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3,206,363

COMPOSITION AND PROCESS FOR SOLVENT DYEING WITH TETRALOWERALKYL UREAS

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15 Claims. (Cl. 167—88)

This invention relates to the coloring of polyamide fibers by the solvent dyeing process. More specifically it relates to such a process that uses certain alkyl derivatives of urea as a solvent.

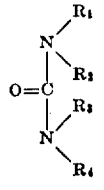
Recently a new process for coloring keratinic fibers including hair has been disclosed by L. Peters and C. B. Stevens, J. Soc. Dyers & Colourists 72, 100, 241, 287 (1956). The process is called solvent dyeing and derives its name from the fact that an organic solvent is added to the dyebath. It is a solvent that has some solvent action on the dye and has some but a limited solubility in water. The dyes that are preferentially employed are the disperse colors and the neutral dyeing metal complexes of azo dyes. Without confining ourselves to any theory we assume that the organic solvent is preferentially adsorbed by the keratin and carries the dye from the aqueous phase through the solvent layer to the keratin. It follows that very hydrophilic and very water soluble organic solvents cannot be used in this process since they tend to stay in the aqueous phase. On the other hand solvents that are entirely insoluble in water are also of no use.

The solvent dyeing process has attracted considerable attention of the textile chemists; cf. L. Peters and C. B. Stevens, The Dyer and Textile Printer 115, 327 (1956); G. H. Lister, Textile Rundscheu 11, 463 (1956); M. Kärrholm and J. Lindberg, Textile Research Journal 26, 528 (1956). However, as far as the dyeing of human hair is concerned the process has suffered from two disadvantages. With the solvents so far disclosed and used the scalp is stained; still worse the scalp is irritated. This is particularly true with benzyl alcohol which otherwise has been the most satisfactory solvent disclosed up to now.

It is a primary object of this invention to overcome these disadvantages, that is to say to employ coloring media which neither stain nor irritate the scalp. This object has been attained by using as solvents certain alkyl derivatives of urea.

This invention can be employed for dyeing either natural or synthetic polyamide fibers such as wool, silk, nylon or animal bristles, and particularly hair attached to the skin such as living human hair, furs, pelts, etc.

The urea derivatives used in this invention correspond to the formula:



wherein R_1 is a (lower) alkyl and each of R_2, R_3, and R_4 is hydrogen or a (lower) alkyl and wherein said urea derivatives have a melting point below 40° C. The term "lower" as used herein to modify alkyl refers to an alkyl having from 1 to 5 carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl, tert. butyl, amyl, and the like. Preferably the water solubility of the urea derivative is less than about 10% at 25° C.

From what has been said above about the solvent dyeing process it becomes clear that the solvent must be a liquid so it can perform the function of a carrier for the dye. The maximum allowable temperature for dyeing hair on the human head is 40° C. and therefore the solvents must be liquid below this temperature. While the prior art has disclosed some alkyl derivatives of urea to be incorporated in dyebaths for human hair none of the disclosed ureas is a liquid and none has a melting point below 40° C. As a matter of fact those ureas disclosed by the prior art have been used in a process for coloring human hair that has nothing to do with the presently contemplated solvent dyeing process.

It is known that urea itself is a salt-like, very polar compound; as a matter of fact urea and thiourea have the character of "Zwitter Ions" (cf. H. Lecher and C. Heuck, Ann. 438, 176 (1924). In alkyl derivatives of urea the polar character is gradually diminished, the melting point decreases and the tetra-lower-alkyl-ureas are distillable liquids. Recent papers by T. Gaumann et al., Helv. Chim. Acta 41 1956, 1971 (1958) disclose dielectric constants and dipole moments of alkyl substituted ureas. To give an extreme example urea itself has a dipole moment μ_D-4.56 while tetramethylurea, tetraethylurea, tetrabutylurea and 1,1-dimethyl-3,3-diethylurea have dipole moments μ_D around 3.45 only and are liquids.

