United States Patent

Bindler

[15] **3,652,201**

[45] **Mar. 28, 1972**

[54] **PROCESS FOR THE PRODUCTION OF DYEINGS ON FIBER MATERIAL CONSISTING OF POLYMERIC OR COPOLYMERIC ACRYLONITRILE**

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[22] Filed: **Apr. 28, 1969**

[21] Appl. No.: **819,976**

[30] **Foreign Application Priority Data**

Apr. 30, 1968 Switzerland 6438/68

[52] **U.S. Cl.** ....**8/172,** 8/177 AB
[51] **Int. Cl.** **D06p 5/06**
[58] **Field of Search** ....8/172, 84, 177 AB

[56] **References Cited**

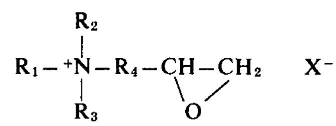
UNITED STATES PATENTS

2,986,444	5/1961	Rokohl et al.	8/177 AB
2,989,361	6/1961	Hees	8/84 X
3,104,933	9/1963	Mendelsohn et al.	8/172 X

Primary Examiner—George F. Lesmes
Assistant Examiner—T. J. Herbert, Jr.
Attorney—Wenderoth, Lind & Ponack

[57] **ABSTRACT**

A process for the production of level dyeings on polymeric or copolymeric acrylonitrile fibers by dyeing said fibers with a dye liquor containing a basic dyestuff and as dye assistant a quaternary ammonium compound of the formula



wherein

R_1 represents an aliphatic hydrocarbon radical with at least eight carbon atoms,
R_2 represents a lower alkyl radical,
R_3 represents a lower alkyl radical optionally substituted by hydroxyl and/or phenyl groups,
R_4 represents a lower alkylene bridge and
X^- represents the anion equivalent of an acid usch as, e.g., Cl^- or Br is, described.

The dyeing process is distinguished from those using known strong cationic retarders by its adequate retarding action without any undue blocking effect.

9 Claims, No Drawings

PROCESS FOR THE PRODUCTION OF DYEINGS ON FIBER MATERIAL CONSISTING OF POLYMERIC OR COPOLYMERIC ACRYLONITRILE

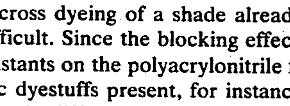
The present invention concerns a process for the production of even dyeings on fiber material consisting of polymeric or copolymeric acrylonitrile, the dye liquor applicable for the process and the material evenly dyed therewith.

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.

In contrast thereto, the claimed quaternary organic nitrogen compounds, in addition to exhibiting the said "blocking effect," are also effective "retarders," that is they exert a reversible restraining effect upon the rate at which the basic dyestuff in the bath dyes the fiber. Consequently, the use of such retarders leads to uniform dyeings from a bath which is virtually exhausted at the end of the dyeing operation.

It has been found that fiber material consisting of polymeric or copolymeric acrylonitrile can be dyed in even shades if this material is dyed using an acid dye liquor, preferably acetic acid dye liquor, which contains at least one cationic dyestuff and a quaternary ammonium compound of the formula



wherein

- R_1 represents an aliphatic hydrocarbon radical with at least eight carbon atoms,
- R_2 represents a lower alkyl radical,
- R_3 represents an lower alkyl radical optionally substituted by hydroxyl and/or phenyl groups,
- R_4 represents a lower alkylene bridge and
- X^- represents the anion equivalent of an acid such as, e.g., Cl^- or Br^-.

The aliphatic hydrocarbon radical R_1 can be saturated or unsaturated, straight or branched. It has at least eight and preferably 12 to 14 carbon atoms. Examples for R_1 are the octyl, decyl, dodecyl or myristyl radical.

The lower alkyl radicals R_2 and R_3 — when the latter represents an lower alkyl group — preferably have one to four carbon atoms and, in particular, they represent the methyl or ethyl radical. If R_3 contains hydroxyl and/or phenyl groups, then these are preferably in the terminal (ω-)position. Such substituted lower alkyl radicals are, e.g., the β-hydroxyethyl, γ-hydroxypropyl and β-hydroxy-β-phenylethyl group.

The alkylene bridge R_4 preferably has at most three carbon atoms and represents especially the methylene group.

