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(54) DYEING PROCESS AND DYE BATH THEREFOR

(71) We, AZIENDE COLORI NAZIONALI AFFINI ACNA S.p.A., of Largo Donegani 1/2, 20121 Milano, Italy, an Italian Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the dyeing of cellulosic fibres and fabrics comprising the same herein referred to broadly as cellulosic material, with anionic dyes in organic solvent-based dye baths. The cellulosic fibres may be natural or artificial or a blend of the two.

The use of organic solvent-based dye baths has been known for a long time, and it has also been proposed to use emulsions or dispersions of aqueous solutions of direct or reactive dyes in chlorinated hydrocarbon solvents. However, this has entailed the use of considerable quantities of water, amounting to some 60—800% by weight with respect to the fibre and concomitantly the use of massive quantities of auxiliary emulsifying or dispersing agents. Further, for the attainment of deep shades, the procedure is restricted to dyes with considerable water solubility, and in general it calls for post treatments such as fixing with e.g. formaldehyde/acetic acid.

It is also known, but the basic fibres such as wool, to incorporate in a chlorinated hydrocarbon-based dye bath, salts or adducts of an anionic dye and an amine having at least eight carbon atoms with an uninterrupted chain of at least three carbon atoms. However, even for the intended fibres which of course have a particular affinity of anionic dyes, it was commented in "Solvent Technology—Update '73" AATCC Symposium 1973 pp 58—64, that the procedure contained 'many problems difficult to overcome before it can be used successfully'.

Moreover, it is known that the longer the hydrocarbon chain of the amine and thus the higher the solubility in the solvent of its salt or complex with the acid dye, the lower will be the degree of exhaustion (loc. cit.).

It is an object of the invention to provide dyeing processes for the above-indicated type of (cellulosic) fibrous material, in which good solubility of a dye-amine salt or complex in the organic solvent of the bath is associated with a high degree of exhaustion potential. It is another object of the invention to provide dyeing processes affording a high intensity of dyeing, reaching even a take-up of 4—5% by weight of dye on the fibre. Yet another object is to enable cellulosic material to be dyed effectively with anionic dyes without large amounts of emulsified water.

In another aspect the invention contemplates a novel dye bath for dyeing cellulosic material.

The invention consists in a process of dyeing cellulosic material with an anionic dye from a moist (i.e. containing at least 0.1% by weight of water) organic solvent-based dye bath, in which the dye is used in the form of its salt or complex with an aliphatic tertiary alkyl, primary or secondary amine of the general formula

$$R—NH—C(R_1,R_3)—R_2$$

wherein R is hydrogen or an aliphatic hydrocarbon radical, and where R_1, R_2 and R_3, which may be the same or different, are aliphatic hydrocarbon radicals the total number of carbon atoms in the amine being from 11 to 29. Suitably, the bath contains a minor proportion of water emulsified or dispersed therein, in an amount of 20%—200%, preferably 40—100%, based on the weight of the cellulosic material being dyed.

The preferred amines are substantially insoluble in water and have at least 12 carbon atoms. They exhibit an ion-exchange function in the liquid phase and are referred to in Helfferich's book "Ion Exchange",

pub. 1962, pp 584. The hydrocarbon radicals may be straight chain or branched, saturated or unsaturated.

The invention also consists in a dye bath suitable for dyeing cellulosic material as aforesaid, comprising a salt or complex of an anionic dyestuff with an amine of said general formula in an organic solvent, preferably a chlorinated hydrocarbon, the bath having 0.2—4% by weight of water dispersed or emulsified therein. Suitably, the salt or complex is prepared separately.

It is believed that the ion exchange propensities of the amines used are of significance in the dyeing process, discharging the dyestuff molecule in the course of an ion exchange process. By suitable adjustment of the pH a progressive and high degree of exhaustion of the bath can be attained. For this purpose material having an alkaline reaction may be added at the commencement of, and/or during the course of the dyeing reaction. Thus, during the dyeing phase it is convenient gradually to add buffer substances and/or salts or substances with an alkaline reaction, suitable for bringing the pH to an optimal value which may be determined experimentally, and optimising the ionic exchange or interchange process of dye exhaustion and penetration of the dye into the textile fibre.

