

1

3,355,243

**PROCESS FOR THE DYEING OF POLYACRYLO-
NITRILE FIBERS****Jakob Bindler, Riehen, and Emanuel Durr, Arlesheim,
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Basel, Switzerland****No Drawing. Filed June 8, 1964, Ser. No. 374,233****Claims priority, application Switzerland,****June 11, 1963, 7,284/63****19 Claims. (Cl. 8—55)**

The present invention concerns a process to attain level dyeings on copolymeric acrylonitrile and especially on acrylic fibers having color saturation values in the range from about 2.5 to 6.5, the dye liquors used therefor as well as, as industrial product, the uniformly dyed material.

Hitherto, in order to dye polymeric or copolymeric acrylonitrile by the exhaustion method with basic dyestuffs and in level shades, a dye liquor has been used which, in addition to basic dyestuffs, contained as dye assistants tertiary, mono- or bis-quaternary organic nitrogen compounds having at least one higher alkyl radical per molecule. As a rule, these assistants detrimentally affect the fastness to light of the dyeings obtained and "block" the fibers, i.e. as soon as a portion thereof has been drawn onto the fiber, they reduce the absorption power of the fiber both for further basic dyestuff and for further dye assistant. This blocking effect on the fiber makes the re-dyeing and in particular the cross dyeing of a shade already attained very much more difficult. Since the blocking effect caused by the known dye assistants on the polyacrylonitrile fiber affects the individual basic dyestuffs present, for instance, in a conventional mixed dye in different degrees, it is also generally impossible to attain or reproduce a desired shade with usually preferred mixtures of basic dyestuffs. Finally the blocking effect has a varying influence on the rate at which the basic dyestuffs draw onto the aforesaid type of fibers which, in practice, easily leads to uneven distribution of the dyestuff. Moreover, since the hitherto used dye assistants which have drawn onto the fiber are very difficult to remove, this blocking effect is generally irreversible.

It has now been found that polymeric, and especially copolymeric acrylonitrile fibers can be dyed in level shades while avoiding the above disadvantages by dyeing these materials in an acid, preferably organic acid and more particularly an acetic acid, dyebath which contains the basic dyestuffs and a polyamine, which latter has three or more, preferably 3 to 5 quaternized basic nitrogen atoms, a polyglycol ether chain and at least one lipophilic substituent, whereafter the dyeing process is completed in known manner.

The polyamines usable in the dyeing treatment according to the invention are, in particular, polyalkylene polyamine compounds the alkylene components of which are preferably of from 2 to 3 carbon atoms each, e.g. 1,2-ethylene, or 1,2- or 1,3-propylene radicals; the number of amino-nitrogens in these amines ranges from 3 to 5 and is preferably 3; for example, diethylenetriamine, tri-

2

ethylenetetramine, tetraethylenepentamine or dipropylenetriamine are compounds from which the polyamines usable according to the invention are derived. The latter polyamines further contain as lipophilic substituent an alkyl or alkenyl radical having, particularly, 14 to 20 carbon atoms. Examples of such radicals are the tetradecyl, hexadecyl, octadecyl or eicosyl or the oleyl radical. The polyglycol ether chain of the polyamines usable according to the invention has about 10 to 50, and preferably from 15 to 20 alkyleneoxy groups; these are mainly ethyleneoxy groups and there may be present in the chain a minor portion, preferably from one to two individual propyleneoxy or styreneoxy groups.

These polyamines are obtained by adding the desired alkylene oxide component and if desired also minor amounts of styrene oxide to the polyamine having at least one lipophilic radical and three or more nitrogen atoms. The addition products thus obtained are then quaternized to form the product to be used according to the invention with an ester derived from a low aliphatic or araliphatic alcohol and a strong acid, e.g. with dimethyl or diethyl sulfate, ethyl chloride or ethyl bromide, or benzyl chloride, arylsulfonic acid alkyl esters such as p-toluene sulfonic acid methyl or ethyl ester, chloroacetic or bromoacetic acid methyl or ethyl ester or chloropropionic or bromopropionic acid methyl or ethyl ester.

