DYESTUFFS FOR DYING AND PRINTING FIBRE MIXTURES WHICH CONTAIN FIBRES CONTAINING ACYLONITRILE

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No Drawing. Application April 18, 1957
Serial No. 653,542

Claims priority, application Germany April 18, 1956
6 Claims. (Cl. 8—21)

This invention relates to new salt-like dyestuffs and especially to those salt-like dyestuffs which are formed by precipitation of dissolved cationic (basic) dyestuffs with dissolved anionic (acid) dyestuffs (or conversely by precipitation of dissolved anionic dyestuffs with dissolved cationic dyestuffs) and which are suitable for dyeing and printing because they pass with precipitation of polyacrylonitrile or of co-polymers of acrylonitrile and fibres capable of being dyed with anionic dyestuffs.

One of the most important problems which has arisen from the increasing importance of modern synthetic fibres is that of dyeing or printing mixtures of these fibres with the natural or regenerated fibre varieties hitherto conventional and also mixtures of various new synthetic fibres with each other. By reason of the differences, which are often very considerable, in the textile and especially the tinctorial properties of modern fibres, it is usually not possible to dye the various components of such fibre mixtures with the same dyestuffs. Hitherto it has often been necessary first to dye one kind of fibre in one dyebath, then to dye the second kind of fibre in a second dyebath, and thus to work consecutively in a plurality of baths. In this way there is not only an increased expenditure for apparatus but there are usually other difficulties, as for example the possibility of the formation of spots and the partial destruction therefore specifically of the dyestuff by the other kinds of fibres which are not to be dyed. Further working operations are therefore unavoidable, serving for example for the stripping of the partially absorbed dyestuff, and by which in some cases the textile properties of the fibres may be unfavorably influenced.

These difficulties exist inter alia also for the range of those fibre mixtures which are composed on the one hand of fibres containing acrylonitrile and on the other hand of natural, regenerated and/or synthetic fibres capable of being dyed with anionic dyestuffs, as, for example, wool, silk, cotton, regenerated cellulose and/or synthetic polyamides. Whereas the polyacrylonitrile and other acrylonitrile-containing fibres may be dyed above all with basic dyestuffs, there are in general used in the case for example of wool, acid dyestuffs; the two kinds of dyestuffs cannot, however, be used side by side in one dyebath because there occurs precipitation which impairs the dyeing process. In order to remedy this defect—without thereby having to resort to the two-bath method—it has been proposed to add to the dyebath, before the addition of the dyestuffs, additives of ethylene oxide as dispersing agents; the mutual precipitation of the acid and basic dyestuffs (which occurs separately) is thereby to be avoided. In this method, therefore, the dyer has to disperse consecutively the dispersing agent, the acid dyestuff and the basic dyestuff, each in a definite dosage, in the dyebath before he can begin dyeing.

It is now known that dyers generally prefer dyestuffs which can be added without further preparation to the dyebath, i.e. are already prepared in admixture with the necessary additives as for example dispersing agents, and with which the dyeing process itself can be commenced immediately afterwards. For example, in contrast to the earlier methods in which azo and azomethine dyestuffs were chromed on the fibre after dyeing, methods have become prevalent in which a ready-prepared chromium-containing dyestuff can be directly used by the dyers in a quite uncomplicated way. Such dyestuffs capable of being used in a simple way have hitherto not been known for dyeing fibre mixtures which contained fibres of polymers containing acrylonitrile.

