United States Patent [19]

Wegmuller et al.

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[45] **Mar. 4, 1975**

[54] **PROCESS FOR THE PRODUCTION OF DIFFERENTIAL EFFECTS ON POLYMERIC OR COPOLYMERIC ACRYLONITRILE FIBERS**

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[21] Appl. No.: **373,292**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 145,582, May 20, 1971, abandoned.

[30] **Foreign Application Priority Data**

May 22, 1970 Switzerland 7573/70

[52] **U.S. Cl.** **8/15,** 8/65, 8/169

[51] **Int. Cl.** **D06p 5/12**

[58] **Field of Search** ..... 8/21, 168 A, 15

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[57] **ABSTRACT**

A process for producing differential effects on polymeric or copolymeric acrylonitrile fibers is provided. The processes carried out by pretreating the fibrous materials with aqueous preparations having a pH-value of between 3 and 5 and containing a colorless cation-active, organic ammonium or sulphonium compound with at least one higher alkyl radical at temperatures of at least 85°C and dyeing the so treated material together with untreated material with at least one cationic dyestuff.

7 Claims, No Drawings

PROCESS FOR THE PRODUCTION OF DIFFERENTIAL EFFECTS ON POLYMERIC OR COPOLYMERIC ACRYLONITRILE FIBERS

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of our patent application Ser. No. 145,582, now abandoned filed May 20, 1971.

The present invention relates to a process for the production of differential effects on fiber material made from polyacrylonitrile or from acrylonitrile copolymers, as well as to the fiber material thus dyed in varying shades.

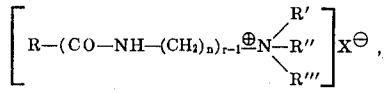
It has already been suggested that resist effects on materials such as fabrics and knitted goods made from hydrophobic fibers, including polyacrylonitrile fibers, be produced by the textile material being treated in the desired areas with a printing paste containing an aromatic amphoteric compound, and subsequently dyed. The effects attainable with such compounds on polyacrylonitrile fiber material have proved, however, to be inadequate.

It has now been found that effectively differential effects can be produced, in a simple manner, on polymeric or copolymeric fibers, wherein said fibers contain at least 80 percent acrylonitrile and having dyesites corresponding to a color saturation value of at least 1 according to the present invention by pretreating said fibers with an aqueous preparation, optionally containing thickeners, of a colorless, cation-active, organic ammonium or sulphonium compound containing at least one higher alkyl radical, i.e., having 8 to 22 carbon atoms at temperatures of at least 85°C, preferably 95° – 110°C, and with a pH-value between 3 and 5, especially between 4 and 4.5; and then dyeing at least one such pretreated fiber material together with untreated said fiber material with at least one cationic dyestuff, wherein the proportion of the dyestuff absorbed by the pretreated fibers and the untreated fibers is within 4:96 to 20:80.

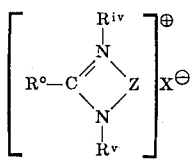
Preferably, the pretreatment is carried out with an aqueous preparation containing a cation-active organic ammonium compound which contains an alkyl radical having 8 to 22 carbon atoms, and of which the cationic part carries only a single positive charge.

Of particular interest is the use of cation-active organic ammonium compounds of the formula:

(1)

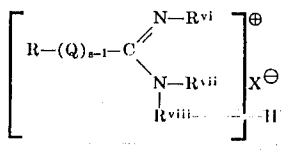


(2)



or

(3)



wherein

R represents an alkyl radical having 8 to 18 carbon atoms,

R′ and R″ each represent hydrogen, lower alkyl, hydroxy-lower alkyl, lower alkoxy-lower alkyl, cyano-lower alkyl; cycloalkyl, or a polyalkylene glycol radical, or

R′ and R″ together with the nitrogen atom binding them represent piperidino or morpholino,

R‴ represents hydrogen, lower alkyl, aralkyl or aralkyl substituted by hydroxyl or lower alkoxy, or

R′, R″ and R‴ together with the nitrogen atom binding them repesents pyridyl or lower alkylpyridyl,

one of the radicals R^{o}, R^{iv} and R^{v} represents an alkyl radical having 8 to 18 carbon atoms, and the others represent hydrogen, alkyl, aralkyl or aralkyl substituted by hydroxyl,

Z represents an alkylene radical having 2 or 3 carbon atoms,

R^{vi}, R^{vii} and R^{viii} each represent hydrogen, lower alkyl, hydroxy-lower alkyl or lower alkoxy-lower alkyl, cycloalkyl or aralkyl,

Q represents sulphur or -NH-,

r and s represent 1 or 2,

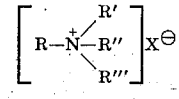
n represents 2 or 3, and

X represents the anion of an organic or inorganic acid.

Good results are obtained, in particular, with a cation-active organic ammonium compound of formula (I).

Of advantage is, in particular, the use of cation-active organic ammonium compounds of the formula

(4)

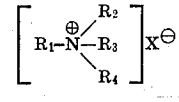


wherein R, R′, R″, R‴ and X have the given meanings.

Of the ammonium and sulphonium compounds to be used, the following **10** types of compounds have proved to be particularly interesting:

1. Compounds of the general formula

(5)



wherein

R_1 represents an unsubstituted alkyl group having 8 to 18, preferably 12 to 18, carbon atoms,

R_2 and R_3 each represent, independently of each other, hydrogen, lower alkyl, hydroxy-lower alkyl, lower alkoxy-lower alkyl, cyano-lower alkyl, cycloalkyl, especially cyclohexyl, or a polyglycol ether chain having 2 to 40, preferably 5 to 20, alkyleneoxy groups, particularly ethyleneoxy groups, and optionally single propyleneoxy groups or phenylethyleneoxy groups, or

R_2 and R_3 together with the nitrogen atom binding them represent piperidino or morpholino,

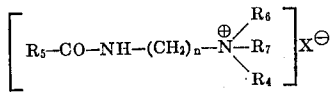
R_4 represents hydrogen, lower alkyl, hydroxy-lower alkyl, lower alkoxy-lower alkyl, or aralkyl, especially benzyl, and

X represents the anion of an organic or inorganic acid, such as the anion of formic, acetic, hydrochloric, hydrobromic, sulphuric, phosphoric or methylsulphuric acid.

Examples of suitable compounds of formula (5) are: salts, as defined, of N-dodecyl-N-cyclohexylamine, N-dodecyl-N-benzylamine, N-cyanoethyl-N-dodecylamine, N,N-bis-(β-hydroxyethyl)-N-dodecylamine, N,N-bis-(β-hydroxyethyl)-N-octadecylamine, N-octadecenyl-piperidine; salts of condensation products of dodecyl, tetradecyl, octadecyl and octadecenylamine having 2 to 40 moles of alkylene oxide, especially ethylene oxide, such as salts, as defined, of condensation products of octadecylamine having 20 moles of ethylene oxide, or of octadecenylamine having 10 moles of propylene oxide. Of the polyethylene oxide addition products, those having short ethylene oxide chains are preferred.