For instance, N - octadecyl - diethylenetriamine condensed with ethylene oxide and permethylated with dimethyl sulfate to a product containing a polyglycol ether chain having 15 to 20 ethyleneoxy groups has an excellent levelling action.

The basic dyestuffs used according to the invention are advantageously of the following dyestuff classes: thiazines, oxazines, diphenylmethanes, triphenylmethanes, rhodamines, azo, anthraquinone dyestuffs and, preferably, monoazo, methine and azamethine dyestuffs, which all contain onium groups, the onium groups being mainly ammonium groups.

As copolymeric acrylonitrile fibers, those fiber materials are used, the fiber-forming substance of which consists of a synthetic long-chain polymer comprising at least 80% by weight of acrylonitrile and which possess sufficient dyestuffs to impart to the fibers a color saturation value above 2, and especially in the range of about 2.5 to 6.5. The acid groups of copolymer effecting the affinity of the dyestuff are mainly the carboxylic acid, carboxylic acid amide or hydroxy groups as well as the sulfonic acid group.

The balance is essentially derived from vinylpyridines and other monomers copolymerizable with acrylonitrile which are described, for instance, in Canadian Patent 557,597, issued May 20, 1958.

Suitable acrylic fibers which satisfy the above requirements are produced from spinnable solutions described for instance in British Patent 830,830, published Mar. 23, 1960, and German Patent 1,075,317, published Feb. 11, 1960.

Commercially available fibers of the above-described type are, for instance, Acrilan 16, Orlon 42 and Dralon.

The polyacrylonitrile fibers can be dyed according to the invention in any form desired, for example as loose material or in the form of tow, top, hanks, or cheeses or, preferably, fabrics. They can also be dyed according to

3

the invention when mixed with other fibers, e.g. with cellulose or polyamide fibers, in particular, however, with wool.

These fibers are dyed by the exhaustion process from short, concentrated dye baths (goods-to-liquor ratio of 1:5) as well as from long dye baths (goods-to-liquor ratio of 1:100) at a temperature of preferably 60 to 100° C. The finished fibers are then rinsed and dried.

Depending on the depth of shade desired, the dosage of the aforesaid polyamine dye assistant in the dye bath ranges between 1 and 2% calculated on the weight of the goods. Deep dyeings require less levelling agent than light shades.

The acid reaction of the liquor is preferably adjusted by addition of organic acid, in particular formic acid, acetic acid or tartaric acid. For instance, to secure pH-values of the dye bath of preferably 3.5 to 5, 80%-acetic acid is added in amounts of 2 to 10%, and in particular 4 to 6%, calculated on the weight of the goods to be dyed in the bath. The dyeings obtained according to the invention on the above described types of acrylic fiber materials are very level and fast to light. They can easily be re-dyed or cross-dyed.

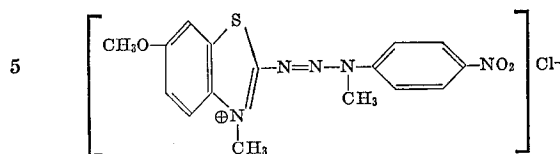
The inventive process for dyeing polymeric and especially copolymeric acrylonitrile fibers has among others the following advantages over similar known processes: It does not block the fibers; it affords a better dyestuff yield, especially in deeper shades; an overdosage of the polyamine used according to the invention does not decrease the dyestuff yield; the process permits an easy cross-dyeing of light shaded parts to deeper shades and does not adversely influence the fastness of dyeings obtained with basic dyestuffs.

The "color saturation value" mentioned in this specification and in the appended claims is the theoretical saturation value of usable acrylic fibers with a basic dyestuff of average affinity for such fibers, expressed in grams of dyestuff per 100 grams of fiber (viz, Surean, *Progrès réalisés dans la teinture des fibres Acryliques*, Teintex, June 1961).