The present invention, however, relates to dyestuffs of salt-like nature which are suitable, by direct application in one dyebath, for the simultaneous dyeing of fibres of polyacrylonitrile and/or other polymers containing acrylonitrile on the one hand and of natural, regenerated and/or synthetic fibres capable of being dyed with anionic dyestuffs on the other hand, i.e. of mixtures of fibres of the said kinds, from a single dyebath. These salt-like dyestuffs can also be used for the simultaneous printing of the said kinds of fibres by means of a single printing paste into which the dyestuffs of the polyacrylonitrile or of the said kind can be prepared, for example, by adding to a solution of a cationic dyestuff, advantageously at ordinary temperatures, the equivalent amount of a solution of an anionic dyestuff (the same effect may naturally also be achieved conversely by precipitation of a solution of an anionic dyestuff with a cationic dyestuff) and filtering, drying and pulverizing the precipitate formed. The pulvulent cationic and anionic dyestuffs may, however, also be mixed with each other, made into a paste with water, dried and powered; in this case the precipitation process takes place during the formation of the paste. In both cases it can be advantageous to incorporate with the salt-like dyestuff formed, from the start, an amount of a dispersing agent which is equal to or greater than the amount of salt-like dyestuff. Examples of dispersing agents are sulfonated high-molecular organic compounds, ethoxylation products of organic substances, dextrines, or organic distillation products of polyacrylonitrile and one anionic dyestuff, two or more of each kind simultaneously. A further important variant of the invention consists in preparing salt-like dyestuffs from cationic and anionic initial dyestuffs of different shades or means of which there may be produced on mixtures of fibres containing acrylonitrile and fibres capable of being dyed with anionic dyestuffs, mixture or shot effects. It may furthermore also be advantageous to replace part of the cationic and/or anionic dyestuff or dyestuffs by colorless cationic and/or anionic substances, for example, dispersing agents, or to coemploy such substances. This is recommended, for example, when, in the use of a dyestuff salt obtained by the reaction of equivalent amounts of cationic and anionic dyestuffs, the shade of color for example of the cationic dyestuff component is more pronounced than is desired in the final dyeing by reason of its preponderant color strength. Moreover, the anionic dyestuff component (or components) may also, be entirely omitted and the cationic dyestuff component (or components) reacted instead only with colorless compound (or compounds).

It is not necessary to react the cationic and anionic colored and colorless components with each other in equimolecular amounts, but, rather excess of cationic or anionic substances may be present in the reaction, the salt-like dyestuff then of course containing this excess as an admixture.

For the production of the new dyestuffs there may be used as cationic or anionic initial dyestuffs all known dyestuffs of cationic or anionic character. For example basic (cationic) azomethine, polymethine or cyanine dyestuffs, including diazacyanine and hemicyanine dyestuffs...
furthermore di- and tri-arylmethane, including indolyl diarylmethane dysstuffs and anthraquinone dysstuffs of cationic character may be used as cationic components. Di-, and tri-arylmethane dysstuffs, anthraquinone dysstuffs, azo, azomethine and complex metal, including 1:1- and 1:2-complex chromium, cobalt and copper compounds of mono- and polyazo- and azomethine dysstuffs, which have an acid (anionic) character may serve inter alia as anionic components.

The new dysstuffs have the general formula:

\[ \text{(K)}^{\ominus} \left(\text{A}^{\ominus}\right)^{\ominus} \]

in which K represents the cation of a cationic dysstuff component and \( A^{\ominus} \) the anion of an anionic dysstuff component. The cationic and the anionic dysstuff components may each consist of a single cationic or anionic dysstuff, but may also include a plurality of cationic or anionic dysstuffs. With the new salt-like dysstuffs there may be dyed or printed with advantage fibre mixtures, as for example flock, threads, woven or knitted fabrics which contain as components on the one hand fibres of polyesylanilin or of copolymers of acylanilin for example with vinyl chloride, vinylidene chloride, vinyl alcohol, vinyl acetate, acrylic esters, methacrylic esters and/or acylamide or methacrylamide, and on the other hand natural, regenerated or synthetic fibres capable of being dyed with anionic dysstuffs, as for example wool, cotton, fibres of regenerated cellulose and/or of synthetic polymides. Fibre mixtures which are composed of a plurality of kinds of fibres containing acylanilidine and a plurality of fibres capable of being dyed with anionic dysstuffs are also suitable for dyeing or printing with the new dysstuffs. In the mixtures, the said fibres can be used in all proportions, i.e. not only in a proportion of 50:50, but also in other proportions as 45:55, 40:60, 30:70, 20:80 or 10:90 and vice versa.