In this specification including the claims the term "lower" is used to denote an alkyl radical having at most five carbon atoms.

The quaternary ammonium compounds, applicable according to the invention, are accessible in various ways, e.g., by reacting 1,3-dichloro-propanol-2, 1,4-dichloro-butanol-3, 1,5-dichloro-pentanol-4- or preferably epihalogen hydrins, such as epibromohydrin or especially epichlorohydrin, with tertiary amines such as N,N-dimethyl-N-octylamine, N,N-diethyl-N-octylamine, N,N-dimethyl-N-dodecylamine, N,N-diethyl-N-dodecylamine, N-methyl-N-isopropyl-N-dodecylamine, N-methyl-N-benzyl-N-dodecylamine, N-methyl-N-β-phenylethyl-N-dodecylamine, N,N-dimethyl-N-myristylamine or with tertiary amines which have been produced by addition of equivalent amounts of alkylene oxide or styrene oxide to a fatty amine having an aliphatic hydrocarbon radical and a lower alkyl radical such as, e.g., N-methyl-N-octylamine, N-methyl-N-dodecylamine, N-ethyl-N-dodecylamine, N-isopropyl-N-dodecylamine, N-propyl-N-dodecylamine, N-butyl-N-dodecylamine or N-methyl-N-myristylamine. The reaction of the tertiary amines with e.g., epihalogen hydrins to give the quaternary ammonium compounds is performed by heating the components to temperatures between 50° and 100° C., optionally in organic solvents, preferably in the presence of aluminum chloride, tin tetrachloride or boron trifluoride. Suitable organic solvents are, optionally, halogenated aromatic hydrocarbons, e.g., benzene, toluene or xylols, chlorobenzene, dichlorobenzene or trichlorobenzene as well as, optionally, halogenated aliphatic hydrocarbons such as carbon tetrachloride, trichloro ethylene or methylene chloride.

Of particular value as levelling agents are the quaternary ammonium salts, applicable according to the invention, wherein R_1 represents an alkyl radical with eight to 14 carbon atoms, R_2 and R_3 each represent the methyl or ethyl group, R_4 the methylene bridge and X^- the chlorine of bromine ion.

An excellent levelling action without the formation of froth is exhibited by quaternary ammonium salts, applicable according to the invention, which are derived from styrene oxide, especially N-methyl-N-dodecyl-N-β-hydroxy-β-phenylethyl-N-2,3-epoxypropyl ammonium chloride.

Suitable as cationic dyestuffs applicable according to the invention are, advantageously, the technically easily accessible salts and metal halides, e.g., zinc chloride double salts of the known basic dyestuffs. These are, e.g., thiazines, oxazines, diphenyl methane, triphenyl methane, rhodamines, azo- or anthra-quinone dyestuffs and preferably monoazo, methine and azomethine dyestuffs, all containing onium groups, whereby as onium groups reference is made, above all, to ammonium groups.

As fiber material consisting of polymeric and copolymeric acrylonitrile, such fiber materials are suitable, the fiber-forming substance of which consists of a synthetic, longchained polymer containing at least 85 acrylonitrile. In the case of the acid groups of copolymeric producing the dyestuff affinity, suitable groups are primarily carboxylic acid groups, carboxylic acid amide groups or hydroxyl groups, and also sulphonic acid groups.

The polyacrylonitrile fibers can be dyed, according to the invention, in any desired form, e.g., as loose material or in the form of slubbing, yarn, hank or on cheeses or as fabrics. They can also be dyed according to the invention in admixture with other fibers, e.g., with cellulose or polyamide fibers, especially however with wool.

The dyeing of the fiber material is performed using the exhaust process from short, concentrated dyebaths (goods/liquor ratio 1:5), and also from long dyebaths (goods/liquor ratio 1:100 at temperatures of preferably 60° to 100° C. The finished fiber material is finally rinsed and dried.

Depending on the desired depth of color, the contents of quaternary ammonium salt, according to the invention, in the dye bath is between 0.02 and 0.5 g. per liter of liquor. Less levelling agent is required for deep dyeings than for light shades.