The dyeing with anionic dye salts or complexes may thus initially be carried out according to procedures analogous with conventional techniques for dyeing with direct dyes, with the preferred additional feature in the final phase involving the addition of alkaline-reacting material in a predetermined manner to promote the reactive dyeing of the fibre.

As buffering and/or alkalizing substances there may be used, for instance, salts of alkali metals or of ammonium with mineral or organic acids, for instance, with phosphoric, carbonic, acetic, oxalic, boric, tartaric or citric acids, and/or hydroxides and alcoholates of alkali metals, in quantities suitably varying from 1% to 20%, preferably 2% to 15% on the weight of the fibre.

The addition of tertiary amines such as trimethylamine, triethylamine, pyridine, will be found in some cases to improve the yield of the dyeing process.

The high attainable degree of exhaustion of the dye and the regenerative properties of the amine materially reduce the pollution problems posed by this type of dyeing process, as well as providing for improved efficiency, lowered costs and improved results.

As already indicated, minor proportions of water are desirably incorporated into the dye bath which should however be homogeneous the water accordingly being emulsified. In this case it may be desirable to incorporate a non-ionic surface-active agent which may be used if desired in conjunction with anionic surface active agents. Mixtures of non-ionic emulsifying agents may be resorted to in order to attain an optional hydrophilic-lyophilic balance (HLB) to stabilise the water-in-oil emulsion. Other blending aids which do not interfere with the dyeing process, such as polar solvents, may be used. The amount of water may vary considerably, depending on the particular fibre to be dyed and on the amount of fibre and the desired tintorial intensity. Thus with an amount of water of from 20% to 200% based on the weight of the fibre the amount of the emulsifier may vary from for example 10% to 20%, also based on the weight of the fibre.

As suitable organic solvents there may be mentioned, for instance: halogenated aliphatic and aromatic hydrocarbons with boiling points of 50° to 180°C such as perchloroethylene, trichloroethylene, 1,1,1-trichloropropane, methylene chloride, methyl chloride, chlorobenzene, chlorotoluene and 1,1,2-trichlorofluorethane sold under the Registered Trade Mark Edifren 113. The two first-mentioned are particularly suitable. Minor amounts of compatible polar solvents may be incorporated to enhance the solubility of the dye-amine adduct and/or to promote the solubility or dispersibility of water in the dye bath.

The salts or complexes (adducts) of the anionic dyes and the amines may be prepared by various conventional methods. For instance, an aqueous solution of the acid dye in the form of its sodium salt may be acidified to pH 2—3 with mineral acid (e.g. H_2SO_4, HCl) and then extracted with a solution containing the equivalent weight at least of liquid anion exchanger amine in a substantially water-soluble organic solvent, suitably a halogenated hydrocarbon. As a rule, each acid group of the dye will be associated with at least a chemical equivalent of the chosen aliphatic amine, preferably from 1 to 1.2 equivalents. After separation of the aqueous phase, the organic phase contains the dissolved salt or complex and may be diluted or concentrated as desired.

Alternatively, it is possible to add to the aqueous dye solution, acidified as indicated above, the chosen amine dissolved in a water-miscible volatile solvent suitably alcohol, the salt or the complex then being taken up in the dye bath solvent after removal of the alcohol.

The salts or complexes used according to the invention are believed to be adducts of

the amine in quaternary form, bonded ionically at the reactive acid group or groups of the dye. Generally, up to four acid groups on the dye molecule may react in this way depending, of course, on the number present. A slight stoichiometrical excess of amine is preferred to a deficiency and is found in some cases to enhance the dye fixation by ion exchange.

Dye usable in the process of this invention belong to various chemical classes, such as for instance the azoic, anthraquinonic, stylbenic and phthalocyaninic dyes. These dyes must however belong to the type of direct dyes, metallised or unmetallised, or of ionic reactive dyes.

The aliphatic amines used as salt-forming or complexing agents are desirably, as already mentioned, substantially insoluble in the aqueous phase and at the same time regeneratable by ionic exchange or interchange whereby they are almost quantitatively recoverable. Suitable amines, available on the market, include N-dodecenyl-(trialkyl-methyl) amine sold as Amberlite LA1, N-lauryl-(trialkyl-methyl) amine sold as Amberlite LA2 ("Amberlite" is a Registered Trade Mark) and containing altogether from 24 to 28 carbon atoms, and the primary trialkyl-methyl-amines having from 12 to 22 carbon atoms such as those sold under the trade name Primene 81—R ("Primene" is a Registered Trade Mark) mainly consisting of from t-$C_{12}H_{25}$—NH_2 up to t-$C_{14}H_{29}$—NH_2 and the Primene JM—T mainly consisting of from t-$C_{18}H_{37}$—NH_2 up to t-$C_{22}H_{45}$—NH_2.

