533 12/1964 Canada 8/173
807,241 1/1959 Great Britain 8/39
1,092,247 11/1967 Great Britain

OTHER PUBLICATIONS

Egli, Textilveredlung Vol. 2; No. 11, pages 856-864,
1967.

Egli, Chem. Abst. 139,597, 1968.

American Dyestuff Reporter, Sept. 25, 1967, pages
749 and 750.

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[57] ABSTRACT

The wet fastness of polyamides dyed with cationic
dyes is improved by treatment with an aqueous solu-
tion containing soluble salts of the condensation prod-
uct of formaldehyde and an aromatic sulfonic acid.

3 Claims, No Drawings

TREATMENT OF DYED POLYAMIDES

DISCLOSURE

This invention relates to polyamides which have been dyed with cationic dyestuffs. More particularly, the invention relates to improving the wet fastness of the dyeings obtained on such material. Even more particularly, the invention provides a treatment for such dyed materials which increases the resistance of the dyeings on the polyamides to degradation by water and perspiration.

The agents used until now to improve the wet fastness properties of the dyeings obtained on polyamides with basic dyestuffs were found to be unsatisfactory, since the improvements achieved were accompanied by an impairment of other properties of the dyeings, e.g., by an impairment of fastness to rubbing and/or brightness of the shades. According to the process of the invention an improvement of the wet fastness properties of the dyeings is obtained without impairing the fastness to rubbing or the brightness of the shades. Furthermore the fastness properties of the dyeings obtained with anionic dyestuffs on standard synthetic polyamides are not impaired by the after-treatment according to the invention. This is important in the after-treating of bi-color dyeings, in which mixtures of standard and anionically modified polyamide materials are dyed simultaneously with cationic and anionic dyestuffs and aftertreated subsequently.

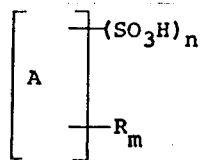
It is, therefore, an object of this invention to provide a method of treating cationically dyed polyamide materials to improve the wet fastness of such materials.

Another object is to improve such wet fastness without impairing rubbing fastness or brightness of the cationically dyed polyamides.

Still another object is to improve the wet fastness of cationic component of bi-color dyeings without impairing the wet fastness of the anionic component.

A further object of the invention is to provide compounds for improving the wet fastness of cationically dyed polyamide materials.

These and other objects of the invention are achieved by applying compounds which comprise alkali or ammonium salts of condensation products of formaldehyde and aromatic sulfonic acids of the formula



in which

A signifies a diphenyl ether radical,

R signifies a lower alkyl radical having 1-4 carbon atoms,

m a whole number from 0-2 and

n a number from 0.5-2.

The process of applying these compounds comprises treating the dyeings produced with cationic dyes on synthetic polyamide with aqueous liquors, which contain alkali or ammonium salts of condensation products of formaldehyde and the aromatic sulfonic acids of formula (I).

The aromatic sulfonic acids adapted for use in this invention as defined by formula (I) are particularly those containing as diaryl ethers (A) components such as diphenyl ether and 4,4'-dimethyl-diphenyl ether.

Sulfonation of these diaryl ether nuclei can be conducted by reaction with sulfonating agents such as sulfuric acid monohydrate or chlorosulfonic acid under the conditions specified in U.S. Pat. No. 2,315,951. The degree of sulfonation can vary as taught in said patent, but the desired aromatic sulfonic acids should contain from ½ to 2 sulfonic acid groups in a position on the aryl nuclei. The sulfonating agent should be present in quantities of about 0.6 to 2.5 mols per mol of diaryl ether.

The sulfonated diaryl ethers may then be condensed with formaldehyde from any suitable source by reacting preferably about ½ to 1 mol of formaldehyde per mol of diaryl ether to form condensation products in the manner disclosed in U.S. Pat. No. 2,315,951. Simultaneously sulfonation and condensation are contemplated by said patent as well as sulfonation and then condensation or condensation followed by sulfonation.

After condensing the sulfonated diaryl ether and formaldehyde, the sulfonic acid salts can be formed by conventional techniques for reacting sulfonic acids with ammonium or alkali metal salts. Particularly suitable bases adapted to yield ammonium or alkali metal salts of the sulfonic acids are ammonia, methylamine, cyclohexylamine, mono-, di- or triethanolamine and alkali hydroxides such as sodium or potassium hydroxide.

After the salt of the condensation product is formed, it can be applied to dyed synthetic polyamide textile materials in such forms as threads, fibers, fibrous or knitted goods, particularly where the synthetic polyamide is an anionically modified synthetic polyamide, e.g., anionically modified ε-polycaprolactam, polyhexamethylene diamine adipate or poly-11-amino-decanic acid. These synthetic polyamide textiles can be previously dyed with any cationic dyestuff including classes of dyes such as the diphenylmethane, triphenylmethane, rhodamine, thiazine, oxazine, methine, azomethine dyes as are described, e.g., in "American Dyestuff Reporter" (1954), pages 432-433, and particularly anthraquinone dyes and azo dyestuffs with a basic or quaternary amino group as described in British Pat. Nos. 785,988; 871,624; 791,932; 930,471; and U.S. Pat. No. 2,716,655.