Suitable examples of quaternary compounds of formula (5) are: N-dodecyl-N,N,N-trimethylammonium-methosulphate, N-dodecyl-N,N-dimethyl-N-benzylammonium chloride, N-dodecyl-N,N-diethyl-N-β-hydroxyethyl-ammonium chloride, N-tetradecyl-N,N-dimethyl-N-benzylammonium chloride, the reaction product of octadecylamine having 10 moles of ethylene oxide, quaternised with dimethyl sulphate, and the reaction product of dodecylamine having 7 moles of ethylene oxide, quaternised with epichlorhydrin.

2. Compounds of the general formula:

(6) 

wherein

R_5 represents unsubstituted alkyl having 11 to 17 carbon atoms,

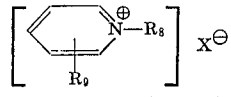
R_6 and R_7 each represent an unsubstituted lower alkyl group, and

n represents 2 or 3, and

R_4 and X have the given meanings.

Examples of suitable compounds of formula (6) are salts, as defined, of compounds obtained by condensation of coconut oil fatty acid chloride with N,N-dimethylpropylenediamine, as well as the salts of quaternary compounds obtainable from the said condensation products by reaction with dimethyl sulphate, glycol chlorohydrin, epichlorohydrin, or benzyl chloride.

3. Compounds of the general formula:

(7) 

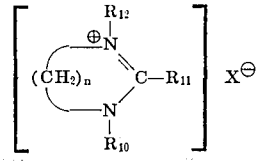
wherein

R_8 represents unsubstituted alkyl having 8 to 18 carbon atoms or an alkyl chain, interrupted by oxygen atoms, having 8 to 18, preferably 12 to 18, carbon atoms, and

R_9 represents hydrogen, the methyl group or ethyl group, and

X has the given meaning.

Examples of suitable compounds of formula (7) are: dodecyl-pyridinium chloride, octadecyl-pyridinium chloride, dodecyl-3- or -4-methylpyridinium chloride and octadecyloxymethylpyridinium chloride. 4. Compounds of the general formula

(8) 

wherein

of R_{10} and R_{11} one represents an unsubstituted alkyl group having 11 to 18 carbon atoms, and the other R represents hydrogen or a lower alkyl radical optionally substituted by hydroxyl groups,

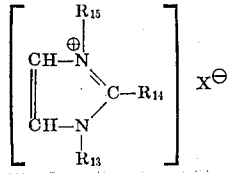
R_{12} represents hydrogen and — if R_{10} or R_{11} do not represent hydrogen — also a lower alkyl radical optionally substituted by hydroxyl groups, or it represents an aralkyl radical, especially the benzyl radical, and

n represents 2 or 3, and

X has the given meaning.

Examples of suitable compounds of formula (8) are: 2-heptadecyl-imidazolinium-acetate, 1-β-hydroxyethyl-2-heptadecyl-imidazolinium chloride, 1-β-hydroxyethyl-2-heptadecyl-3-methylimidazolinium-methosulphate, 1-undecyl-2-methyl-imidazolinium chloride, and 2-heptadecenyl-tetrahydropyrimidinium chloride.

5. Compounds of the formula

(9) 

wherein

R_{13} represents an unsubstituted alkyl group having 12 to 18 carbon atoms,

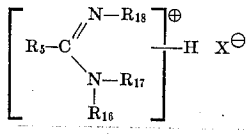
R_{14} represents hydrogen, an unsubstituted alkyl group having up to 18, preferably 1 to 4, carbon atoms, or the unsubstituted phenyl radical,

R_{15} represents an unsubstituted lower alkyl group, or the benzyl radical, and

X_1 represents the anion of hydrochloric or hydrobromic acid, or of methylsulphuric acid.

Mentioned as examples of compounds of formula (9) are: 1-dodecyl-3-benzyl-imidazolium chloride and 1-hexadecyl-2-isopropyl-3-methylimidazolium-methosulphate.

6. Compounds of the general formula

(10) 

wherein

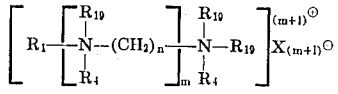
R_5 represents an unsubstituted alkyl group having 11 to 17 carbon atoms, and

R_{16}, R_{17} and R_{18} each represent, independently of each other, hydrogen, a lower alkyl radical optionally substituted by hydroxyl or lower alkoxy groups; a cycloalkyl or an aralkyl group, especially the cyclohexyl or benzyl radical, and

X has the given meaning.

Examples of suitable compounds of formula (11) are: heptadecenyl-amidinium chloride, undecyl-N-benzyl-amidinium chloride, heptadecyl-N,N,N'-trimethyl-amidinium-methosulphate and heptadecyl-N-β-methoxypropyl-amidinium chloride.

7. Compounds of the formula

(11) 

wherein

R_{19} represents a lower alkyl radical optionally substituted by hydroxyl groups, especially the methyl radical, or a polyglycol ether chain having 2 to 40, preferably 5 to 20 alkyleneoxy groups, particularly ethyleneoxy groups, and optionally single propyleneoxy groups or phenylethyleneoxy groups,

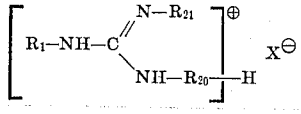
n represents 2 or 3, and

m represents a whole number from 1 to 4, and

R_1, R_4 and X have the given meanings.

Examples of suitable compounds of formula (12) are: salts, as defined, of N-substituted derivatives of dodecyl-, tetradecyl-, octadecyl-, octadecenyl-ethylenetriamine, -propylenediamine, -diethylenetriamine, -dipropylenetriamine and -tetraethylenepentamine, such as dichlorohydrate of N-dodecyl-N-methyl-N',N'-dimethylpropylenediamine, or an addition product quaternised with dimethyl sulphate of 15 to 20 moles of ethylene oxide with N-octadecyl-diethylenetriamine.

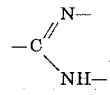
8. Compounds of the formula

(12) 

wherein

R_1 represents an unsubstituted alkyl group having 8 to 18, preferably 12 to 18, carbon atoms, and

R_{20} and R_{21} each represent, independently of each other, hydrogen, or a lower alkyl radical optionally substituted by hydroxyl or lower alkoxy groups, whereby R_{20} and R_{21} together with the group

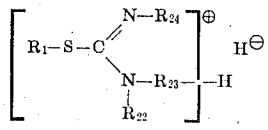


can also form the radical of a partially saturated ring, particularly of a diazoline or tetrahydrodiazine ring, and

X has the given meaning.

Mentioned as examples of suitable compounds of formula (12) are: N-octadecyl-guanidinium chloride, N-hexadecyl-N'-methyl-N''-β-hydroxyethyl-guanidinium chloride, and 2-octylamino-imidazolinium acetate.