The new dysstuffs, if desired containing the said cationic or anionic admixtures, are simply added to the dyebaths with which fibre mixtures of the above-mentioned kind can then be directly dyed by known methods. The dyeing can be carried out at temperatures of 95° to 130° C., preferably at 97° to 110° C.; at temperatures lying above 100° C., dyeing is under a pressure of up to 2.5 atmospheres over pressure. Printing with the new dysstuffs may also be carried out by known methods. During the course of the dyeing or printing process, the cations formed by dissociation from the dysstuff salts go on to the fibres containing acylanilinidy polymers and the anions also formed go on to the fibres capable of being dyed with them. Obviously there may also be co-employed inorganic salts, and auxiliaries, as for example fatty alcohol sulfonates, in the dyebaths and printing pastes. Following the dyeing or printing there may advantageously be carried out a treatment of about a quarter of an hour with anionic auxiliaries, as for example sulfonation products of high molecular organic compounds, at a temperature range of about 40° to 60° C. (but not above 90°).

With the aid of the new dysstuffs it is possible to obtain unitary, fullshade dyeings and prints of all tones and excellent fastness properties, on fibre mixtures of individual fibres of any kind in a simple way.

The following examples will further illustrate this invention but the invention is not restricted to these examples. The parts specified are parts by weight.

**Example 1**

5 parts of the cationic dysstuff of the formula:

\[ \text{HCO-O-S-S-N=N-N} \]

1 part of the anionic dysstuff of the formula:

\[ \text{HCO-O-N=O-N} \]

both in the powdered state, are mixed with 10 parts of the condensation product derived from 2 moles of the sodium salt of naphthalene-2-sulfonic acid and 1 mol of formaldehyde, the resultant mixture made into a paste with 20 to 40 parts of water, dried and ground in a ball mill. A blue dispersion dysstuff is obtained which can readily be dispersed in water and gives dyeings of excellent fastness properties on fibre mixtures of fibres containing acylanilin and fibres capable of being dyed with anionic dysstuffs.

In the same way dispersion dysstuffs can be prepared from the dysstuffs described in the co-pending U.S. patent applications Ser. No. 587,503, filed May 28, 1956, by Helmut Pfitzner, Hans Baumann, Julius Eisele and Wilhelm Federkiel, and Ser. No. 617,706, filed October 23, 1956, by Wilhelm Brunkhorst, Emil Kern and Hans Baumann as cationic initial dysstuffs and the 1:1-complex chromium compound of the monoazo dysstuff of the formula

\[ \text{HCO-O-S-N=N-N} \]

or a dysstuff described in the U.S. patent specifications Nos. 2,708,193 and 2,685,595 and in the copending U.S. patent applications Ser. No. 403,446, filed January 11, 1954, by Helmut Pfitzner and Otto Kaufmann, and No. 472,244, filed November 30, 1954, by Helmut Pfitzner and Otto Kaufmann, as anionic initial dysstuffs.

**Example 2**

A dispersion dysstuff is prepared as described in Example 1 from a cationic dysstuff of the formula

\[ \text{HCO-O-S-S-N=N-N} \]

and the water-soluble 1:1-complex chromium compound of the monoazo dysstuff of the formula

\[ \text{HCO-O-S-N=N-N} \]

The resultant red dysstuff disperses readily in water and gives on mixtures of fibres containing acylanilin and fibres capable of being dyed with anionic dysstuffs, dyeings of excellent fastness properties. In a similar way, the anionic dysstuff described in Example 1 may be used instead of the said acid dysstuff as the initial dysstuff.
Example 3

For the production of a dispersion dyestuff there are used as initial dyestuffs a cationic dyestuff of the formula

and an anionic 1:1-complex chromium compound of the monoazo dyestuff of the formula

as described in Example 1. The resultant yellow dyestuff may be dispersed readily in water and gives dyeings of excellent fastness properties on mixtures of fibres containing acrylonitrile and fibres capable of being dyed with anionic dyestuffs.