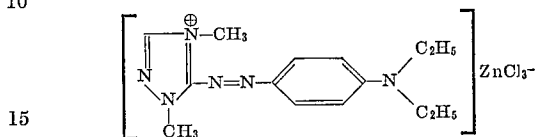
The following non-limitative examples illustrate the invention. The temperatures are given therein in degrees centigrade. C.I. means Colour Index, Second Edition, 1956, published by The Society of Dyers and Colourists, Bradford, England and The American Association of Textile Chemists and Colorists, Lowell, Mass., U.S.A.

4

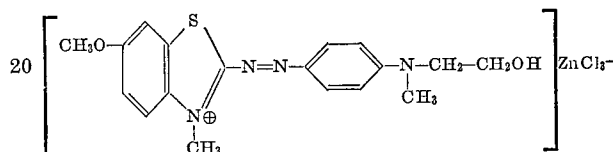
liquor (liquor ratio 1:50) which contains 0.7% of C.I. Basic Yellow 19, i.e. dyestuff of the formula



0.3% of C.I. Basic Red 22, i.e. dyestuff of the formula



and 2% of C.I. Basic Blue 41, i.e. dyestuff of the formula



as well as 5% of acetic acid (100%), 10% of sodium sulfate and 2% of the condensation product of 15 to 20 equivalents of ethylene oxide with N-octadecyl diethylenetriamine, quaternized with dimethyl sulfate, all percentages being calculated on the weight of the fibers. The liquor is heated to 80° within 10 minutes and then the temperature is raised at the rate of half a degree centigrade per minute to the boil. The material is left in the liquor for 2 hours at this temperature and then the liquor is allowed to cool to 60° within 30 minutes. The material so dyed is then taken out of the dyebath, and rinsed first with lukewarm and then with cold water.

The hanks of polyacrylonitrile are dyed a very level grey color, and have good fastness to light. The dyeings can easily be cross-dyed.

When the condensation product of 15 to 20 equivalents of ethylene oxide with N-octadecyl diethylenetriamine quaternized with dimethyl sulfate is replaced in the above example by corresponding amounts of the dye assistants listed in Table I below and otherwise the procedure described in the above example is followed, then dyeings having similarly good properties are obtained.

TABLE I

No.	Dye assistant condensation product of X mol of ethylene oxide with 1 mol of polyamine, quaternized			
	X	Alkylene oxide	Polyamine	Quaternizing agent
2	15-20 1	Ethylene oxide plus propylene oxide.	N-octadecyl-diethylenetriamine.	Dimethyl sulfate.
3	15-20	Ethylene oxide.	do.	Diethyl sulfate.
4	15-20	do.	do.	Benzyl chloride.
5	15-20	do.	do.	Toluene sulfonic acid methyl ester.
6	20	do.	do.	Dimethyl sulfate.
7	12	do.	N-oleyl-triethylenetetramine.	Do.
8	15	do.	N-hexadecyl-tetraethylenepentamine.	Do.
9	15-20	do.	N-octadecyl-dipropylenetriamine.	Do.
10	18-20 2	Ethylene oxide plus styrene oxide.	N-octadecyl-diethylenetriamine.	Do.

EXAMPLE 1

Hanks of polyacrylonitrile fibers which were produced from the spinnable solution obtained as described in Example 1 of British Patent 830,830 (or of Acrilan 16, Orlon 42 or Dralon) are introduced at 60° into a dye

When the same procedure as in Example 1 is followed, but, instead of the, in all, 3% of the dyestuff mixture given in Example 1, corresponding parts of the dyestuffs listed in Column II of Table II are used, then dyeings of the shades given in Column III of that table are obtained, which have similar satisfactory properties.