9. Compounds of the formula

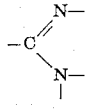
(13) 

wherein

R_1 represents an unsubstituted alkyl group having 8 to 18, preferably 12 to 18, carbon atoms, and

R_{22}, R_{23} and R_{24} each represent, independently of each other, a lower alkyl radical optionally substituted by hydroxyl or lower alkoxy groups; a cycloalkyl or aralkyl radical, especially the cyclohexyl or benzyl radical, or

R_{22} and R_{23} together with the group

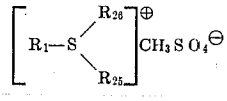


form the radical of a partially saturated ring, particularly of a diazoline or tetrahydrodiazine ring, and

X has the given meaning, and preferably represents the chloride or bromide ion.

Examples of suitable compounds of formula (13) are: salts, as defined, of S-dodecyl-isothiourea, S-octadecyl-N,N',N'-tripropyl-isothiourea, S-dodecyl-N-benzyl-isothiourea, S-dodecyl-N-cyclohexyl-isothiourea, and S-octadecyl-N-γ-methoxypropyl-N',N'-dimethyl-isothiourea.

10. Compounds of the formula

(14) 

wherein

R_1 represents an unsubstituted alkyl group having 8 to 18, preferably 12 to 18, carbon atoms, and

R_{25} and R_{26} each represent a lower alkyl radical optionally substituted by hydroxyl groups.

An example of such a compound is: S-dodecyl-S-methyl-S-β-hydroxyethyl-sulphoniummethosulphate.

In the foregoing, the term "lower" in connection with alkyl or alkoxy groups denotes, as a rule, a radical having not more than 4 carbon atoms. By higher alkyl radicals are meant, as a rule, radicals having about 8 to 22 carbon atoms. In the process according to the invention it is possible to use mixtures of the cation-active compounds. Of the compounds of formulae 5 to 14, those of formula 5 are especially preferred.

The cation-active compounds, as defined, are advantageously used in amounts of at least 1 per cent by weight, especially 2 to 10 per cent by weight, relative to the weight of the fiber material to be treated.

The aqueous preparation usable in the process according to the invention optionally contains the usual thickeners for the printing of fiber material made from polyacrylonitrile, or acrylonitrile copolymers, such as solubilised types of rubber, e.g. that known as "crystal rubber," or thickeners with a cellulose base, such as locust bean flour, galactomannans, tragacanth, British gum, polysaccharides, or cellulose derivatives such as methyl cellulose, or soluble salts of carboxymethyl cellulose. Preferred are thickeners made from locust bean flour and galactomannans.

For the purpose of adjusting to the desired pH-value, it is possible to add to the aqueous preparation usable according to the invention the usual auxiliaries, especially organic acids such as formic or acetic acid, buffer substances such as ammonium salts or alkali metal salts, e.g. ammonium, sodium or potassium acetate, -propionate or -citrate, as well as, optionally, neutral salts such as sodium sulphate or sodium chloride.

As fiber material made from polyacrylonitrile or from acrylonitrile copolymers the commercially known types of fibers can be used. In the case of acrylonitrile copolymers, the proportion of acrylonitrile should be advantageously at least 35 per cent by weight and preferably at least 80 per cent by weight of the copolymer. Furthermore, they possess sufficient dyesites to impart to the fibers a color saturation value of at least 1 and especially in the range of about 1.1 to 3.5. Suitable comonomers include other vinyl compounds, e.g. vinylidene chloride, vinylidene cyanide, vinyl chloride, methacrylate, methylvinylpyridine, N-vinylpyrrolidone, vinylacetate, vinyl alcohol, or styrenesulphonic acids.

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 decribed, for instance, in Canadian Pat. No. 557,597, issued May 20, 1958.

Suitable acrylic fibers which satisfy the above requirements are produced from spinnable solutions described for instance in British Pat. No. 830,830, published Mar. 23, 1960, and German Pat. No. 1,075,317, published Feb. 11, 1960.

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

This fiber material can be pretreated and/or dyed in any stage of processing, e.g. it can be in the form of loose material, rovings, yarns or knitted goods, such as knitted fabrics, fabrics or fiber fleece materials, as well as textile floor coverings such as woven, tufted, or felted carpets.

As cationic dyestuffs for the dyeing of the fiber material pretreated according to the invention and made from polyacrylonitrile or acrylonitrile copolymers, together with untreated acrylonitrile polymers fiber material, can be used the usual such compounds, generally chromophorous systems the cationic character of which comes from an onium group such as a carbenium, ammonium, cyclammonium, oxonium, or sulphonium grouping, and which are in the form of water-soluble salts. These dyestuffs have advantageously a saturation value of 0.15 to 2, especially 0.18 to 1. Examples of cationic dyestuffs containing such chromophorous systems are: acrylazo, anthraquinone, methine, azamethine, azine, oxazine, thiazine, xanthene, acridine, polyarylmethane and coumarin dyestuffs.

Fibre material made from polyacrylonitrile or acrylonitrile copolymer pretreated according to the invention can, optionally, be processed and dyed (with application of suitable dyestuffs having affinity to fibres) not only together with untreated acrylonitrile polymer fibre materia, but also with other untreated fibre material. Suitable for this purpose are, in particular, fibre materials made from linear high-molecular esters of aromatic polycarboxylic acids with polyfunctional alcohols, such as polyethylene glycol terephthalate fibres, and synthetic polyamide fibre material, as well as the corresponding acid modified fibres. Particularly interesting multi-colour effects are obtained, for example, by the dyeing of fibre mixtures made up of pretreated polyacrylonitrile fibres, untreated polyacrylonitrile fibres, and nonmodified polyester fibres or synthetic polyamide fibres using a combination of the above mentioned cationic dyestuffs and the usual dispersion dyestuffs. The dyeing of such fibre mixtures may also be carried out by dyeing first with dispersion dyestuffs and afterwards with cationic dyestuffs. Such dispersion dyestuffs can belong to any desired classes of dyestuffs; thereby suitable are, in particular, azo dyestuffs, or also anthraquinone, nitro, methine, styryl, azastyryl, naphthoperinone, quinophthalone, or naphthoquinoneimine dyestuffs.

The pretreatment of the fibre material made from polyacrylonitrile or acrylonitrile copolymers with the aqueous preparation (optionally containing thickeners) of a cation-active compound as defined above can be carried out by methods common for the dyeing or printing of acrylonitrile fibre material, that is, for example, by the so-called exhaust process in a long liquor (ratio of goods to liquor ca. 1:10 to 1:50), optionally under pressure, at temperatures between 85°C and about 110°C, preferably 95° to 110°C, for 30 to 180 minutes; by impregnation, particularly by padding, e.g. in the form of slubbing, at temperatures below 80°C, especially at 30° to 40°C, and subsequent heat treatment such as steaming, preferably using neutral saturated steam, and optionally under pressure, at temperatures of, for example, 98°to 140°C for 3 to 30 minutes; or, finally, also by printing, such as by roller printing, and subsequent steaming, preferably under pressure at temperatures of ca. 105° to 140°C for 3 to 30 minutes.