The chemical and physical characteristics of the amines used according to the invention are in high degree attributable to the tertiary alkyl group which imparts their high solubility in the organic solvents, at the same time making them substantially insoluble in water, enabling them to function as liquid phase anion exchangers.

A suitable dyeing temperature is from 40° to 90°C, depending on the nature of the fibre and on the dyes. The immersion (dwell) times at dyeing temperature may vary widely, e.g. from 20 to 90 minutes.

The process of this invention is, as indicated above, applicable to cellulosic materials. In particular it is applicable to cotton fibres with various degrees of mercerization, polynosic fibres, viscose fibres and blends of these. Moreover, it is in general possible in accordance with the invention to dye blends of cellulosic material with fibrous materials containing basic groups such as wool and nylon.

The process of the invention may also be applied to the optical bleaching of cellulosic materials, by using salts or complexes of the amines with anionic optical bleaching agents.

The following examples illustrate how the invention may be carried into effect. The parts and percentages indicated are by weight, unless otherwise indicated.

EXAMPLE 1

100 parts of mercerized cotton yarn were immersed at room temperature into a dye bath consisting of: 0.5 parts of the salt of Amberlite LA2 with the C.I. dye Direct Violet 7, No. 27,855 (corresponding to 1 part of commercial dye at a standard tinctorial concentration of 100%), and 40 parts of water emulsified with 8 parts of an emulsifier composed of 15.9% Tween 80 and 84.1% Span 80 into 3200 parts of commercial perchloroethylene. ("Tween" and "Span" are Registered Trade Marks).

The temperature of the bath was brought to 90°C over a period of 30 minutes in a closed dyeing apparatus with circulating provision for the dye bath and fitted with a pressure feed.

During the heating phase there were gradually added small portions, amounting in all to 2 parts by weight, of Na_2CO_3. The bath was maintained at 90°C for 40 minutes. At the end of the dyeing phase the exhaustion of the dye bath was almost complete. Thereupon the bath was cooled, discharged and the dyed yarn washed with perchloroethylene containing small quantities of emulsified water, after which the yarn was taken out and dried.

There was obtained a dyeing of a violet tinge, well equalized, comparable with that obtained by dyeing in an aqueous bath, with a good bath exhaustion.

EXAMPLE 2

100 parts of a blend of mercerized cotton and polynosic fabric (hosiery) were immersed at room temperature into a dye bath consisting of:

0.93 parts of the salt of Amberlite LA1 with the C.I. dye Direct Yellow 12, No. 24895 (corresponding to 2 parts of commercial dye at a standard tinctorial concentration of 100%), and

50 parts of purified water (pH 8.5) emulsified with

10 parts of the emulsifier of example 1 plus

2 parts of Amberlite LA1 into

3200 parts of commercial perchloroethylene.

The temperature of the bath was brought to 85°C during 20 minutes in a circulating bath apparatus as in Example 1, and was held at that level for 45 minutes.

At the completion of the dyeing, the bath was discharged and the dye fabric after

washing with perchloroethylene containing emulsified water was dried.

The bath exhaustion amounted to 91%, while dyeing from an aqueous bath resulted in a bath exhaustion of only 71%.

EXAMPLE 3

100 parts of mercerized cotton yarn were immersed at room temperature into a dye bath consisting of: 0.35 parts of the salt of Amberlite LA2 with the C.I. dye Direct Blue 86, No. 74,180 (corresponding to 1 part of commercial dye at a standard tinctorial concentration of 100%), and 40 parts of purified water (pH 8.5), emulsified with 8 parts of emulsifier as in example 1 together with 2 parts of Amberlite LA2 into 3200 parts of commercial perchloroethylene.

The temperature of the bath was then brought upto 85°C over 20 minutes in a circulating bath apparatus, and was maintained at that level for 45 minutes.