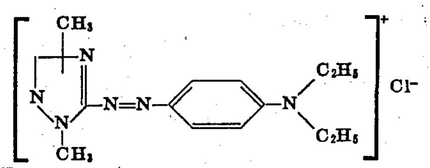
The acid reaction of the liquor is adjusted preferably using organic acid, especially acetic acid. For example, 40% acetic acid is added in quantities of 0.5 to 5 ml. per liter of liquor. In addition, in order to ensure pH values of the liquor of preferably from 3.5 to 5, small amounts of sulphuric acid and/or neutral salts, such as sodium sulphate or sodium chloride, are added to the dye bath.

The dyeings obtained according to the invention on polymeric and copolymeric acrylonitrile fibers are characterized by a very good uniformity. Of particular advantage is the fact that the quaternary ammonium salts applicable according to the invention, compared with known cationic retarding agents of similar constitution, also have, in addition to an adequate retarding action, a lower blocking action. They are therefore very suitable for correcting faulty dyeings and for cross-dyeing, without impairing the dyestuff yield and the fastness properties of the obtained dyeings.

The following Examples illustrate the invention, whereby the temperature are given in degrees Centigrade C.I. denotes COLOR 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. USA.

EXAMPLE 1

25 g. of polyacrylonitrile yarn are introduced at 50° into a liter of dye liquor containing 0.12 g. of the cationic dyestuff of the formula



0.05 g. of N,N-dimethyl-N-dodecyl-N-2,3-epoxypropyl ammonium chloride and 0.5 ml. of 40% acetic acid. The temperature of the dye bath is raised to boiling point and the dye bath is held at this temperature for 1 hour. After cooling to 60°, the dyed material is taken out and it is then rinsed with lukewarm and cold water.

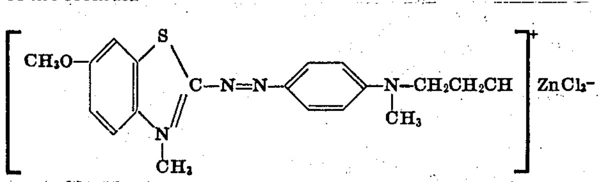
A red dyed yarn is obtained of excellent uniformity.

The N,N-dimethyl-N-dodecyl-N-2,3-epoxypropyl ammonium chloride used in the first section can, for example, be produced as follows:

68 g. of N,N-dimethyl-N-dodecylamine together with 0.1 g. of aluminum chloride are heated to 98°–100°. 30 g. of epichlorohydrin are then added dropwise within 30 minutes. After stirring for 3 hours at 100°–105°, a thick brown paste is obtained, which dissolves in water in a practically clear form.

EXAMPLE 2

25 g. of polyacrylonitrile fabric are introduced at 50° into a liter of dye liquor containing 0.075 g. of the cationic dyestuff of the formula

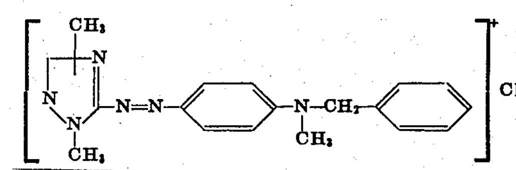


0.125 g. of N,N-dimethyl-N-dodecyl-N-2,3-epoxypropyl ammonium chloride, 0.040 ml. of 98% sulphuric acid, 1.5 ml. of 40% acetic acid and 2.5 g. of anhydrous sodium sulphate. The temperature of the dye bath is raised to the boiling point and dyeing proceeds at this temperature for 1 hour. The thus dyed material is then taken out and rinsed with lukewarm and cold water. A very uniform, blue dyeing on polyacrylonitrile fabric is obtained.

If, instead of 0.125 g. of N,N-dimethyl-N-dodecyl-N-2,3-epoxypropyl ammonium chloride, the same amounts are used of N,N-diethyl-N-dodecyl-N-2,3-epoxypropyl ammonium chloride, N-methyl-N-β-hydroxy-ethyl-N-dodecyl-N-2,3-epoxypropyl ammonium chloride or N-methyl-N-γ-hydroxypropyl-N-dodecyl-N-2,3-epoxypropyl ammonium chloride, using otherwise the procedure given in the example, dyeings of good uniformity are obtained.