It was most surprising to obtain the high differential effect merely by treating one portion of the fibers by the process according to the invention. The untreated fibers take up much as 80 to 96 percent of the total ab-

sorbed dyestuff whereas the treated fibers only take up the remaining 4 to 20 percent.

This magnitude of differential effect could not be expected from a consideration of the prior art because under extended dyeing conditions, the prior art ammonium compounds do not block the fiber permanently and enable level dyeings on acrylic fibers. Such compensation is one of the prerequisites of a leveler.

By contrast the ammonium compounds employed according to the invention permit retention of a strong blockage over extended dyeing periods. Consequently, also by a prolongation of the dyeing duration the proportion of the differential effects obtained according to the invention remains unchanged.

The fiber material pretreated in such a manner is subsequently advantageously rinsed both with warm and with cold water, and then dried; the said fibre material is then dyed together with untreated fibre material made from polyacrylonitrile or acrylonitrile copolymers, in a manner known per se, with at least one cationic dyestuff. Preferably, the dyeing is performed from an aqueous liquor by the exhaust process (ratio of goods to liquor ca. 1:10 to 1:50), at temperatures of ca. 85° to 110°C, with the addition of the usual dyeing auxiliaries, such as organic acids, particularly acetic acid, for the purpose of adjusting the pH-value of the dye liquor to between 3.5 and 5. The fibre material can, however, also be dyed continuously, i.e., by impregnation with a thickened dye liquor containing standard dyeing auxiliaries, such as dye carriers and acid, and subsequent heat treatment, especially steaming at temperatures of ca. 98° to 105°C.

Depending on the nature of the pretreatment and combination of fiber material made from polyacrylonitrile or acrylonitrile copolymers pretreated according to the invention with untreated fiber material made from polyacrylonitrile or acrylonitrile copolymers, as well as, optionally, with other untreated fiber material, very effective two- and multi-shade effects can be obtained. Fiber material pretreated according to the invention can be stored as desired and processed at any time, and dyed in the desired shades, thus the expensive storage of large amounts of pre-dyed material can be avoided. The process according to the invention also renders possible the dyeing, in a simple manner, of fiber material of the same quality in varying shades, an aspect which, especially in the case of the manufacture of carpets, is of great importance, since carpets can thereby be produced which, with respect to stability and lustre of the nap, present a uniform and harmonious appearance.

The "color saturation value" of the acrylic fibers mentioned in this specification is the constant saturation value of usable acrylic fibers with a basic dye-stuff of average affinity, for example, malachite green for such fibers, expressed in grams of dyestuff per 100 grams of fiber.

The "saturation value" of the dyestuff mentioned in this specification corresponds to the quotient from the saturation value of the fiber and the saturation concentration value of the dyestuffs. This latter value represents the amount of the dyestuff absorbed by the fiber when saturation point is attained. The saturation concentration value of the dyestuff is given in grams pro 100 grams of fiber.

The temperatures are given in degrees Centigrade in the following examples.

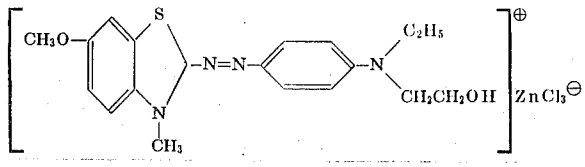
EXAMPLE 1

An amount of 50 g of polyacrylonitrile yarn, e.g. Orlon 42 yarn, is introduced into a pretreatment bath containing 2.5 g of octadecylamine acetate, 2 ml of 40 percent acetic acid, and 1 g of sodium acetate dissolved in 1,000 ml of water. The temperature of the dye liquor is raised, with continuous movement of the textile material, within about 30 minutes up to the boiling point, and boiling is then maintained for 90 minutes. The treated polyacrylonitrile yarn is afterwards rinsed with warm water and then dried.

The thus pretreated 50 g of polyacrylonitrile yarn are processed together with 50 g of untreated polyacrylonitrile yarn on a knitting machine to produce a knitted fabric.

The knitted material pretreated in this manner is now dyed for 60 minutes at boiling temperature in a fresh bath containing, in 2,000 ml of water, 1.25 g of the dyestuff of the formula

(101)



4 ml of 40 percent acetic acid, and 10 g of crystallised sodium sulphate. The dyed material is subsequently rinsed with lukewarm water and then with cold water, and afterwards dried.

In this manner a knitted fabric displaying a clear light-blue/dark-blue two-shade effect is obtained. By means of reflection measurement the following color distribution was established. The polyacrylonitrile yarn part, pretreated according to the present invention, had taken up 8 percent of the total absorbed dyestuff; and the untreated polyacrylonitrile yarn part 92 percent of the absorbed dyestuff.

If, in the above example, the 2.5 g of octadecylamine acetate are replaced by the stated amounts (shown in the second column of the following Table I) of the pretreatment agents listed in the third column, the pretreatment and the dyeing being then carried out under the conditions described in Example 1, then similar light-blue/dark-blue effects are obtained on the knitted fabric. The proportions of dyestuff absorbed by the pretreated fibres and by the untreated fibres are given in Columns 4 and 5.

TABLE I

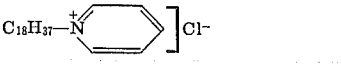
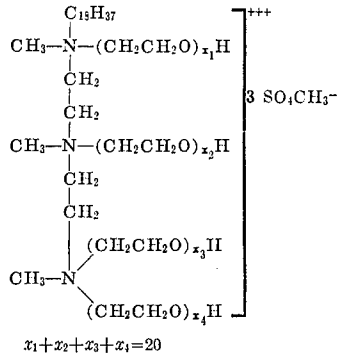
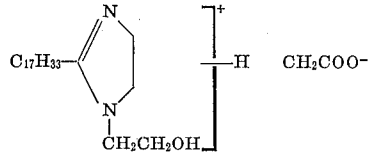
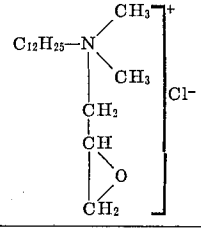
Example No.	Amount in g.	Pretreatment agent	Absorbed dyestuff in percent: Pretreated polyacrylonitrile yarn	Absorbed dyestuff in percent: Untreated polyacrylonitrile yarn
2	1.5		4	96