Instead of the said cationic dyestuff there may be used in the same way another of the dyestuffs described in the co-pending U.S. patent application Ser. No. 653,296, filed April 17, 1957, by Hans Baumann, Friedrich Arnemann, Julius Eisele and Wilhelm Federtiel for The Dyeing of Polyacrylonitrile and Copolymers of Acrylonitrile as initial dyestuff. Similarly the dispersion dyestuff can be prepared from the cationic dyestuffs described in this example and the anionic dyestuffs of U.S. patent specification No. 1,801,745.

Example 4

The procedure of paragraph 1 of Example 3 is followed, but instead of the cationic dyestuff therein specified there is used a dyestuff of the formula

A yellow dispersion dyestuff is obtained which gives dyeings of excellent fastness properties on the said fibre mixtures.

Example 5

A solution of 5 parts of the cationic dyestuff specified in Example 4 in 250 parts of water is precipitated with a solution of 5 parts of the 1:1-complex chromium compound formed by chroming from the monoazo dyestuff of the formula

reacted with 1 mol of 1-carboxy-2-hydroxybenzene-5-sulfonic acid phenylamide, in 280 parts of water at room or somewhat elevated temperature, the precipitate formed is separated, dried and powdered. A yellow dispersion dyestuff is obtained.

Further dispersion dyestuffs can be prepared in the same way from the cationic dyestuffs specified in Examples 1 to 3 and the anionic dyestuff described in the second paragraph of Example 2.

Example 6

A dispersion dyestuff is prepared as described in Example 1 from the cationic dyestuff of paragraph 1 of Example 3 and an anionic dyestuff of the formula

It gives yellow dyeings of very good fastness properties on the fibre mixtures previously described.

In the same way dispersion dyestuffs may be prepared from the cationic dyestuffs specified in Examples 1 to 5 and the anionic dyestuffs specified in French patent specification No. 1,026,865.

Example 7

By the method of Example 1 there is obtained from the cationic dyestuff specified in paragraph 1 of Example 2 and the anionic dyestuff of the formula

a red dispersion dyestuff which gives on the said fibre mixtures dyeings of very good fastness properties. In the same way a red dispersion dyestuff is obtained by using as anionic dyestuff the 1:2-chromium complex of the monoazo dyestuff of the formula

Further dispersion dyestuffs can be prepared from the cationic dyestuffs specified in paragraph 1 of Example 2 and the anionic dyestuffs described in French patent specification No. 894,039 and the co-pending U.S. patent application Serial No. 515,554, filed June 14, 1955, by Helmut Pfitzner and Otto Kaufmann.

Example 8

A dispersion dyestuff is prepared as described in Example 1 from the cationic dyestuff specified therein (in paragraph 1) and the direct dyeing anionic dyestuff of the formula

A blue dyestuff is obtained which may be readily dispersed in water. Instead of the said cationic dyestuff there may similarly be used also the cationic dyestuff of Example 2.
and Example 3, paragraph 1, and instead of the said anionic dyestuff, the dyestuffs of the formulae

\[
\begin{align*}
&\text{H}_3\text{C} & \text{N} & \text{N} & \text{OH} & \text{SOH} \\
&\text{N} & \text{H} & \text{CO} & \text{NH} & \text{CO} & \text{CH}_3 \\
&\text{N} & \text{SOH} & \text{H}_3\text{C} & \text{N} & \text{N} & \text{OH} & \text{SOH}
\end{align*}
\]

and

\[
\begin{align*}
&\text{H}_3\text{C} & \text{N} & \text{N} & \text{HN} & \text{CO} & \text{CH}_3 & \text{CO} & \text{CH}_3 \\
&\text{N} & \text{SOH} & \text{H}_3\text{C} & \text{N} & \text{N} & \text{HN} & \text{CO} & \text{CH}_3 & \text{CO} & \text{CH}_3
\end{align*}
\]
as initial dyestuffs.