The dyes used in the process of our invention are soluble in the urea derivative solvent and have a higher solubility in the urea solvents of this invention than in water. Generally such dyes have a low solubility in water such as less than about 0.5% and preferably less than 0.1% at 25° C.

The preferred dyes used in this invention are the disperse dyes and the neutral premetallized dyes. Disperse dyes are well-known to the textile art and are used for dyeing cellulose acetate and other polyester fibers, and nylon. They are structurally characterized by the absence of solubilizing sulfonic acid groups. Aside from this requirement, they may belong to various chromphoric classes, such as to nitrodiphenylamines, as for example, Disperse Orange 15 (C.I. 10350), to azo dyes, as for example, C.I. Disperse Orange 5 (C.I. 11100), and to anthraquinones, as for example, Disperse Violet 4 (C.I. 61105). The disperse dyes are well described in the textile literature. A list of disperse dyes can be found in the 1961 Technical Manual of the American Association of Textile Chemists and Colorists, vol. 38, pages 292–293; in The Chemistry of Synthetic Dyes and Pigments (1955) by H. A. Lubs, pages 167–174 and 417–426; and in K. Vankataraman, The Chemistry of Synthetic Dyes (1952) vol. I pages 639–646 and vol. II pages 803–812.

The neutral premetallized dyes, also referred to herein as neutral dyeing metallized azo dyes, comprise particularly chromium and cobalt complexes of azo dyes with appropriate chelating groups, the ratio of metal: azo dye being 1:2. They are further characterized by the absence of solubilizing sulfonic acid groups. Such dyes are sold under a variety of tradenames, such as Cibalans, Irgalans, Irgacets, Capracyls, Lanasyns and others. Irgalans have been described in an article by G. Schetty, J. Soc. Dyers & Colourists 71, 705 (1955). As an example there can be mentioned Irgalan Orange RL which is the sodium-ammonium salt of the chromim complex of the azo dye obtained from diazotized 3-amino-4-hydroxyphenyl-methylsulfone coupled on 3'-chloro-1-phenyl-3-methyl-pyrazolone-5 (Example 8 of U.S. Patent 2,551,056). Irgalan Gray BL described in Example 13 of the same patent uses the same diazo component but the coupling component is the methylurethane of 1-amino-7-hydroxynaphthalene.

Cibalans are dealt with in an article by C. Weidmann, Am. Dyestuffs Reporter 43, 167 (1954). As an example may be mentioned Cibalan Orange RL which is a chromium complex of 2-aminophenol-4-sulfonamide coupled on 1-p-tolyl-3-methyl-pyrazolone-5.

The dyeing process of this invention can be employed over a wide pH range such as that of about 2 to 9, the preferred pH depending on the class of dye employed. In the case of the neutral premetallized dyes, where the acid form of these dyes is less water-soluble than the salt form, an acid pH in the range of about 3–6 is preferred. The pH can be adjusted to the preferred value by the addition to the dyeing composition of various inorganic or organic acids or acid-salts, as for example, hydrochloric acid, sulfuric acid, ammonium sulfate, acetic acid, formic acid, citric acid, lactic acid or tartaric acid.

Illustrative of the urea derivatives employed in this invention which have a melting point less than 40° C. there can be mentioned: tetrapropylurea; tetraethylurea; 1,1-dipropyl - 3,3 - diethylurea 1,1 - dibutyl-3 - ethylurea; 1-ethyl-1 - methyl-3-ethyl-3 - methylurea; 1-ethyl-1-propyl-ethyl-3,1-methyl-3-ethyl-3-methylurea; 1-ethyl-1-propyl-3 propylurea; tetrabutylurea; and 1,1-dimethyl-3,3-diethylurea. Preferably the urea derivative is a tetraalkyl urea having from 2 to 3 carbon atoms in each alkyl chain, tetraethyl urea being preferred.