EXAMPLE 3

25 g. of polyacrylonitrile yarn are introduced at 50° into a liter of dye liquor 85% 0.2 g. of the cationic dyestuff of the formula



0.125 g. of N-dodecyl-N-methyl-N-2,3-epoxypropyl-N-β-hydroxy-β-phenylethyl ammonium chloride and 0.5 ml. of 40% acetic acid. The temperature of the dye bath is raised to the boiling point and the dye bath is held at this temperature for 1 hour. After cooling to 60°, the dyed material is taken out and then rinsed with lukewarm and cold water.

A very uniformly red dyed polyacrylonitrile yarn is obtained.

The N-dodecyl-N-methyl-N-2,3-epoxypropyl-N-β-hydroxy-β-phenylethyl ammonium chloride used in the first section can, for example, be produced as follows: 37 g. of styrene oxide are added dropwise at 45°–50°, while stirring, to a solution of 60 g. of N-methyl-N-dodecylamine in 300 g. of chlorobenzene. The reaction mixture is heated to boiling and is refluxed for 10 hours at boiling temperature. The chlorobenzene is then distilled off in vacuo and the residue is distilled under reduced pressure at B.P.$_{0.1mm}$ 153°–155°.

76.8 g. of N-methyl-N-dodecyl-N-β-hydroxy-β-phenylethylamine are obtained in the form of a yellowish oil. 0.1 g. of aluminum chloride is added at 45° to 62 g. of N-methyl-N-dodecyl-N-β-hydroxy-β-phenylethylamine. To this mixture are then added at 90°–95°, within 40 minutes, 18 g. of epichlorohydrin. The temperature of 95°–100° is held for a further 6 hours, whereupon a viscous substance is formed which is dissolved in isopropyl alcohol and diluted with water. A stable, non-frothing emulsion is then formed.

Very uniform dyeings are obtained on polyacrylonitrile fibers by using, instead of 0.125 g. of the N-dodecyl-N-methyl-N-2,3-epoxypropyl-N-β-hydroxy-β-phenylethyl ammonium chloride given in Example 3, but applying otherwise the same procedure, corresponding amounts of quaternary ammonium salts, which have been produced by reacting the tertiary amines given in column III of the following table I, with epichlorohydrin, using the method described in Example 3, section 3.

TABLE I

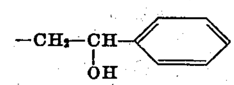
	G. amounts of the quaternary ammonium salts	Tertiary amine of the formula $R_1-N(R_3)-R_2$: R_1	R_2	R_3	Boiling point of the tertiary amine in ° C.
Example No.:					
4	0.05	$-C_8H_{17}$	$-CH_3$		B.P.$_{0.14mm}$ 121–123
5	0.125	$-C_{14}H_{29}$	$-CH_3$	do	B.P.$_{0.15mm}$ 171–172

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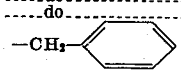
Table I—Continued

	G. amounts of the quaternary ammonium salts	Tertiary amine of the formula $R_1-N(R_3)-R_2$ R₁	R₂	R₃	Boiling point of the tertiary amine in ° C.
Example No.:					
6	0.06	$-C_{12}H_{25}$	$-C_2H_5$	do	B.P. $_{0.15mm.}$ 160–161
7	0.08	$-C_{12}H_{25}$	$-CH(CH_3)-CH_3$	do	B.P. $_{0.1mm.}$ 163–166
8	0.06	$-C_{12}H_{25}$	$-CH_2CH_2CH_3$	do	B.P. $_{0.7mm.}$ 160–162
9	0.06	$-C_{12}H_{25}$	$-C_4H_9$	do	B.P. $_{0.2mm.}$ 166–169
10	0.05	$-C_{12}H_{25}$	$-CH_3$		B.P. $_{0.01mm.}$ 135–140

If, instead of 0.2 g. of the dyestuff given in example 3, corresponding amounts of the dyestuffs listed in table II, column II, are used, applying otherwise the same procedure, then dyeings are obtained in the shades given in column III having similar properties.

