Patented June 11, 1935 2,004,476

UNITED STATES PATENT OFFICE

2,004,476

DYEING OF TEXTILES

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No Drawing. Application October 14, 1931, Serial No. 568,870. In Switzerland October 16, 1930

11 Claims. (Cl. 8—5)

It is known that dyeings produced by means of so-called direct dyestuffs on fibres of vegetable origin, such as cotton or artificial silk from regenerated cellulose, have at best but little fastness to water. This is a difficulty in the way of their use for many purposes, and indeed may exclude their use.

According to this invention the fastness to water and to wet ironing, of dyeings obtained with such dyestuffs, and in many cases the fastness to top dyeing with such dyestuffs, is quite generally improved by an after-treatment with water-soluble salts of organic bases which are characterized by their containing, on the one part, at least one basic nitrogen-containing residue x, and, on the other part, at least one aliphatic residue R consisting of at least 10 carbon atoms.

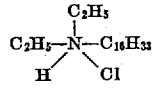
This property of the water-soluble salts is quite generally inherent in the just defined bases. It is in a particularly high measure existing with those bases in which the aliphatic residue R consists of 12 or more carbon atoms. It is also indifferent whether the residues R and x are directly bound to each other, or whether they are indirectly linked by a bridge consisting of an oxygen or nitrogen atom.

Such products in which the residues R an x are directly bound to each other, thus corresponding to the general formula

anion—x—R

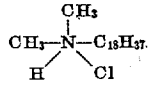
in which x and R have the above identified significations, are the salts of higher aliphatic amines, such as

diethylcetylamine hydrochloride

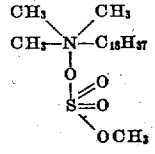


(cf. Reychler, chemisches Zentralblatt, [1913], II, page 1376)

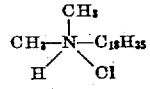
dimethyloctodecylamine hydrochloride



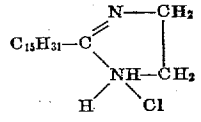
octodecyltrimethylammoniumsulfomethylate



dimethyloctodecenylamino hydrochloride



pentadecyldihydroimidazol hydrochloride

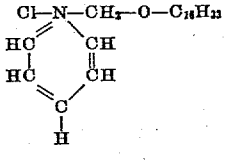


(cf. Patent 1,958,529) etc.

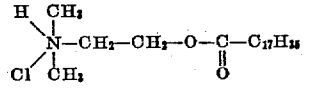
Such products in which the two residues R and x are indirectly linked are ethers, esters or amides. Such products correspond for example to the general formula

anion—x—O—R

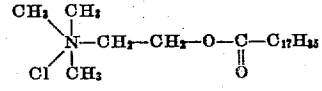
wherein x stands for the residue of an organic base, O means a bridge consisting of an oxygen atom, and R stands for an aliphatic residue consisting of at least 10 carbon atoms. Such compounds are for example the mixed ethers from cetylalcohol and N-hydroxymethylpyridinium chloride of the formula



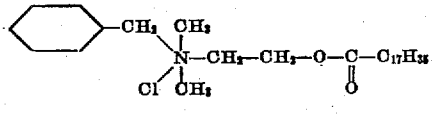
the stearic acid dimethyl- or diethylaminoethanolester hydrochloride of the formula



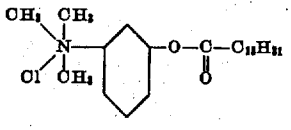
the stearoylcholine chloride of the formula



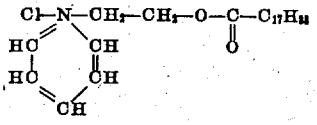
(cf. Fourneau, Bull. Soc. Chim. France [4], 15, page 549) the corresponding benzyl derivative of the formula



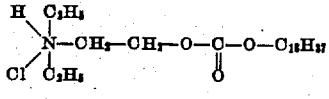
the palmitic acid ester of the 1-hydroxyphenyl-3-trimethyl-ammonium chloride of the formula



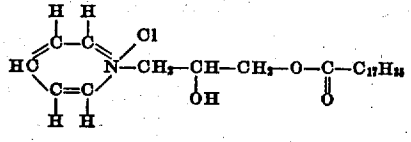
the stearic acid ester of the hydroxyethylpyridinium chloride of the formula



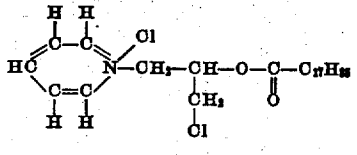
the hydrochloride of the diethylaminoethyloctodecyl carbonate of the formula



the stearyl ester of the addition product of the glycerinemono-chlorhydrine or of the $\alpha:\alpha'$-glycerinedichlorhydrine to pyridine of the formulas