On completion of the dyeing the bath was discharged, the material was washed with perchloroethylene containing emulsified water, and then was dried. There was obtained a turquoise dyeing with a bath exhaustion amounting to 85%.

The same dyeing in an aqueous bath gave an exhaustion of only 60%. The fastnesses are equivalent in the two types of dyeing.

EXAMPLE 4

100 parts of non-mercerized cotton yarn were immersed at room temperature into a dye bath containing:

0.58 parts of the salt of Amberlite LA2 with the C.I. dye Direct Yellow 12, No. 24,895 (corresponding to 1.25 parts of commercial dye at standard tinctorial concentration of 100%),

2 parts of sodium acetate dissolved in

40 parts of purified water (pH 8.5) emulsified with

8 parts of emulsifier as in Example 1 into

2000 parts of commercial perchloroethylene.

Thereupon the temperature of the bath was brought up to 85°C over half an hour in a circulating bath apparatus, and was maintained at that level for 45 minutes. At the end of this time the procedure of Example 1 was followed, giving an exhausted dyeing, of a yellow tinge, which was well equalized and similar to the dyeing obtained from an aqueous bath.

EXAMPLE 5

100 parts of viscose staple yarn were immersed at room temperature into a dye bath containing:

0.49 parts of the salt of Amberlite LA2 with the C.I. dye Direct Yellow 50, No. 29,025 (corresponding to 0.5 parts of commercial dye at a standard tinctorial concentration of 100%), and

80 parts of water containing

2 parts of sodium carbonate emulsified with

15 parts of emulsifier as in Example 1 into

3200 parts of commercial perchloroethylene.

The material was dyed in a closed circulating bath apparatus, bringing the temperature up to 90°C over a period of 40 minutes and keeping it at that level for 40 minutes. The procedure of Example 1 was then followed, giving a well exhausted and equalized yellow dyeing.

EXAMPLE 6

100 parts of cotton hosiery were immersed at room temperature into a dye bath consisting of:

2.17 parts of the salt of Amberlite LA2 with the C.I. dye Direct Orange 49 No. 29,050 (corresponding to 2 parts of commercial dye at Standard Tinctorial Concentration of 100%), and

1 part of sodium acetate dissolved in

40 parts of purified water (pH 8.5) emulsified with

8 parts of the emulsifier of Example 1 into

3200 parts of commercial perchloroethylene.

The material was dyed in a closed apparatus with provision for circulating the bath, the temperature being brought over a period of 30 minutes upto 90°C. There was then added, in small increments, a total of 1 part of anhydrous sodium carbonate previously dissolved in 20 parts of water containing 5 parts of the emulsifier of Example 1.

The temperature of 90°C was maintained for 40 minutes after which the procedure of Example 1 was followed. There was obtained a well exhausted and equalized orange dyeing.

EXAMPLE 7

100 parts of mercerized cotton fabric were immersed at room temperature into a dye bath consisting of:

2.7 parts of the salt of Amberlite LA2 with the C.I. dye Reactive Orange 27 (corresponding to 3 parts of commercial dye at Standard Tinctorial Concentration of 100%), and

2 parts of sodium acetate dissolved in

80 parts of water emulsified with 16 parts of the emulsifier of Example 1 into

3200 parts of commercial perchloroethylene.

the material was treated in a closed circulating bath apparatus, bringing the temperature up to 85°C over a period of half an hour.

After a dwell at this temperature of 10 minutes there was ascertained an

exhaustion of the dye already on the material. Then 4 parts of sodium carbonate were added gradually and the dyeing was continued for 40 minutes at 85°C.

In this way there was obtained a reactive dyeing of the material. The bath was then discharged and the material was washed at 60°C for 5 minutes with an emulsion consisting of:

300 parts of water emulsified with

50 parts of emulsifier as described in Example 1, into

2850 parts of commercial perchloroethylene.

The material was then soaped for 10 minutes at 95°C in an emulsion consisting of:

300 parts of water emulsified with

49 parts of the emulsifier described in Example 1, and

1 part of Aerosol OT(sodium sulfosuccinate of 2-ethylhexyl alcohol) into

2850 parts of commercial perchloroethylene.

There was obtained a well fixed dyeing of a yellow tinge and with characteristics equivalent to those of a dyeing from an aqueous bath, but with a greater bath exhaustion.