TABLE II

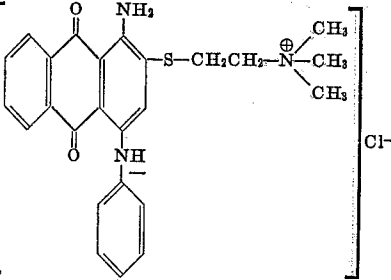
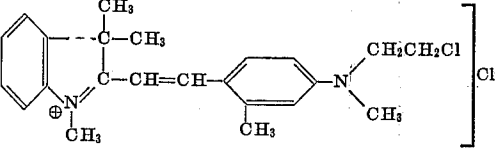
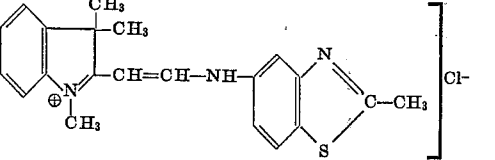
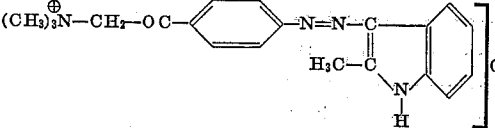
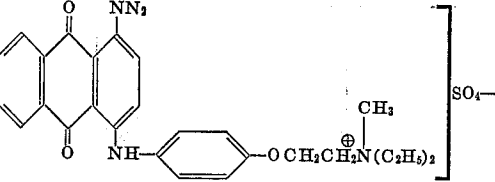
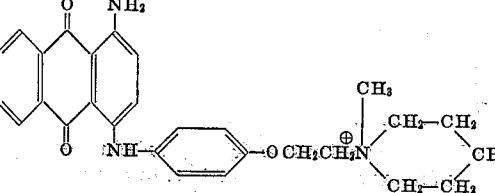
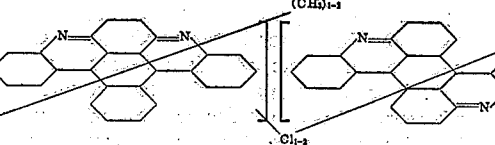
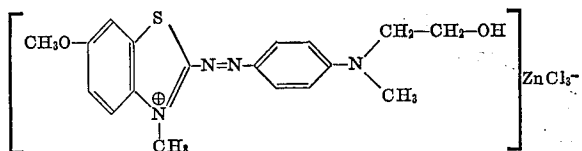
I No.	II Dyestuff	III Shade on polyacrylo- nitrile fibers
11.....	C.I. Basic Blue 49 	Blue.
12.....	C.I. Basic Red 14 	Red.
13.....	C.I. Basic Yellow 13 	Yellow.
14.....	C.I. Basic Green 1 (42040)	Green.
15.....	Deorlin Light Yellow 4RL 	Yellow.
16.....	Deorlin Light Blue BL 	Blue.
17.....	C.I. Basic Blue 5 (42140)	Do.
18.....	C.I. Basic Blue 44 	Do.
19.....	C.I. Basic Blue 1 (42025)	Do.
20.....	C.I. Basic Green 6 	Olive.