TABLE I—Continued

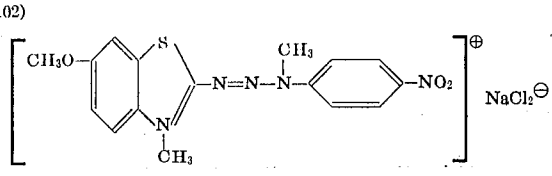
Example No.	Amount in g.	Pretreatment agent	Absorbed dyestuff in percent: Pretreated polyacrylonitrile yarn	Absorbed dyestuff in percent: Untreated polyacrylonitrile yarn
3	2.5		20	80
4	2.5		14	86
5	2.5		6	94

EXAMPLE 6

An amount of 1 kg of polyacrylonitrile flock (Orlon 42) is introduced into a dyeing apparatus. A dye liquor is prepared separately containing, dissolved in 15 litres of water, 30 g of octadecylpyridinium chloride 40 ml of 40 percent acetic acid, and 20 g of sodium acetate. This pretreatment dye liquor is then pumped into the dyeing apparatus; the temperature of the dye liquor is subsequently raised, within ca. 20 minutes, up to the boiling point, and boiling is maintained for 90 minutes. The pretreated polyacrylonitrile flock is afterwards rinsed with warm water, centrifuged, dried, and then spun to obtain a carpet yarn. The thus obtained carpet yarn having low affinity to cationic dyestuffs is subsequently processed together with 1 kg of untreated polyacrylonitrile yarn of the same quality, on a tufting machine, into a carpet.

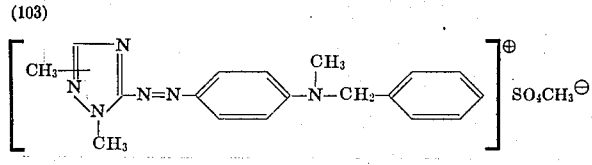
A piece weighing 1 kg of this carpet is then fed into a winch vat and stitched at the ends. On to the material to be dyed are poured ca. 30 litres of water at 40°, and 100 g of crystallised sodium sulphate are added. Separately, in ca. 4 litres of water containing 40 ml of 40 percent acetic acid, are dissolved 10 g of the dyestuff of the formula

(102)



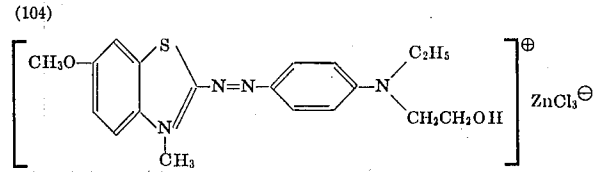
2 g of the dyestuff of the formula

(103)



and 1.5 g of the dyestuff of the formula

(104)



The obtained dyestuff solution is thereupon carefully added to the dye liquor. The temperature of the dye liquor is then raised within 45 minutes to 95°, and dyeing carried out for 60 minutes with slight boiling of the dye liquor. The dyed carpet is first rinsed with warm water and afterwards with cold water, and dried. In this manner is obtained a carpet having a light-brown and dark brown pattern.

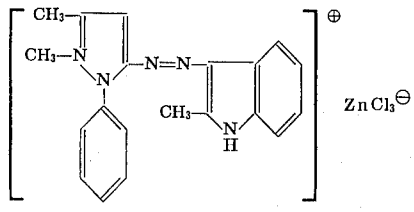
By means of reflection measurements was determined the following colour distribution: Drawn on to the untreated polyacrylonitrile yarn part was 4% of the total absorbed dyestuff, and on to the untreated polyacrylonitrile yarn part 96 percent of the total absorbed dyestuff.

Similar effects are obtained by using instead of Orlon 42 flock, with otherwise the same procedure, polyacrylonitrile flock made from Acrilan, Crilenka, Dralon, or Exlan.

EXAMPLE 7

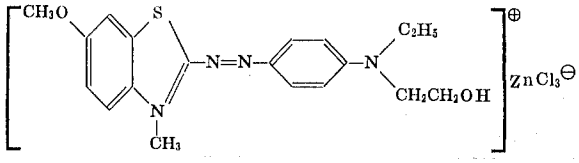
If, in the preceding Example 6, the 30 g of octadecylpyridinium chloride are replaced by 50 g of the pretreatment agent according to Example 3, the pretreatment being otherwise carried out as described in Example 6, and the carpet obtained by processing of the treated and untreated fibre material is then dyed under the conditions given in Example 6, whereby is used, however, instead of the dyestuff combination mentioned in the preceding example, a dyestuff mixture consisting of 6 g of the dyestuff of the formula

(105)



and 6 g of the dyestuff of the formula

(106)

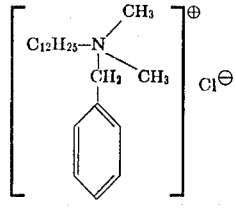


then is obtained a carpet dyed light-green/dark green. The reflection measurements gave the following values; Absorbed on the pretreated fibre part is 19 percent, on the untreated part 81 percent of the total absorbed dyestuff.

EXAMPLE 8

If in Example 6 are used, instead of the 30 g of octadecylpyridinium chloride, 50 g of the pretreatment agent of the formula

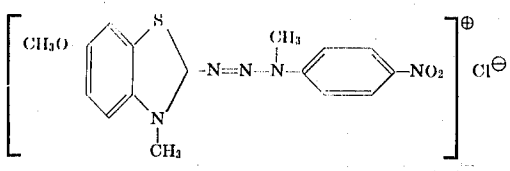
(107)



the pretreatment being carried out as described in Example 6, and the polyacrylonitrile fibre material which has been processed in the same manner into a carpet then dyed, under the dyeing conditions given in Example 6, with a dyestuff mixture consisting of

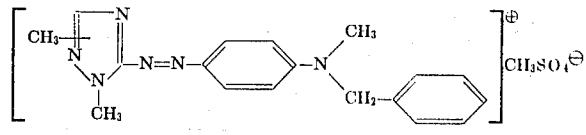
4 g of the dyestuff of the formula

(108)



and 8 g of the dyestuff of the formula

(109)



then is obtained a carpet made up

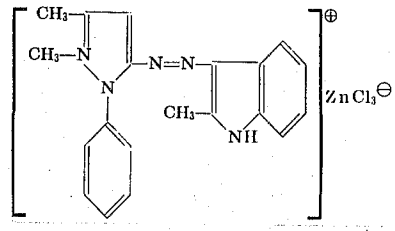
a. of untreated polyacrylonitrile yarn dyed an intense scarlet red, and

b. of pretreated polyacrylonitrile yarn dyed slightly yellowish red. The ratio of the amount of dyestuff absorbed by the treated polyacrylonitrile fibre material to the amount absorbed by the untreated polyacrylonitrile material is 20 : 80.