EXAMPLE 8

100 parts of mercerized cotton yarn were immersed at room temperature into a dye bath consisting of:

2.18 parts of the salt of Amberlite LA2 with the C.I. dye Reactive Orange 54 (corresponding to 2 parts of commercial dye at a Standard Tinctorial Concentration of 100%),

3 parts of sodium acetate dissolved in

50 parts of water emulsified with

16 parts of the emulsifier of Example 1 into

3200 parts of commercial perchloroethylene.

The material was dyed in a closed apparatus with a circulating bath, which was heated up to 80°C in the course of 30 minutes. Then, 4 parts of trisodium phosphate dissolved in 30 parts of water were added gradually in incremental amounts and the dyeing was continued for 40 minutes at 80°C.

On completion of the dyeing the bath was discharged and the material was washed as described in Example 7, followed by soaping for 15 minutes at 95°C with an emulsion consisting of:

300 parts of water,

30 parts of the emulsifier described in Example 1,

10 parts of anionic UN 100, (condensation product of octylphenol with 11 mols of ethylene oxide) and

2000 parts of commercial perchloroethylene.

There was thus obtained a well fixed orange dyeing comparable, as regards equalization and fastness, to the dyeing in an aqueous bath, in comparison to which it showed a greater bath exhaustion.

EXAMPLE 9

100 parts of cotton poplin were wound onto a core and introduced into a circulating bath apparatus containing a dye bath consisting of:

3.52 parts of the salt of Amberlite LA2 with the dye Reacna Brilliant Orange T2R (corresponding to 2 parts of a commercial dye with a Standard Tinctorial Concentration of 100%), and

1 part of sodium acetate dissolved in

80 parts of water emulsified with

16 parts of the emulsifier of Example 1 into

2880 parts of commercial 1,1,2-trichloroethane.

The temperature of the bath was then brought upto 80°C in the course of half an hour and was maintained at this level for 10 minutes, after which there were slowly incorporated, in incremental portions 6 parts of anhydrous sodium carbonate dissolved in 25 parts of water. After this the dyeing was continued for 40 minutes at the same temperature.

On completion the bath was discharged and the washing and soaping treatments of the material were carried out as described in Example 8. There was obtained a well fixed orange shade, equivalent as regards equalization and fastness, to a dyeing from a normal aqueous bath, and with respect to which the dyeing according to the present invention showed a greater bath exhaustion.

EXAMPLE 10

100 parts of cotton hosiery fabric wound on a core were introduced into a closed circulating bath apparatus charged with a dyeing bath consisting of:

6.57 parts of the salt of Amberlite LA1 with the dye Reacna Brilliant Scarlet TR (corresponding to 4 parts of a commercial dye with a Standard Tinctorial Concentration of 100%), and 80 parts of water containing

2 parts of sodium acetate and

1 part of sodium carbonate emulsified with

16 parts of emulsifier of Example 1 into

2880 parts of commercial 1,1,2-trichloroethane.

The temperature of the bath was then brought to 80°C in the course of 40 minutes and then, slowly, there were incorporated in incremental portions 10 parts of anhydrous sodium carbonate; after this the dyeing was continued for 50 minutes at the same temperature.

On completion of the dyeing, the dye bath was discharged and the dyed fabric washed and soaped as in Example 8.

There was thus obtained a well equalized and deep scarlet tinge, having fastness characteristics comparable with those derived from an aqueous dyeing bath.

EXAMPLE 11

100 parts of cotton poplin were wound onto a core and introduced into a closed circulating bath apparatus charged with a dye bath consisting of:

3 parts of the salt of Amberlite LA2 with the C.I. dye Reactive Red 61 (corresponding to 2 parts of a commercial dye with a Standard Tinctorial Concentration of 100%) and

2 parts of sodium acetate dissolved in

40 parts of water emulsified with

8 parts of the emulsifier of Example 1 into

3200 parts of commercial perchloroethylene.

The temperature of the dye bath was then brought upto 60°C over 20 minutes and there were then gradually incorporated 2 parts of anhydrous sodium carbonate dissolved on 20 parts of water containing 4 parts of emulsifier as in Example 1. Then, the temperature was brought up in the course of 20 minutes to 85°C, when there were gradually added 4 parts of anhydrous sodium carbonate dissolved in 20 parts of water.