TABLE II—Continued

I No.	II Dyestuff	III Shade on polyacrylo- nitrile fibers
21.....	C.I. Basic Orange 21 (48035).....	Orange.
22.....	C.I. Basic Orange 22 (48040).....	Do.
23.....	C.I. Basic Red 13 (48015).....	Pink.
24.....	C.I. Basic Violet 7 (48020).....	Red-violet.
25.....	C.I. Basic Violet 20.....	Blue-violet.
	$\left[\begin{array}{c} \text{CH}_3-\text{N}^+=\text{C}-\text{C}_6\text{H}_4-\text{N}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{O}-\text{C}_2\text{H}_5 \\ \text{C}_6\text{H}_5 \\ \text{CH}_3\text{SO}_4^- \end{array} \right]$	
26.....	C.I. Basic Violet 21.....	Violet.
	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{OOC}-\text{C}_6\text{H}_3-\text{C}-\text{CH}_3 \\ \quad \quad \\ \text{C}=\text{CH}-\text{CH}-\text{C}_6\text{H}_4-\text{N}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{OCH}_2\text{CH}_3 \\ \quad \quad \\ \text{N}^+ \quad \quad \text{CH}_3 \\ \text{CH}_3 \end{array} \right] \text{Cl}^-$	
27.....	C.I. Basic Yellow 12 (48065).....	Yellow.
28.....	C.I. Basic Yellow 20.....	Do.
	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{C}-\text{CH}_3 \\ \quad \quad \\ \text{C}=\text{CH}-\text{CH}-\text{HN}-\text{C}_6\text{H}_3(\text{CH}_3\text{O})-\text{OCH}_3 \\ \quad \quad \\ \text{N}^+ \quad \quad \text{CH}_3 \end{array} \right] \text{Cl}^-$	
29.....	C.I. 48013.....	Pink.
30.....	C.I. Basic Blue 6 (51175).....	Blue.
31.....	C.I. Basic Yellow 3 (41005).....	Yellow.
32.....	C.I. Basic Green 4 (42000).....	Green.
33.....	C.I. Basic Red 1 (45160).....	Red.
34.....	C.I. Basic Yellow 19, C.I. Basic Blue 41 (1:1).....	Green.
	$\left[\begin{array}{c} \text{CH}_3\text{O}-\text{C}_6\text{H}_3-\text{S}-\text{N}=\text{N}-\text{N}(\text{CH}_3)-\text{C}_6\text{H}_4-\text{NO}_2 \\ \quad \quad \\ \text{N}^+ \quad \quad \text{CH}_3 \end{array} \right] \text{Cl}^-$ <p>and</p> $\left[\begin{array}{c} \text{CH}_3\text{O}-\text{C}_6\text{H}_3-\text{S}-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{N}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{OH} \\ \quad \quad \\ \text{N}^+ \quad \quad \text{CH}_3 \end{array} \right] \text{ZnCl}_3^- (1:1)$	

EXAMPLE 35

3 grams (g.) of C.I. Basic Blue 41, i.e. dyestuff of the formula



are pasted at room temperature with 5 g. of 80%-acetic acid. Then 250 milliliters (ml.) of hot water are poured

in. This solution is added to a solution of 10 g. of sodium sulfate and 2 g. of an adduct, quaternized with dimethyl sulfate, of 20 mols of ethylene oxide and 2 mols of styrene oxide to N-octadecyl diethylene-triamine in 1250 ml. of water. After heating the liquor thus obtained to 60°, a polyacrylonitrile fabric containing about 15% of dyesites-affording copolymer, e.g. a Dralon fabric, is introduced. The liquor is heated within 10 minutes to 80° and then at a rate of half a degree per minute up to 98°. It is maintained at this temperature for 2 hours, whereupon it is allowed to cool within 30 minutes to 60°. The fabric dyed in this way is rinsed several times in

40°-warm water and in cold water, then treated with an aqueous solution of 4 g./liter of an antistatic cation-active fatty acid imidazoline derivative, and finally dried.

A level, deeply blue dyeing is obtained.

We claim:

1. A process for the production of level dyeings on copolymeric acrylonitrile fibers having dyesites corresponding to a color saturation value above 2, comprising dyeing this material with an acid dye liquor which contains at least one basic dyestuff and, as dye assistant, a polyamine the molecule of which consists of a polyalkene polyamine moiety having from three to five quaternized basic nitrogen atoms, a polyglycol ether chain of from 10 to 50 ethyleneoxy groups and at least one lipophilic substituent, and steaming and rinsing the resulting dyeing.

2. A process according to claim 1, wherein the dye assistant is a permethylated N-octadecyl-diethylene triamine which contains a polyglycol ether chain having 15 to 20 ethyleneoxy groups.