EXAMPLE 9

If the pretreatment of the polyacrylonitrile flock is carried out as described in Example 6, using, however, 50 g of the quaternisation product of N-dodecyl-N,N-dimethylamine with epichlorhydrin instead of the 50 g of octadecylpyridinium chloride used in Example 6, and the fibre material is processed in the same manner into a carpet, the said fibre material consisting of identical parts of pretreated material and untreated material, and dyed, under the dyeing conditions described in Example 6, with 5 g of the dyestuff of the formula

(110)



then is obtained a patterned carpet made up

a. of untreated polyacrylonitrile yarn dyed an intense yellow, and

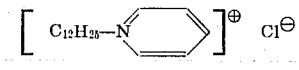
b. of pretreated polyacrylonitrile yarn dyed slightly yellow.

The reflection measurement gives the following dye distribution: Absorbed on the untreated polyacrylonitrile fibre part is 9 percent of the total absorbed amount of dyestuff; on the untreated part 91 percent of the total dyestuff.

EXAMPLE 10

A printing paste containing 50 g/l of the pretreatment agent of the formula

(111).



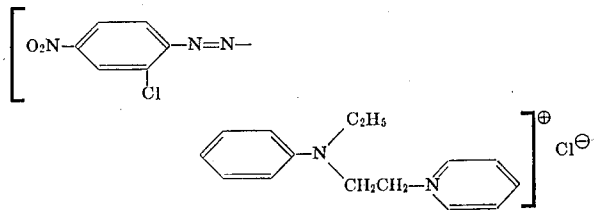
5 g/l of locust bean flour thickener, and 5 ml/l of 80 percent acetic acid is applied, with the aid of a roller printing machine, to a fabric made from polyacrylonitrile fibres. The liquor applied amounts to ca. 100 percent printing paste, relative to the dry weight of the fabric.

The fabric printed with the pretreatment agent is afterwards steamed for 15 minutes at a temperature of 120° and at 1 atmosphere, whereupon the steamed material is rinsed with warm water and then dried.

A piece of this pretreated polyacrylonitrile fibre fabric weighing 1 kg is then fed into a winch vat and stitched at the ends. Into the winch vat are then poured 35 litres of water at ca. 40°, and 100 g of crystallised sodium sulphate are added.

To about 3 litres of water are added, in a separate operation, 40 ml of 40 percent acetic acid, whereupon are added 10 g of the dyestuff of the formula

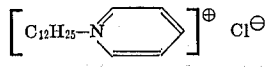
(112)



The thus prepared dyestuff solution is now carefully added to the dye liquor. The temperature of the dye bath is then raised within ca. 50 minutes to 95°–97°. Dyeing is subsequently carried out for 1 hour with gently boiling. In this manner is obtained a colour printing whereby the area printed with the pretreatment agent are dyed slightly red, the non-printed areas, however, being dyed an intense red.

If, in this example, the 50 g of the pretreatment agent of the formula

(113)



are replaced by the identical amount of one of the pretreatment agents listed in the following Table II, in the second column, the procedure for the pretreatment and for the subsequent dyeing being as described in Example 10, then likewise are obtained colour printings having a slightly red/intense red pattern.

TABLE II

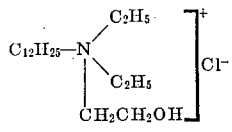
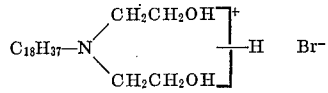
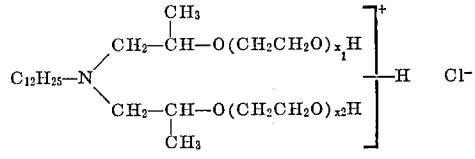
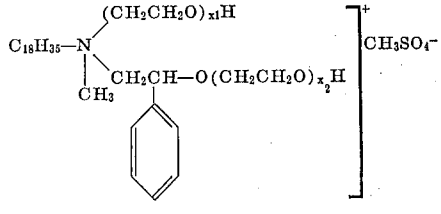
Example No.	Pretreatment agent
11	
12	
13	
14	 $x_1+x_2=10$
15	 $x_1+x_2=40$

Table II – Continued

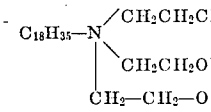
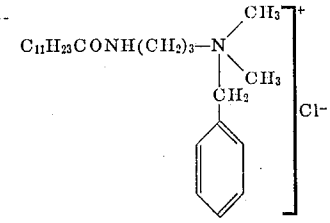
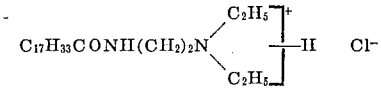
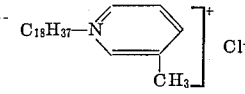
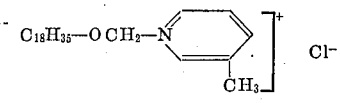
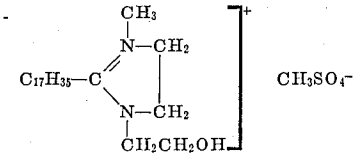
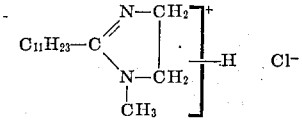
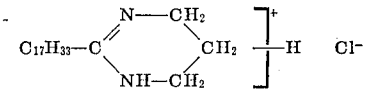
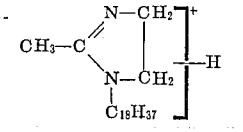
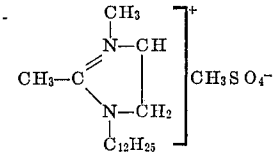
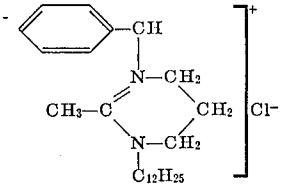
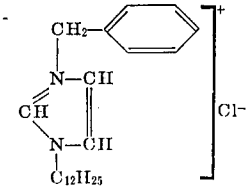
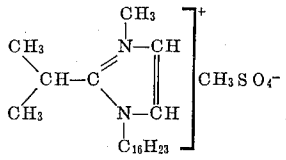
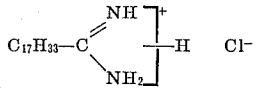
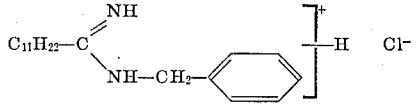
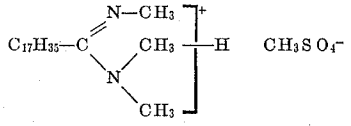
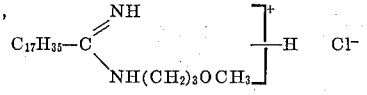
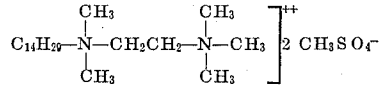
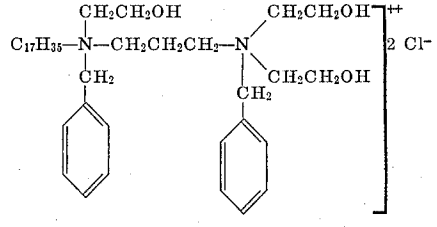
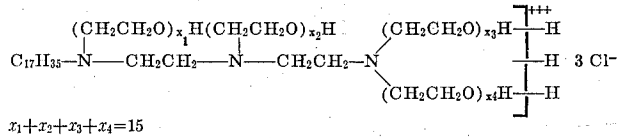
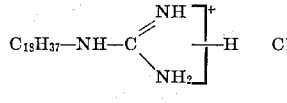
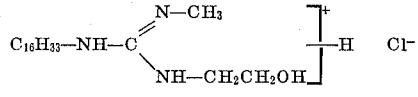
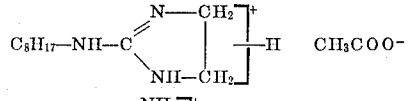
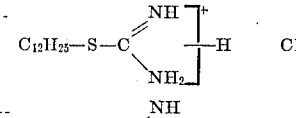
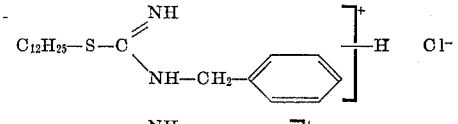
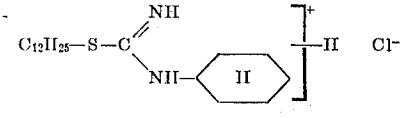
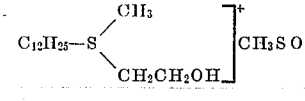
Example No.	Pretreatment agent
16	
17	
18	$C_{18}H_{35}OCH_2CH_2CH_2N(CH_3)_3]^+CH_3SO_4^-$
19	
20	
21	
22	
23	
24	
25	
26	
27	
28	