TABLE II

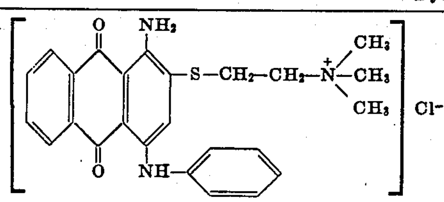
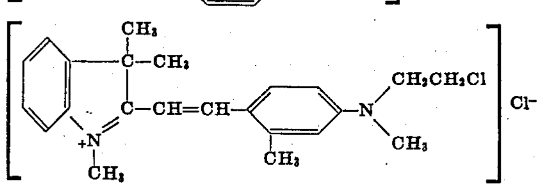
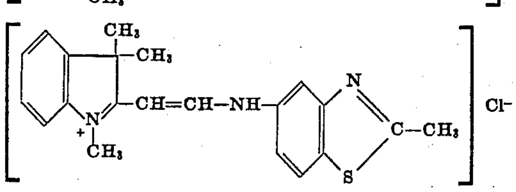
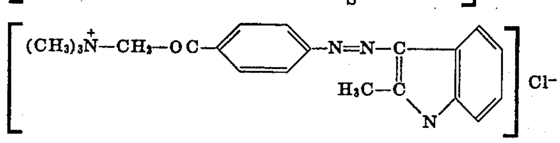
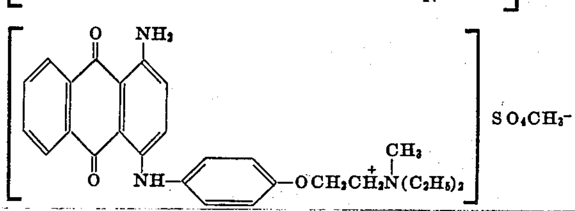
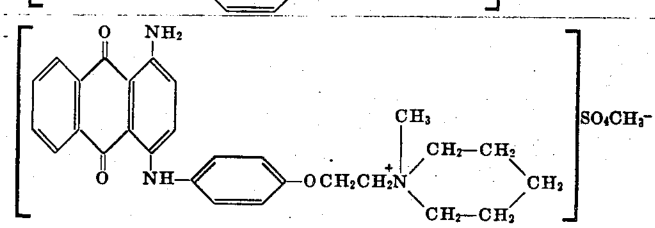
I. Nr.	II. Dyestuff	III Shade on polyacrylonitrile fibres
11		Blue.
12		Red.
13		Yellow.
14		Do.
15		Blue.
16		Do.

TABLE II

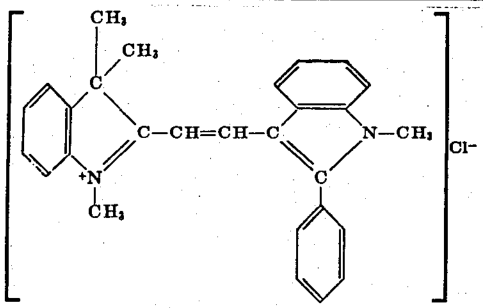
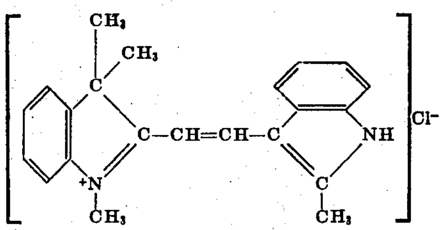
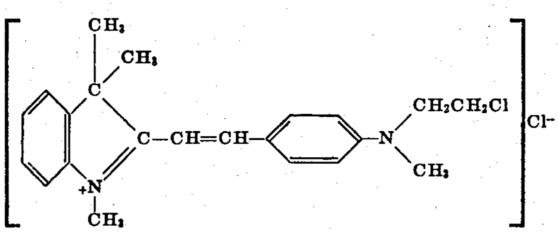
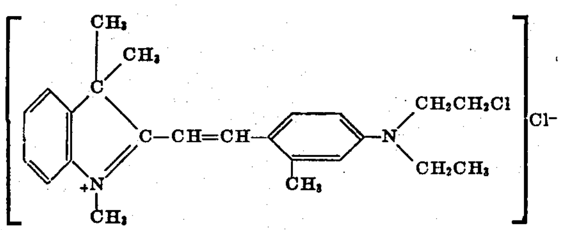
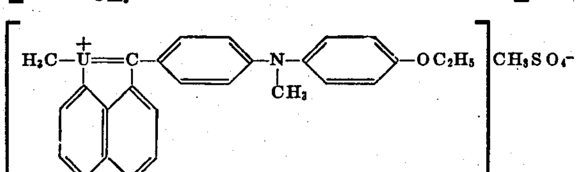
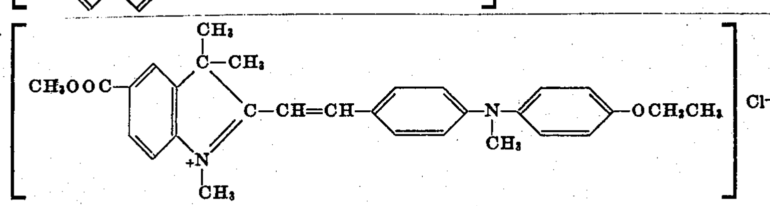
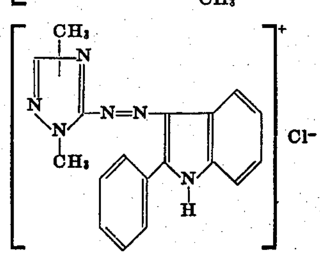
I. Nr.	II. Dyestuff	III Shade on polyacrylonitrile fibres
17		Orange.
18		Do.
19		Red.
20		Red.
21		Violet.
22		Do.
23		Reddish yellow.