Formulation of the solutions of the compounds of formula (I) should contain from 1-5 percent by weight based on the weight of the goods to be dyed and should have a pH of from 2-8. The pH is adjusted by adding organic acids such as formic acid. While in the solution, the goods should be slightly agitated as by moving for a period of about 10-60 minutes while the solution is maintained at a temperature of about 30°-100°C, preferably 40°-70°C.

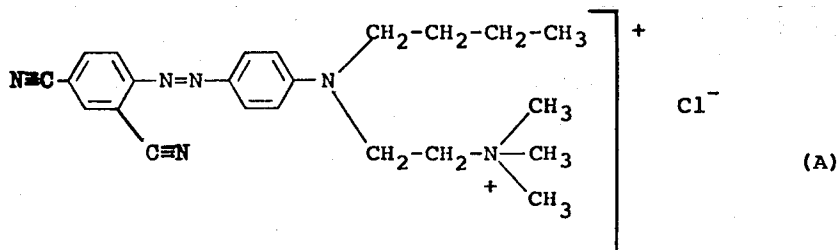
The invention will be more fully understood by reference to the following illustrative examples:

EXAMPLE 1

1a. Threads formed from anionically modified polyhexamethylene diamine adipate, were dyed with 1 percent by weight of a cationic dyestuff corresponding to the formula:

3

4



A part of these threads are reserved for a CONTROL and a second part was treated as follows: One part by weight of the threads was placed in 40 parts by weight of an aqueous solution and moved for 60 minutes at 40°C.

The aqueous liquid contains per liter of liquid:

0.35 g 85 percent formic acid and

1 g of the sodium salt of the condensation product of formaldehyde, diphenyl ether, and sulfuric acid monohydrates prepared by reaction in a mol ratio of 0.75:1:1.5 under the conditions of U.S. Pat. No. 2,315,951.

Subsequently, the threads were rinsed with fresh water and dried.

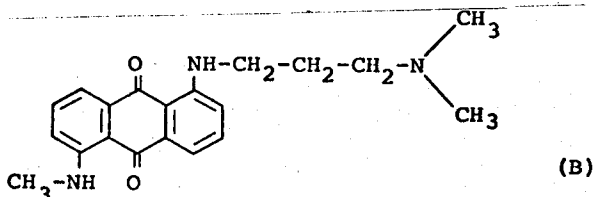
After the above treatment, the dyeing has the following wet fastness values (determined by evaluation of the bleeding of standard white ϵ -polycaprolactam according to Draft-ISO-Recommendation No. 117, Part 3):

TREATED THREADS

TREATED THREADS	CON-TROL
Washing fastness 3 (determined according to ISO/R 105/IV-1968, Part 10): 5	(4-5)
Fastness to water b (determined according to ISO/R 105/I-1959, Part 22): 4-5	(3)
Fastness to perspiration acid (determined according to ISO/R 105/IV-1968, Part 4): 4	(2-3)
Fastness to perspiration alkaline (determined according to ISO/R 105/IV-1968, Part 4): 3-4	(2)

The numbers in the parentheses state the corresponding wet fastness values of the control dyeing which was not aftertreated according to this invention.

1b. A similar improvement of the wetting fastness properties was also achieved in the case of pink dyeings which had been produced on threads formed from anionically modified polyhexamethylene diamine adipate with 0.5 percent by weight of a cationic dyestuff of the formula:



and which was after treated according to the procedure of Example 1a.

EXAMPLE 2

2a. 2 hanks of equal weight, one consisting of an unmodified, and another consisting of an anionically modified polyhexamethylene diamine adipate were dyed together in a dye bath with 1 percent by weight of the anionic dyestuff color index number

61135 and 1 percent by weight of the cationic dyestuff (A) of Example 1; 1 part by weight of these hanks was moved for 45 minutes in 40 parts by weight of an aqueous liquor at 60°C, which contains per liter of liquid:

0.35 g 85 percent acid and

0.75 g condensation product of Example 1. The liquor contained 2.5 percent of the condensation product based on the weight of the hanks. Subsequently, the hanks were rinsed in fresh water and dried.

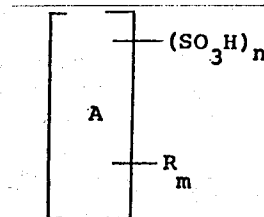
Upon subjecting the hanks to the testing procedure of Example 1, the hank which was anionically modified shows considerable improvement in fastness to water, washing, and perspiration, whereas the fastness properties of the dyed unmodified material remain unaffected. The properties of the anionic dye component are thus not impaired by the after-treatment of this invention.

2b. A similar result was obtained in the case of the after-treatment of yarns from unmodified and anionically modified polyhexamethylene diamine adipate threads which had been dyed with 1 percent by weight of the anionic dyestuff color index number 61590 and 1 percent by weight of the cationic dyestuff (B) given in Example 1.

Having described the invention by way of non-limiting examples in full, clear, and concise terms, what is to be protected is defined by the following claims.

We claim:

1. Process for the improvement of the wet fastness properties of anionically modified synthetic polyamide textile materials dyed with cationic dyestuffs comprising treating the materials with aqueous liquors, which contain alkali or ammonium salts of formaldehyde condensation products of aromatic sulfonic acids of the formula:



in which

A signifies diphenyl ether radical,

R signifies an alkyl radical containing 1-4 carbon atoms,

m a whole number from 0-2 and

n a number from 0.5-2.

2. Process of claim 1 wherein m is 0.

3. Process of claim 1 wherein R is methyl and m is 2.

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