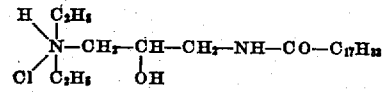


or

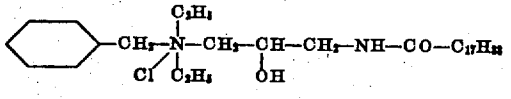


In such compounds the stearoyl or the palmitoyl residue may be replaced by the residues of other acids such as oleic acid, capric acid, lauric acid, myristic acid or ricinoleic acid. Further the alcoholic residue, such as the residue of the cetyl alcohol, may be replaced by the alcoholic residues which correspond to the above named acids, such as oleic alcohol etc.

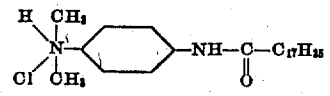
Further compounds in which the two residues R and x are not directly bound to each other are for example the salts of such partially acylated polamines which have been acylated with such acids which themselves contain the above defined residue R, it being indifferent whether the non-acylated amino groups of the polyamine are present in the form of a primary, secondary or tertiary base or in the form of a quaternary ammonium compound. Such partially acylated polyamines are inter alia disclosed in the U. S. Patents 1,534,525 and 1,737,458. Other partially acylated polyamines are for example such which derive from diamines containing OH-groups, for example the hydrochloride of oleoyl-β-hydroxy-γ-diethylamino-propyl-amide of the formula



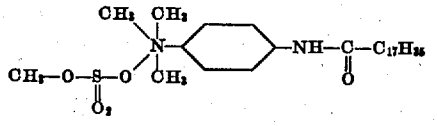
(cf. Patent 1,805,355, Example 1) and the ammonium compounds thereof, such as



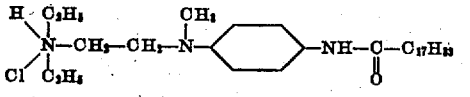
as also such which derive from cyclic diamines, such as the stearoyl-para-amino-dimethyl-aniline hydrochloride of the formula



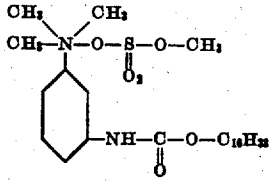
(cf. German Patent 559,500, Example 10) and the ammonium compounds deriving therefrom, such as the addition product of dimethyl-sulfate to the above compound of the formula



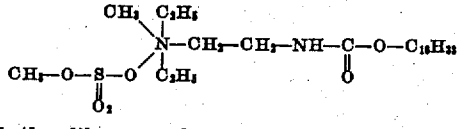
the 4-oleoyl-amino-(diethyl-amino-ethyl-methyl)-aniline hydrochloride of the formula



(cf. Patent 1,894,375, Example 4) suitable monoacyl-piperazine salts (cf. Fourneau, Bull. Soc. Chim. France [4], 45, Pages 1172–1189), further basic urethanes, such as, for example, the dimethyl sulfate addition product to m-dimethyl-amino-phenyl-cetylurethane of the formula



or to diethylamino-ethyl-cetylurethane of the formula



and the like. Such acylated polyamines may further be produced by partially acylating compounds, such as diethylenetriamine, triethylenetetramine, $NH_2—CH_2—CH_2—NH—CH_2—CH_2—NH_2$, $NH_2—CH_2—CH_2—NH—CH_2—CH_2—NH—CH_2—CH_2—NH_2$, etc., and other similar compounds, and their alkylation or aralkylation products, or the ammonium compounds thereof.

Among these products those are particularly valuable which derive from high molecular acids. Among these there may be mentioned capric acid, palmitic acid, stearic acid, and oleic acid, lauric acid, and the like (cf. Patent 1,947,951).

The improvement in the fastness to water is not limited to direct dyeings, but it is to be observed also in the case of dyeings which are subsequently developed, for instance by after-treatment with formaldehyde, or by diazotization and coupling on the fibre.

The invention opens the door for the use of direct dyestuffs for dyeing hat bands, umbrella silks, batique goods, half-wool goods or half-silk goods which must be dyed by the two-bath process, namely first with the direct dyestuff and then as a top dyeing with an acid dyestuff in an acid bath, and also to other applications of such dyestuffs, the improvement constituting a considerable industrial advance.