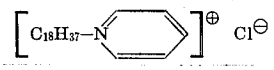
Table II – Continued

Example No.	Pretreatment agent
29	
30	
31	
32	
33	
34	
35	
36	 $x_1+x_2+x_3+x_4=15$
37	
38	
39	
40	
41	
42	
43	

If in Example 1 is used, instead of the 2.5 g of octadecylamine acetate, the same amount of the pretreatment agent stated in the preceding Examples 10 to 43, the pretreatment being carried out as described in Example 1, and the knitted fabric which has been produced in an analogous manner then dyed under the conditions given in Example 1, then a knitted fabric is obtained displaying a similarly good light-blue/dark blue two-shade effect.

EXAMPLE 44

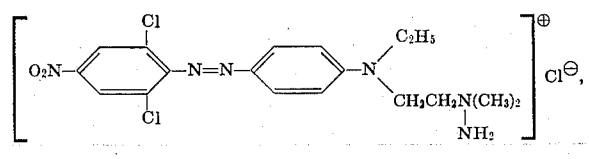
Into a pretreatment bath containing 1.5 g of the pretreatment agent of the formula

(114) 

2 ml of 40 percent acetic acid and 1 g of sodium acetate dissolved in 1,200 ml of water are introduced 50 g of polyacrylonitrile yarn. With continuous movement of the textile material, the dye liquor temperature is then raised withinn ca. 30 minutes to 95°, and boiling is subsequently maintained for 90 minutes. The treated polyacrylonitrile yarn is afterwards rinsed with warm water and then dried.

An amount of 50 g of untreated polyacrylonitrile yarn is then combined with the polyacrylonitrile yarn pretreated in the above described manner and processed on a knitting machine into a tricot.

In a fresh bath containing, dissolved in 2,000 ml of water, 0.5 g of the dyestuff of the formula

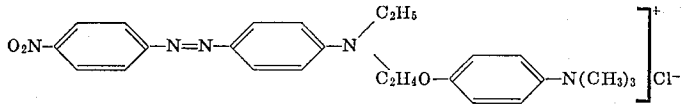
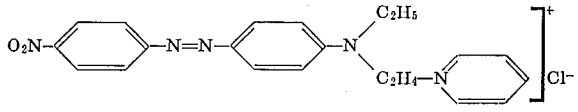
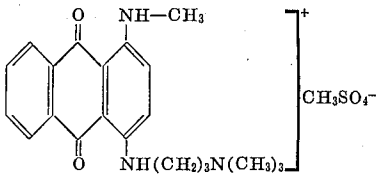
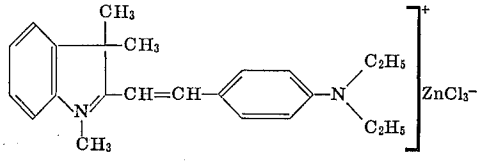
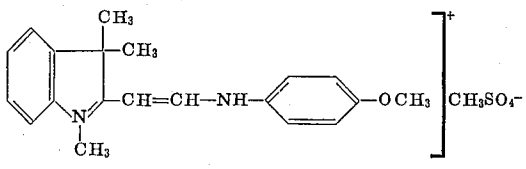
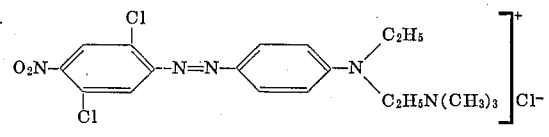
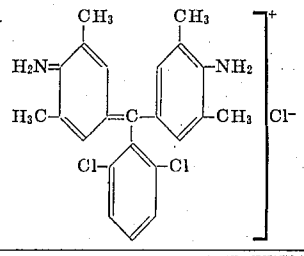
(115) 

4 ml of 40 percent acetic acid and 10 g of sodium sulphate is then dyed the knitted fabric for 60 minutes at boiling temperature. The dyed material is afterwards rinsed with warm water and then with cold, and finally dried.

In this manner is obtained a knitted fabric presenting a slightly yellow brown/intensely yellow brown two-shade effect. By means of reflection measurements, the following colour distribution was determined: The polyacrylonitrile yarn part pretreated in the described manner has absorbed 9 percent of the total absorbed dyestuff, and the untreated part 91 percent of the total absorbed dyestuff.

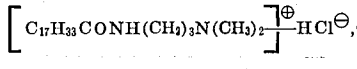
If polyacrylonitrile yarn is pretreated according to the information given in Example 44, and combined with untreated polyacrylonitrile yarn; and if is used for the dyeing of the finished knitted fabric, instead of the 0.5 g of the dyestuff mentioned in the preceding Example 44, in each case 1 g of one of the dyestuffs listed in Column 2 of the following Table III, then is obtained knitted fabric dyed in the shades given in Columns 3 and 4.

TABLE III

Example No.	Dyestuff	Shade on polyacrylonitrile yarn: Pretreated	Shade on polyacrylonitrile yarn: Untreated
45		Slightly bluish red.	Intensely bluish red.
46		Slightly yellow brown.	Intensely yellow brown.
47		Slightly blue.	Intensely blue.
48		Slightly pink.	Intensely pink.
49		Slightly yellow.	Intensely yellow.
50		Light-brown.	Dark-brown.
51		Light-blue.	Intensely blue.