The dyeing was then continued for 40 minutes at 85°C. On completion of the dyeing the dyeing bath was discharged and the material was washed and soaped as described in Example 8.

There was thus obtained a well-exhausted and well-equalized red dyeing with fastness characteristics comparable with those obtained using an aqueous dyeing bath.

EXAMPLE 12

100 parts of a polynosic fibre yarn were introduced into a closed circulating bath dyeing apparatus containing:

4.86 parts of the salt of Amberlite LA2 and the dye Ruby Brilliant Reacna TR (corresponding to 2.5 parts of a commercial dye with a Standard Tinctorial Concentration of 100%), and

60 parts of water emulsified with

12 parts of the emulsifier of Example 1 into

3200 parts of commercial perchloroethylene.

The dye bath was then brought up to 60°C over a period of 20 minutes, and then there were gradually added:

1 part of anhydrous sodium carbonate and

4 parts of trisodium phosphate crystals dissolved in

40 parts of water containing

4 parts of the emulsifier of Example 1.

The dyeing was then continued for 50 minutes at 80°C. On completion, the dye bath was discharged and the yarn subjected to washing and soaping as described in Example 8. A well-exhausted and equalized dyeing of a ruby tinge was obtained.

EXAMPLE 13

Proceeding as in Example 12, but substituting the Amberlite LA2/Ruby Brilliant Reacna TR salt by 5.73 parts of an Amberlite LA2/Ruby Reacna TB salt, analogous results were obtained.

EXAMPLE 14

100 parts of mercerized cotton yarn were introduced into a closed circulating bath dyeing apparatus containing a dye bath consisting of:

3.74 parts of the salt of Amberlite LA1 with the dye Blue Brilliant Reacna SG (corresponding to 2 parts of a commercial dye with a Standard Tinctorial Concentration of 100%), and

40 parts of water containing

2 parts of sodium acetate emulsified with

8 parts of the emulsifier of Example 1 into

3200 parts of commercial perchloroethylene.

This dye bath was then brought to 80°C over 30 minutes whilst adding gradually, in the course of heating,

2 parts of sodium acetate and

2 parts of anhydrous sodium carbonate dissolved in

20 parts of water.

After 10 minutes at 80°C, there were gradually added

4 parts of anhydrous sodium carbonate and

4 parts of trisodium phosphate crystals.

There upon the dyeing was continued for 60 minutes at 80°C, after which the dye bath was discharged and the yarn washed and soaped as in Example 8.

There was obtained a well equalized dyeing of a blue tinge.

EXAMPLE 15

Proceeding as in Example 14, but substituting the Amberlite LA1/Blue Brilliant Reacna SG salt by 1.8 parts of an Amberlite LA1/C.I. dye Reactive Blue 47 salt, similar tinctorial results were obtained.

EXAMPLE 16

100 parts of a viscose staple yarn were introduced into a closed circulating bath apparatus charged with a dye bath consisting of:

8.75 parts of the salt of Amberlite LA2/with the C.I. dye Reactive Red 102 (corresponding to 4 parts of a commercial

dye with a Standard Tinctorial Concentration of 100%), and

2 parts of sodium acetate dissolved in 60 parts of water emulsified with 12 parts of emulsifier as in Example 1 into 3200 parts of commercial perchloroethylene.

This bath was brought to 85°C in the course of 30 minutes whilst adding incrementally the following substances to a total of:

5 parts of sodium acetate dissolved in 30 parts of water containing 6 parts of the emulsifier of Example 1.

After dyeing had proceeded for 10 minutes at 85°C, there were added 3 parts of anhydrous sodium carbonate dissolved in 15 parts of water.

After a further 10 minutes the same addition was repeated and then dyeing was continued for 40 minutes at 85°C. After this the dye bath was discharged and the yarn was washed and soaped as in Example 8.

There was obtained a well exhausted dyeing of a deep brown tinge.

EXAMPLE 17

100 parts of cotton poplin were wound onto a core and then introduced into a closed circulating bath dyeing apparatus containing a bath consisting of:

9.47 parts of the salt of Amberlite LA2 with the C.I. dye Reactive Black 5 (corresponding to 6 parts of commercial dye with a Standard Tinctorial Concentration of 100%), and

2 parts of sodium acetate dissolved in 60 parts of water emulsified with 12 parts of the emulsifier of Example 1 into 3200 parts of commercial perchloroethylene.