Not only can the fastness towards water of dyeings on cellulosic textile materials, this expression comprising textiles from natural cel-

lulose, such as cotton, ramie, linen, jute etc., or from regenerated cellulose, such as so-called viscose silk or cuprammonium silk, be improved by this invention, but similar effects can be produced on other materials, such as paper or wood. More or less pronounced effects can also be obtained on other textiles or other materials, such as wool and acetate silk, even if they have been dyed with dyestuffs other than direct dyeing dyestuffs, for example acid dyestuffs. The after-treatment of the dyed material may occur during any of the operations which follow dyeing, for example, in the finishing operation, the water-soluble salts of the bases containing the above mentioned residues x and R being added to the appropriate treatment bath.

The following examples illustrate the invention:—

Example 1

100 kilos of cotton yarn are dyed with
2 kilos of Cotton yellow CH (Schultz 1923, No. 304) and
20 kilos of crystallized Glauber's salt.

The dyeing operation is conducted for 1 hour near the boiling temperature in a bath of 2000 liters of water. The material is then rinsed and after-treated in a bath containing 1 kilo of octodecyl-diethylamine hydrochloride, followed by hydroextracting and drying. A water test shows that the yarn after-treated in this manner is considerably faster to water than that which is not so treated.

Example 2

10 kilos of viscose tricot are dyed in the usual manner at boiling temperature with
0.2 kilo of Chlorantine red 8BN (Schultz 1923, No. 358)

in a bath containing Glauber's salt. After rinsing the material is after-treated for 20 minutes in a cold solution of 100 grams of the cethylether of the N-hydroxymethylpyridinium chloride in 200 liters of water, hydroextracted and dried. The fastness towards water of the knitted fabric has become essentially better.

Example 3

Cotton piece goods which have been dyed as usual with 2 per cent. of Direct sky blue green shade (Schultz 1923, No. 424) are after-treated in a fresh bath with a solution of 1 per cent. (calculated on the weight of the goods) of the oleic acid ester of the hydroxy-ethylpyridinium chloride and dried, the operation being as indicated in Example 2. The dyed material is fast towards water.

Example 4

50 kilos of cotton yarn are dyed with
1.5 kilos of Direct Saframine RW (Color Index Supplement 1928, page 39)
1000 litres of water,
0.5 kilo of crystallized sodium carbonate and
15 kilos of crystallized sodium sulfate,

for one hour at boiling temperature, then rinsed and treated in a bath consisting of 1000 litres of water and 0.5 kilo of the trimethylammonium-methylsulfate of monostearoyl-para-phenylenediamine for 20–30 minutes at 45–50° C., and finally rinsed for a short time and dried. The dyeing thus after-treated has an essentially improved fastness to water.

Example 5

Bleached cotton material is dyed in a neutral bath containing Glauber's salt for one hour at boiling temperature with 3 per cent. of direct fast violet BL (a dyestuff comparable with No. 325 of the Color Index) and then rinsed. The dyed fabric is then after-treated in the manner described in Example 4 in a bath containing 1 per cent. of trimethylammonium-methylsulfate of monostearoylethylenediamine (cf. Patent 1,737,458).

During this treatment, a remarkable change in the shade from blue-violet towards violet-red is observed. Examination of the after-treated dyeing shows an essential improvement in the fastness to water as compared with the dyeing which has not been after-treated.

Example 6

A mixed fabric of viscose artificial silk and cotton is dyed in the usual manner in a bath containing Glauber's salt with 2.5 per cent. of Rigan blue G (Melliands Textil-Berichte 1930, page 642) for one hour at 70–80° C. and is then after-treated in a further bath with 1 per cent. of the acetate of oleoyl-β-hydroxy-γ-diethylamino-propylamide (cf. specification 1,805,355, Example 1), as in Example 4. In this case also there is an essentially improved fastness to water.

Example 7

100 kilos of viscose thread are dyed for one hour at 80° C. with 6 kilos of Melantherine BH (Color Index No. 401), 1 kilo of crystallized sodium carbonate and 40 kilos of crystallized sodium sulfate. After rinsing well the material is treated with a solution of 0.6 kilo of trimethylammonium-methyl sulfate of mono-oleoylethylenediamine in 2000 litres of water for 30 minutes at 45° C. It is then rinsed and dried.

Example 8

10 kilos of half-silk ribbon (cotton and silk) are dyed with 0.25 kilo of Chlorantine fast brown BRL (Color Index Supplement, page 31), 0.150 kilo of Chlorantine fast blue 8GL (Color Index Supplement, page 31) 0.100 kilo of Diamine fast orange R (Color Index, page 349) 0.2 kilo of marseilles soap and 4 kilos of crystallized sodium sulfate in 400 litres of water at approximately boiling point for one hour. After thorough rinsing the goods are after-treated as described in Example 4 in a liquor which contains 0.06 kilo of the acetate of mono-oleoyl-diethyl-ethylenediamine (cf. specification 1,534,525, Example 9) in 200 litres of water. In this case also there is an essential improvement in the fastness to water.