EXAMPLE 52

In a closed laboratory dyeing apparatus are placed 300 g of polyacrylonitirle yarn in the form of a cheese. A pretreatment liquor is prepared separately containing, in 4.5 litres of water, 30 g of the pretreatment agent of the formula

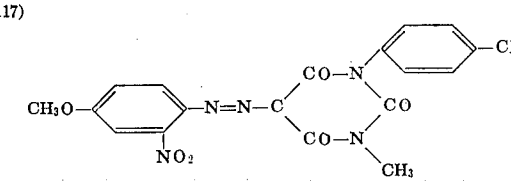
(116) 

12 ml. of 40 percent acetic acid, and 6 g of sodium acetate. This pretreatment liquor is then transferred to the dyeing apparatus; the temperature is raised within ca. 45 minutes to 105°- 107°, and this temperature is maintained for 90 minutes. The pretreatment liquor is afterwards cooled to room temperature, the dyed material rinsed with warm water, centrifuged, and then dried.

The thus pretreated polyacrylonitrile yarn is then combined with 500 g of untreated polyacrylonitrile yarn and with 500 g of yarn made from polyethylene glycol terephthalate, and the whole processed, on a knitting machine, into a knitted article.

The thus produced knitted article is then fed into a winch vat. An amount of ca. 40 litres of water is poured in, and as swelling agent are added 80 g of an emulsion of the sodium salt of o-phenylphenol, as well as 80 g of diammonium sulphate. With continual movement of the textile material, the temperature of the dye bath is raised within 15 mintues to about 60°.

In a separate operation 26 g of a dyestuff preparation containing, in finely dispersed form, the dyestuff of the formula

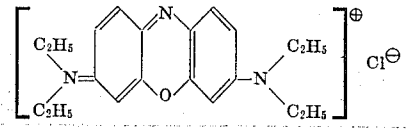
(117) 

are suspended in ca. 500 ml of water. The obtained dyestuff dispersion is then carefully added to the dye liquor, whereupon the temperature of the liquor is raised, within ca. 30 minutes, from 60° to 95°. Dyeing is subsequently carried out for 90 minutes with gentle

boiling. The dyed material is rinsed with hot water, then soaped, and again rinsed with water.

The cross-dyeing of the treated and the untreated polyacrylonitrile yarn part is performed as follows:

Into the winch vat are again placed 40 litres of water at ca. 40°, and to this are added 100 g of crystallised sodium sulphate. In ca. 5 litres of water containing 32 ml of 40 percent acetic acid are dissolved, in a separate operation, 10 g of the dyestuff of the formula

(118) 

The obtained dyestuff solution is now carefully added to the dye liquor. The temperature of the liquor is thereupon raised within 1 hour to 95°, and dyeing is subsequently carried out for 60 minutes with gentle boiling; the knitted article is thereupon rinsed with warm water, centrifuged, and finally dried. with observance of the above conditions is obtained a knitted article which is made up of

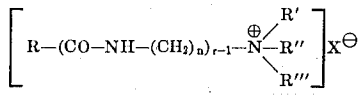
a. polyethylene glycol terephthalate yarn dyed greenish yellow,

b. pretreated polyacrylonitrile yarn dyed light-green, and

c. untreated polyacrylonitrile yarn dyed an intense bluish green.

We claim:

1. Process for the production of differential effects on copolymeric acrylonitrile fibers, wherein said fibers containing at least 80 percent by weight of acrylonitrile a) are treated at temperatures of at least 85°C with a pH-value of between 3 and 5, with an aqueous perparation consisting essentially of at least one cation active organic ammonium compound of the formula:



wherein

R represents an alkyl radical having 8 to 18 carbon atoms,

R′ and R″ each represent hydrogen, lower alkyl, hydroxy-lower alkyl, lower alkoxy-lower alkyl, cyano-lower alkyl, cycloalkyl, or a polyalkylene glycol radical, or

R′ and R″ together with the nitrogen atom binding them represent piperidino or morpholino,

R‴ represents hydrogen, lower alkyl, aralkyl, or aralkyl substituted by hydroxyl or lower alkoxy, or

R′, R″ and R ‴ together with the nitrogen atom binding them represent pyridyl or lower alkyl-pyridyl,

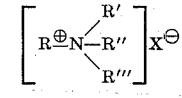
r represents 1 or 2,

n represents 2 or 3, and

x represents the anion of an organic or inorganic acid,

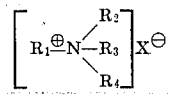
and b) said acrylic fibers, treated according to a), are dyed together with untreated material made from said acrylic fibers in a dyebath consisting essentially of an aqueous liquor with at least one cationic dyestuff, wherein the proportion of the dyestuff absorbed by the fibers pretreated according to a) and by the untreated fibers is within 4:96 to 20:80.

2. Process according to claim **1**, wherein the treatment a) is carried out with an aqueous preparation containing, as cation-active organic ammonium compound, a compound of the formula:



wherein R, R′, R″, R‴ and X have the meanings given in claim **1**.

3. Process according to claim **2**, wherein the cation-active ammonium compound has the formula:



wherein

R_1 represents an unsubstituted alkyl group having 8 to 18 carbon atoms,

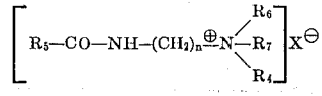
R_2 and R_3 each represent, independently of each other, hydrogen, lower alkyl, hydroxy-lower alkyl, lower alkoxy-lower alkyl, cyano-lower alkyl, cycloalkyl, or a polyglycol ether chain having 2 to 40 alkyleneoxy groups, or

R_2 and R_3 together with the nitrogen atom binding them represent piperidino or morpholino,

R_4 represents hydrogen, lower alkyl, hydroxy-lower alkyl, lower alkoxy-lower alkyl or aralkyl, and

X represents the anion of an organic or inorganic acid.

4. Process according to claim **1**, wherein the cationactive ammonium compound has the formula



wherein

R_4 represents hydrogen, lower alkyl, hydroxy-lower alkyl, lower alkoxy-lower alkyl or aralkyl,

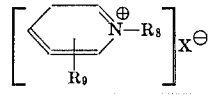
R_5 represents unsubstituted alkyl having 11 to 17 carbon atoms,

R_6 and R_7 each represent unsubstituted lower alkyl,

n represents 2 or 3, and

X represents the anion of an organic or inorganic acid.

5. Process according to claim **1**, wherein the cationactive ammonium compound has the formula:



wherein

R_8 represents unsubstituted alkyl having 8 to 18 carbon atoms or an alkyl chain interrupted by oxygen atoms, having 8 to 18 carbon atoms,

R_9 represents hydrogen, methyl or ethyl, and

X represents the anion of an organic or inorganic acid.

6. Process according to claim **1**, wherein the cationactive ammonium compound is octadecylamine acetate.

7. The fiber material made from polyacrylonitrile or from acrylonitrile copolymers, dyed according to claim **1** in differential shades.

* * * * *