**Example 9**

A red dispersion dyestuff is prepared by the method of Example 1 from a cationic dyestuff of the formula

\[
\text{O}_2\text{N} \quad \text{N} \quad \text{N} \quad \text{N}
\]
and the anionic dyestuff specified in Example 2.

**Example 10**

A salt-like dispersion dyestuff is prepared according to the process of Example 1 from Spirit Blue (Schulz-Lehmann, Farbstofftabellen, 1931, volume 1, No. 792: Colour Index, 1924, No. 689) as cationic initial dyestuff and one of the anionic dyestuffs specified in Example 1 or the dyestuff Orange II (Schulz-Lehmann, loc.cit., No. 189: Colour Index No. 151) as anionic initial dyestuff.

In the same way, dispersion dyestuffs can be prepared from the cationic dyestuffs specified in Example 1 and Orange II.

**Example 11**

Dispersion dyestuffs can be prepared from the cationic dyestuffs specified in Example 1 by the use of copper, nickel or cobalt phthalocyanine tetra-sulfonic acids or their carboxylic acids as anionic initial dyestuffs, as described.

**Example 12**

The dispersion dyestuffs specified in Examples 1 to 4 and 6 to 11 may also be prepared by the method of claim 1 but without the addition of the dispersing agent therein described.

**Example 13**

Instead of the dispersing agent specified in Example 1, there may also be used for the preparation of the dispersion dyestuffs in Examples 1 to 4 and 6 to 11 10 parts of the condensation product of cresol formaldehyde resin with the sodium salt of 2-hydroxynaphthalene-6-sulfonic acid, sodium sulfate and formaldehyde or 10 parts of dextrine.

**Example 14**

Into a dyebath of 1 part of the dyestuff salt prepared according to Example 1, 1 part of the condensation product of 10 parts of naphthalene-2-sulfonic acid with 1 part of formaldehyde and 4 parts of 85% formic acid in 5,000 parts of water, 100 parts of a fabric of 50 parts of polyacrylonitrile fibres and 50 parts of wool is introduced at about 50° C. The bath is heated to 100° C. and dyeing continued for 90 minutes at this temperature; the fabric is then rinsed and dried in the usual way. Powerful dyeings of excellent fastness properties are thus obtained on both kinds of fibres.

Mixed woven and knitted fabrics and mixed threads of from 10 to 90 parts of polyacrylonitrile fibres and 90 to 10 parts of wool or of 10 to 90 parts of polyacrylonitrile fibres and 90 to 10 parts of fibres of polyhexamethylene diamine adipate or of polypropyram in general can be dyed in the same way. The salt-like dispersion dyestuffs specified in Examples 1 to 13 can be used.

**Example 15**

100 parts of one of the fibre mixtures specified in Example 14 are dyed for 2 hours at 100° C. in a bath of 1 part of a dispersion dyestuff prepared according to Example 2, 1 part of the sodium salt of oleyl polyglycol ether sulfate, 20 parts of sodium sulfate and 2 parts of sulfuric acid in 4,000 parts of water. Mixed fabrics of 45 parts of wool and 55 parts of a copolymer of 93 parts of acrylonitrile and 7 parts of methyl methacrylate can be dyed similarly.

**Example 16**

100 parts of mixed woven or knitted fabric of 60 parts of a copolymer of 93 parts of acrylonitrile and 7 parts of methyl methacrylate on the one hand and 40 parts of wool or 40 parts of fibres of polypropyram or of polyhexamethylene diamine adipate on the other hand are dyed for 20 minutes at 109° C. in a high temperature dyeing apparatus in a bath of 0.2 part of the salt-like dispersion dyestuff prepared according to paragraph 1 of Example 3, 1 part of the sodium salt of oleyl polyglycol ether sulfate, 20 parts of sodium sulfate and 2 parts of sulfuric acid in 4,000 parts of water. Fibre mixtures of all of the kinds described in Examples 1 to 7 and 9 to 13 can be dyed in the same way.