Thereupon the bath temperature was brought up in the course of 30 minutes to 60°C, when there were added 2 parts of anhydrous sodium carbonate dissolved in 20 parts of water.

After dyeing had proceeded for 10 minutes at 60°C, there were gradually added, in incremental amounts, 6 parts of trisodium phosphate crystals dissolved in 30 parts of water.

The dyeing was then allowed to continue for 60 minutes at 60°C, whereupon the dye bath was discharged and the dyed poplin washed and soaped as in Example 8. There was obtained a well exhausted and equalized black shade.

EXAMPLE 18

Proceeding as indicated in Example 11, but substituting the Amberlite LA2/Reactive Red 61 salt by 2.7 parts of the corresponding Primene JMT/salt, the results obtained were comparable with those obtained in Example 11.

WHAT WE CLAIM IS:—

1. A process of dyeing cellulosic fibrous material with an anionic dye from an organic solvent-based dye bath containing at least 0.1% by weight of water, in which the dye is used in the form of a salt or complex with an aliphatic tertiary alkyl, primary or secondary amine of the general formula

$$R—NH—C(R_1, R_3)—R_2$$

where R is hydrogen or an aliphatic hydrocarbon radical, and R_1, R_2 and R_3, which may be the same or different, are aliphatic hydrocarbon radicals the total number of carbon atoms in the amine being from 11 to 29.

2. A process according to claim 1 in which the tertiary alkyl, primary or secondary amine is added to the bath as a pre-formed salt or complex with the dye.

3. A process according to claim 1 or 2 in which the amine has at least 12 carbon atoms in the molecule, is substantially insoluble in water and manifests an ion-exchange function in the liquid phase.

4. A process according to claim 1, 2 or 3 in which the amine used is an N-dodecyl (trialkyl-methyl) or N-lauryltrialkyl-methyl) amine of 24—28 carbon atoms or a primary (trialkyl-methyl) amine of 12—22 carbon atoms.

5. A process according to any of claims 1—4 in which the amine is present in at least one chemical equivalent proportion with respect to the anionic dye.

6. A process according to claim 4 in which the amine is present in from 1 to 1.2 chemical equivalent proportions.

7. A process according to any of claims 1—6 in which the organic solvent is a chlorinated hydrocarbon.

8. A process according to any of the foregoing claims in which the dye bath contains 20—200% of water, based on the weight of the fibre, emulsified therein.

9. A process according to claim 8 in which the amount of water is from 40% to 100% by weight of the fibre being dyed.

10. A process according to any preceding claim in which material having an alkaline reaction is added at the commencement of, and/or during the course of, the dyeing reaction.

11. A process according to claim 10 in which the amount of said alkaline material is from 1% to 20% by weight of the cellulosic material being dyed.

12. A process according to claim 11 in which said amount is from 2% to 15% by weight of the cellulosic material.

13. A process according to any preceding claim in which, after dyeing, the amine is regenerated by ionic exchange or interchange and reused.

14. A process according to claim 1, substantially as described in any of the foregoing examples.

15. A dye bath suitable for dyeing cellulosic fibrous material comprising a salt or complex of an anionic dyestuff with a primary or secondary amine as defined in claim 1, 2 or 3, dissolved in an organic solvent, and 0.2—4% by weight of a separate aqueous phase emulsified therein.

16. A dye bath according to claim 15 in which the solvent is a chlorinated hydrocarbon.

17. A dye bath according to claim 16 in which the solvent is perchlorethylene or 1,1,2-trichloroethylene.

18. A dye bath according to claim 16 or 17 containing 0.01—0.4% of an alkaline material.

19. A dye bath according to claim 16, 17 or 18 incorporating a minor amount of a tertiary amine.

20. A dye bath according to claim 15, substantially as described in any of the examples.

21. Cellulosic material when dyed by a process according to any of claims 1—14, or in a dye bath according to any of claims 15—20.

22. A process according to any of claims 1—14, or a dye bath according to any of claims 15—20, or cellulosic material according to claim 21, in which the anionic dye used belongs to one of the chemical classes hereinbefore referred to.

23. A process of dyeing cellulosic fibrous material, or a dye bath or a material according to claim 22, in which the dye is one of those hereinbefore specifically mentioned.

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