3. A process as defined in claim 1, wherein the pH of the dye liquor is within the range between 3.5 and 5.

4. An acid dye liquor for use in the production of level dyeings on copolymeric acrylonitrile fibers having dyesites corresponding to a color saturation value above 2, said acid dye liquor containing at least one basic dyestuff for coloring said fibers and, as dye assistant, a polyamine the molecule of which consists of a polyalkene polyamine moiety having from three to five quaternized basic nitrogen atoms, a polyglycol ether chain of from 10 to 50 ethyleneoxy groups and at least one lipophilic substituent.

5. A dye liquor as defined in claim 4, wherein the pH of said liquor at introduction of said fibers is within the range between 3.5 and 5.

6. A process as defined in claim 1, wherein said polyamine dye assistant is the condensation product of 15 to 20 equivalents of ethylene oxide with N-octadecyl diethylenetriamine quaternized with dimethyl sulfate.

7. A process as defined in claim 1, wherein said polyamine dye assistant is the condensation product of 20 mols of ethylene oxide and 2 mols of styrene oxide with N-octadecyl diethylenetriamine, per mol of the latter, quaternized with dimethyl sulfate.

8. A process as defined in claim 1, wherein said polyamine dye assistant is the condensation product of 15 to 20 mols of ethylene oxide and 1 mol of propylene oxide with 1 mol of N-octadecyl-diethylenetriamine, quaternized with dimethyl sulfate.

9. A process as defined in claim 1, wherein said polyamine dye assistant is the condensation product of 20 mols of ethylene oxide with 1 mol of N-octadecyl-diethylenetriamine, quaternized with dimethyl sulfate.

10. A process as defined in claim 1, wherein said polyamine dye assistant is the condensation product of 12 mols of ethylene oxide with 1 mol of N-oleyl-triethylenetetramine, quaternized with dimethyl sulfate.

11. A process as defined in claim 1, wherein said polyamine dye assistant is the condensation product of 15 mols of ethylene oxide with 1 mol of N-hexadecyl-tetraethylenepentamine, quaternized with dimethyl sulfate.

12. A process as defined in claim 1, wherein said polyamine dye assistant is the condensation product of 15 to 20 mols of ethylene oxide with 1 mol of N-octadecyl-dipropylenetriamine, quaternized with dimethyl sulfate.

13. A dye liquor according to claim 4, wherein said polyamine dye assistant is the condensation product of 15 to 20 equivalents of ethylene oxide with N-octadecyl diethylenetriamine quaternized with dimethyl sulfate.

14. A dye liquor according to claim 4, wherein said polyamine dye assistant is the condensation product of 20 mols of ethylene oxide and 2 mols of styrene oxide with N-octadecyl diethylenetriamine, per mol of the latter, quaternized with dimethyl sulfate.

15. A dye liquor according to claim 4, wherein said polyamine dye assistant is the condensation product of 15 to 20 mols of ethylene oxide and 1 mol of propylene oxide with 1 mol of N-octadecyl-diethylenetriamine, quaternized with dimethyl sulfate.

16. A dye liquor according to claim 4, wherein said polyamine dye assistant is the condensation product of 20 mols of ethylene oxide with 1 mol of N-octadecyl-diethylenetriamine, quaternized with dimethyl sulfate.

17. A dye liquor according to claim 4, wherein said polyamine dye assistant is the condensation product of 12 mols of ethylene oxide with 1 mol of N-oleyl-triethylenetetramine, quaternized with dimethyl sulfate.

18. A dye liquor according to claim 4, wherein said polyamine dye assistant is the condensation product of 15 mols of ethylene oxide with 1 mol of N-hexadecyl-tetraethylenepentamine, quaternized with dimethyl sulfate.

19. A dye liquor according to claim 4, wherein said polyamine dye assistant is the condensation product of 15 to 20 mols of ethylene oxide with 1 mol of N-octadecyl-dipropylenetriamine, quaternized with dimethyl sulfate.

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