Example 9

In half-wool the cotton is dyed as usual with 3 per cent. of Chlorantine fast blue GLN (Color Index Supplement, page 31), then rinsed and after-treated with 0.6 per cent. of trimethylammonium-methylsulfate of mono-oleoylethylenediamine for half-an-hour at 40–50° C. and washed. The wool is then dyed with 2 per cent. of its weight of Kiton fast orange G (Color Index No. 27), 2 per cent. of sulfuric acid and 10 per cent. of Glauber's salt for ¾ hour at the boil. By after-treatment with trimethylammonium-methylsulfate of mono-oleoylethylenediamine the direct dyestuff becomes fast to top dyeing.

Example 10

Half-wool material is first dyed in an acid bath in the usual manner with 1 per cent. of Tartrazine (Color Index No. 640). It is then well rinsed, and

the cotton is dyed at 55° C. with 3 per cent. of Direct sky blue green shade (Color Index No. 518), with or without addition of a reserving agent, such as the material known by the registered name Katanol W.

The half-wool material which has thus been dyed in a two-color effect is rinsed and then treated in a separate bath for 20 minutes at 45° C. with 1 per cent. of the trimethylammonium-methylsulfate of monostearoylethylenediamine (cf. Patent 1,737,458), rinsed and dried. The dyeings on the after-treated material are fast to water.

Example 11

Difficulties exist in obtaining pure white or colored discharges on material dyed with substantive dyestuffs, in the washing operation which follows steaming. If on the other hand the goods are passed after steaming through a solution containing for example 0.3 gram of the trimethyl-ammonium-methylsulfate of mono-oleoylethylenediamine per litre, the dyeing becomes fast to water, so that it can be washed thoroughly with water. For example, if cotton velvet dyed with 3 per cent. of Direct Safranine B (Color Index, page 351) is discharged in the known manner by means of sodium sulfoxylate, and then passed through the aforesaid trimethylammonium-methylsulfate solution, the velvet may be allowed to remain overnight in luke warm water without fear that the color will run.

A like result is obtained if the treatment with the trimethylammonium-methylsulfate of mono-oleoylethylenediamine is interposed between the dyeing and printing operations.

Example 12

Cotton fabric is printed with printing color having for example the following composition:—

10	grams of Chlorantine fast blue RL (Color Index, page 345)
670	grams of water
300	grams of solid British gum
20	grams of sodium phosphate
1000	grams

The material is steamed twice in a quick steamer or for half an hour in a vessel at ordinary pressure. It is then passed through a bath containing per litre 0.3 gram of oleoylaminoethyl-diethylmethylammoniumsulfomethylate (cf. Patent 1,737,458, Example 2), rinsed and dried. There is obtained a blue print of good fastness to water.

Similar effects are also attained if the acylated diamines used in the foregoing example are replaced by others, such as the trimethylammonium-methyl sulfate of monostearoyl-metaphenylenediamine (cf. German Patent 559,500); the addition product of dimethyl sulfate and ortho-, meta or para-dimethylaminophenylcarbamic acid hexadecyl or octodecyl ester; the hydrochloride of diethylaminoethylimino-dicarboxylic acid dimenthyl ester (cf. Patent 1,527,868, Example 4) or the corresponding addition product with dimethyl sulfate; and the like.

Similar effects are also attained if the water-soluble salts of the bases containing the residues R and x mentioned in the introduction, and used in the foregoing examples, are replaced by other compounds also containing these two residues, such as for example those which have been mentioned or suggested in other examples or in the introduction.

Example 13

Silk paper is dyed by the immersion process by padding with a dyestuff solution containing 10 grams of Direct Safranine B (Color Index, page 351) per litre. It is then treated, either after drying or without drying, in a bath containing 1 gram of oleoylaminoethyl-diethylmethylammoniumsulfomethylate (cf. Patent 1,737,458, Example 2) per litre. The material is thus dyed a red shade which is fast to water. If instead of Direct Safranine B there is used in the process of this example Kiton blue A (Color Index Supplement, page 44) there is obtained a blue dyeing fast to water.