**Example 17**

100 parts of a mixed woven or knitted fabric of 50 parts of a copolymer from 93 parts of acrylonitrile and 7 parts of methyl methacrylate and 50 parts of regenerat cellulose are dyed with a solution of 0.4 part of the salt-like dyestuff obtained by the method of Example 1 from the cationic dyestuff named in Example 3, section 1 and the anionic dyestuff of the formula

\[
\begin{align*}
&\text{SOH} & \text{H}_3\text{C} & \text{N} & \text{N} & \text{HN} & \text{CO} & \text{CH}_3 & \text{CO} & \text{CH}_3 \\
&\text{SOH} & \text{H}_3\text{C} & \text{N} & \text{N} & \text{HN} & \text{CO} & \text{CH}_3 & \text{CO} & \text{CH}_3
\end{align*}
\]
9

1.4 parts of the anionic dyestuff of the aforesaid formula and 20 parts of sodium sulfate in 4,000 parts of water. The salt-like dyestuff described in Example 4 can also be used.

Example 18

10 parts of the salt-like dyestuff named in Example 3, section 1, but prepared by the method described in Example 12 in the absence of a dispersing agent, 20 parts of thioglycol, 20 parts of tartaric acid, 650 parts of crystal gum and 300 parts of water of 80° C. are made into a paste in known manner and this paste is used for printing a mixed fabric of 50 parts of wool and 50 parts of fibres made of a copolymer from 93 parts of acrylonitrile and 7 parts of methyl methacrylate. For finishing the prints are dried and steamed for 30 minutes at 101° to 102° C.

We claim:

1. A salt-like dyestuff of the general formula

\((K^{\oplus})(A)^{\ominus}\)

in which K represents the cation of a member of the group of triphenylmethane dyestuffs free from sulfonic acid groups and of cationic character, cyanine and diazacyanine dyestuffs and A represents the anion of a member of the group consisting of indolyl diphénylméthane, azo dyestuffs and their complex compounds with a metal of an atomic number between 24 and 29 which azo dye-stuffs and complex compounds contain at least one watersolubilizing group selected from the class consisting of sulfonic acid, carboxylic acid, sulfonic acid amido and carboxyhydroxybenzene sulfonic acid amido substituent dyestuffs having anionic character.

2. The salt-like dyestuff obtained by the reaction of the cationic dyestuff of the formula

\(\text{Cationic Dyestuff} \quad \text{Anionic Complex} \quad \text{Salt-like Dyestuff}\)

and the anionic dyestuff of the formula

3. The salt-like dyestuff obtained by the reaction of the cationic dyestuff of the formula

\(\text{Cationic Dyestuff} \quad \text{Anionic Complex} \quad \text{Salt-like Dyestuff}\)

4. The salt-like dyestuff obtained by the reaction of the cationic dyestuff of the formula

\(\text{Cationic Dyestuff} \quad \text{Anionic Complex} \quad \text{Salt-like Dyestuff}\)

5. The salt-like dyestuff obtained by the reaction of the cationic dyestuff of the formula

\(\text{Cationic Dyestuff} \quad \text{Anionic Complex} \quad \text{Salt-like Dyestuff}\)

6. A method of dyeing polymeric acrylonitrile-containing fibres and wool fibres in mixed textiles which comprises precipitating from an aqueous suspension a salt of a cationic dyestuff and an anionic dyestuff in the presence of a dispersing agent, incorporating said water-wetted precipitated salt in a finely divided suspension in an aqueous dyebath and subjecting the mixed fibre textile to contact with said salt suspension at a temperature of from 95°-130° C. for a time sufficient to color the fibres in said textiles.

References Cited in the file of this patent

**UNITED STATES PATENTS**

2,760,841 Salvin et al. August 28, 1956
2,767,166 Strabel et al. October 16, 1956

**FOREIGN PATENTS**

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,922,690 January 26, 1960

Roland Mueller et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 44, for that portion of the formula reading "N-CH=CH-N" read -- C-CH=CH-N --; column 10, line 35, claim 5, for that portion of the formula reading "N-CH=CH-N" read -- C-CH=CH-N --.

Signed and sealed this 11th day of October 1960.

(SEAL)
Attest:
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