TABLE II

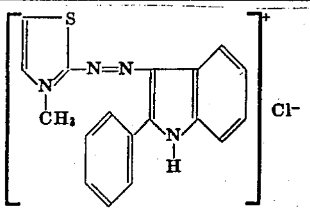
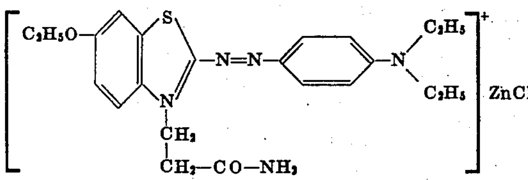
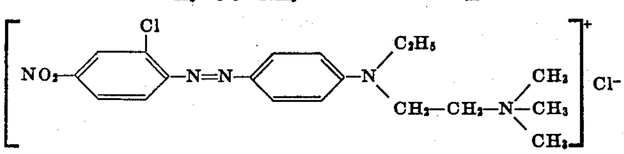
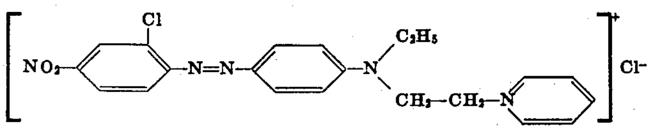
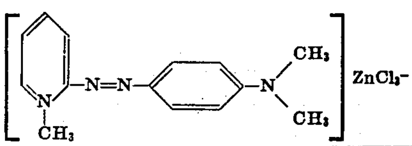
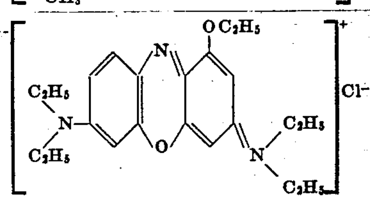
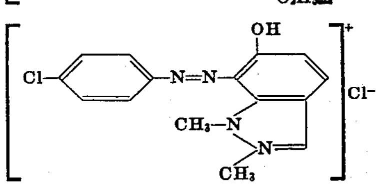
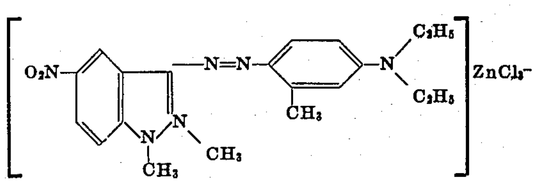
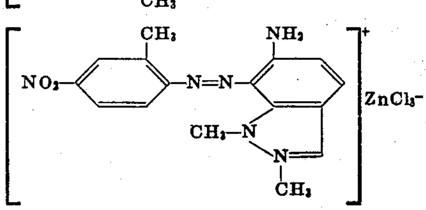
I. Nr.	II. Dyestuff	III Shade on polyacrylonitrile fibres
24		Red.
25		Blue.
26		Red.
27		Red.
28		Violet.
29		Blue.
30		Yellow.
31		Blue.
32		Orange.