Example 14

Loaded silk piece goods are dyed for ¾ hour at 90° C. with 2.5 per cent of Alizarin Fast blue BB (Color Index Supplement, page 26) and 4 per cent of acetic acid. They are then rinsed in cold water and after-treated for 20 minutes at 40–45° C. with 1 per cent of the trimethylammonium-methylsulfate of mono-oleoylethylenediamine. The blue dyeing is rendered essentially faster towards water by the after-treatment.

What we claim is:—

1. A process for improving the fastness of dyeings produced on materials by means of water-soluble dyestuffs, which consists in subjecting the dyed material to an after-treatment with water-soluble salts of organic bases which bases are characterized by containing at least one basic nitrogen-containing residue and an aliphatic residue consisting of at least 10 carbon atoms.

2. A process for improving the fastness of dyeings produed on textile materials by means of water-soluble dyestuffs, which consists in subjecting the dyed material to an after-treatment with water-soluble salts of organic bases which bases are characterized by containing at least one basic nitrogen-containing residue and an aliphatic residue consisting of at least 10 carbon atoms.

3. A process for improving the fastness of dyeings produced on textile materials by means of water-soluble dyestuffs, which consists in subjecting the textile material dyed with direct dyeing dyestuffs to an after-treatment with water-soluble salts of organic bases which bases are characterized by containing at least one basic nitrogen-containing residue and an aliphatic residue consisting of at least 10 carbon atoms.

4. A process for improving the fastness of dyeings produced on textile materials by means of water-soluble dyestuffs, which consists in subjecting the textile material dyed with direct dyeing dyestuffs to an after-treatment with water-soluble salts of organic bases which bases are characterized by containing at least one basic nitrogen-containing residue and an aliphatic residue consisting of at least 12 carbon atoms,

5. A process for improving the fastness of dyeings produced on cellulosic textile materials selected from the group consisting of native and regenerated cellulose by means of water-soluble direct dyeing dyestuffs, which consists in subjecting the cellulosic textile material dyed with direct dyeing dyestuffs to an after-treatment with water-soluble salts of organic bases which bases are characterized by containing at least one basic nitrogen-containing residue and an aliphatic residue consisting of at least 12 carbon atoms.

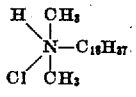
6. A process for improving the fastness of dyeings produced on cellulosic textile materials selected from the group consisting of native and

regenerated cellulose by means of water-soluble dyestuffs, which consists in subjecting the cellulosic textile materials dyed with direct dyeing dyestuffs to an after-treatment with a water-soluble salt of the formula

anion—x—R

in which x stands for a basic nitrogen-containing residue, and R for an aliphatic residue consisting of at least 12 carbon atoms.

7. A process for improving the fastness of dyeings produced on cellulosic textile materials selected from the group consisting of native and regenerated cellulose by means of water-soluble dyestuffs, which consists in subjecting the cellulosic textile materials dyed with direct dyeing dyestuffs to an after-treatment with a water-soluble salt of the formula

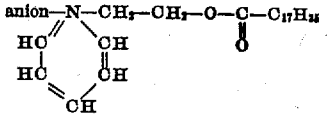


8. A process for improving the fastness of dyeings produced on cellulosic textile materials selected from the group consisting of native and regenerated cellulose by means of water-soluble dyestuffs, which consists in subjecting the cellulosic textile materials dyed with direct dyeing dyestuffs to an after-treatment with a water-soluble salt of the general formula

anion—x—O—R

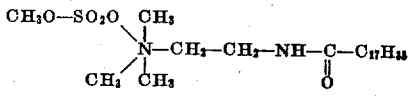
in which x stands for the residue of an organic base, O constitutes a bridge consisting of an oxygen atom, and R stands for an aliphatic residue containing at least 12 carbon atoms.

9. A process for improving the fastness of dyeings produced on cellulosic textile materials selected from the group consisting of native and regenerated cellulose by means of water-soluble dyestuffs, which consists in subjecting the cellulosic textile materials dyed with direct dyeing dyestuffs to an after-treatment with a water-soluble salt of the formula



10. A process for improving the fastness of dyeings produced on cellulosic textile materials selected from the group consisting of native and regenerated cellulose by means of water-soluble dyestuffs, which consists in subjecting the cellulosic textile materials dyed with direct dyeing dyestuffs to an after-treatment with a water-soluble salt of such partially acylated polyamines which have been acylated with such acids which contain an aliphatic residue consisting of at least 12 carbon atoms.

11. A process for improving the fastness of dyeings produced on cellulosic textile materials selected from the group consisting of native and regenerated cellulose by means of water-soluble dyestuffs, which consists in subjecting the cellulosic textile materials dyed with direct dyeing dyestuffs to an after-treatment with a water-soluble salt of the formula



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