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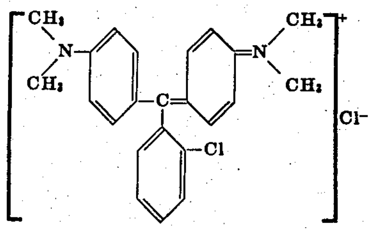
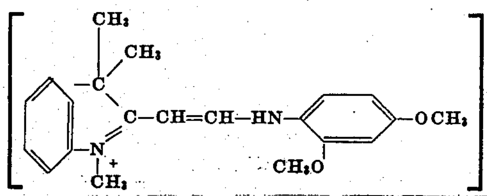
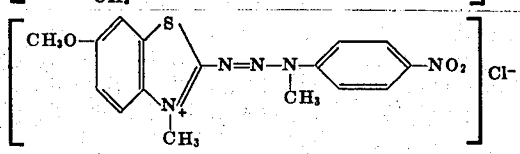
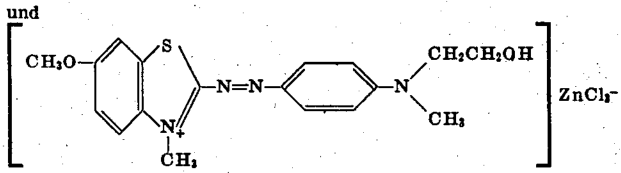
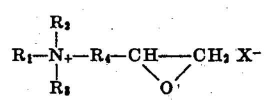
TABLE II

I. Nr.	II. Dyestuff	III Shade on polyacrylonitrile fibres
33		Blue.
34		Yellow.
		
35	und 	Green.
36	C.I. Basic Green 1 (42040)	Do.
37	C.I. Basic Blue 4 (42140)	Blue.
38	C.I. Basic Blue 1 (42025)	Do.
39	C.I. Basic Orange 21 (48035)	Orange.
40	C.I. Basic Orange 22 (48040)	Do.
41	C.I. Basic Red 13 (48015)	Pink.
42	C.I. Basic Violet 7 (48020)	Red-violet.
43	C.I. Basic Yellow 12 (48065)	Yellow.
44	C.I. 48013	Pink.
45	C.I. Basic Blue 6 (51175)	Blue.
46	C.I. Basic Yellow 3 (41005)	Yellow.
47	C.I. Basic Green 4 (42000)	Green.
48	C.I. Basic Red 1 (45160)	Red.

We claim:

1. Process for the production of level dyeings on polymeric or copolymeric acrylonitrile fibers, said fibers containing at least 85% acrylonitrile, comprising dyeing this material with an acid dye liquor having a pH in the range between 3.5 to 5 which contains at least one basic dyestuff and a quaternary ammonium compound of the formula



wherein

R_1 is an aliphatic hydrocarbon radical of at least eight carbon atoms,

R_2 is a lower alkyl radical,

R_3 is a lower alkyl radical any substituent of which is selected from hydroxy and phenyl and

R_4 is a lower alkylene bridge and

X^- represents the anion of an acid.

2. A process as described in claim 1 wherein R_4 is $-CH_2-$.

3. A process as described in claim 1 wherein R_1 is alkyl of from eight to 14 carbon atoms.

4. A process as described in claim 3 wherein R_2 is methyl or ethyl.

5. A process as described in claim 4 wherein R_3 is selected from methyl, ethyl, β-hydroxyethyl, γ-hydroxypropyl and β-hydroxy-β-phenylethyl group.

6. A process as described in claim 1 wherein in the formula of said compound R_1 is alkyl of from eight to 14 carbon atoms, each of R_2 and R_3 represents methyl or ethyl and X represents chlorine or bromine.

7. A process as described in claim 1 wherein said compound is N-methyl-N-dodecyl-N-β-hydroxy-β-phenylethyl-N-2,3-epoxy-propyl-ammonium chloride.

8. A process as described in claim 6, wherein said compound is N,N-dimethyl-N-dodecyl-N-2,3-epoxypropyl-ammonium chloride.

9. An acid dye liquor for level dyeing on polymeric or copolymeric acrylonitrile fibers containing at least 85% acrylonitrile, which liquor contains at least one basic dyestuff for coloring said fibers, and as a dye assistant a quaternary compound of the formula as described in claim 1.

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