The dyeing compositions of this invention contain a dye of low water solubility which also has some solubility in the solvent (such as a dye from the various classes of dyes mentioned hereinabove which are suitable for this invention), water and the alkyl urea solvent. Additionally the compositions can contain conventional dye additives such as thickeners, detergents, etc.

The quantity of the various ingredients in the dyeing composition can vary over a wide range. Illustratively the quantity of the urea derivative can preferably vary from about 0.1% to about 10% and particularly from about 1% to about 5% by weight of the dyeing composition. The dye can vary over a wide range such as that from about 0.001% to 5% and preferably from about 0.01% to about 2% by weight of the composition. The compositions are aqueous since they contain some water. The quantity of water is not critical and can vary over a wide range such as that from about 30%–99%, and particularly from 75% to 99% based on the weight of the composition. Preferably water is the major ingredient of the composition e.g., the composition contains at least 50% of water.

The dyeing compositions of this invention can be formulated in conventional forms such as solutions, gels, pastes, emulsions, dispersions, and the like, and can be prepared by the conventional methods used in the dyeing art. Thus they can be prepared by dissolving or dispersing the dye in the urea derivative and adding this mixture to the water. Also, all the ingredients can be mixed simultaneously. A conventional blender or dispersing apparatus can be employed in order to facilitate solution or dispersion.

The dyeing compositions can be applied to polyamide fibers by the conventional techniques known in the art. Illustratively when applied to living hair on the human head, they can be applied to the hair with a brush, sponge, or other means of contact until the hair is properly dyed. The reaction time or time of contact of the dyeing composition with the polyamide fibers is not critical and can vary over the wide range used in the dyeing art such as periods of about 5 minutes to two hours or more, and preferably from about 10 to 60 minutes when used for dyeing living human hair. As mentioned hereinabove the dyeing on live hair is preferably effected at temperatures below 40° C. such as those from 15° C. to 40° C. and preferably at ambient room temperatures such as those of about 20° C. to 35° C.

The Colour Index (C.I.) designations as given herein are conventional in the art for designating a dye and the structural formula of the dye. Reference to the Colour Index (C.I.) can be found in Colour Index, Second Edition (1956) which is published by the Society of Dyers and Colourists and The American Association of Textile Chemists and Colorists. The percent values given herein for the quantities of the various ingredients are on a weight basis.

Example 1

A homogeneous paste is prepared containing 0.2 g. of the dye, C.I. Disperse Violet 4 (C.I. 61105) which is 1-amino-4-methylamino-anthraquinone, 3 g. tetraethylurea, 0.1 g. citric acid, and 4 g. carboxymethylcellulose, as a thickening agent, in 100 ml. water. The pH is adjusted to 3.5 with an additional small quantity of citric acid. The paste is poured on living normal gray hair on the human head and dyeing is allowed to proceed for 20 minutes at room temperature. The hair is then shampooed, rinsed and dried. The hair shows a strong, level violet color which is fast to rubbing and shampooing. When a similar experiment is performed, except that the tetraethylurea is omitted, the hair shows no uptake of dye. The above procedure and composition can be used with bleached hair and permanent-waved hair in place of normal gray hair, and the effect of adding tetraethylurea (as against the blank control) is even more pronounced with respect to the strength of dyeing observed.

Example 2

The procedure of Example 1 is followed, except that in place of the dye of that example, there is used 0.2 g. of the ammonium salt of the 2:1, dye-to-metal, chromium complex, of the dye obtained by coupling 3-amino-4-hydroxyphenyl methyl sulfone diazo to N-carbomethoxy-8-amino-2-naphthol. Normal gray hair, permanent-waved hair and bleached hair are all dyed a uniform medium silver shade when the dyeing is performed in the presence of tetraethylurea. In the absence of tetraethylurea, there is obtained only a faint tint to a very weak dyeing.

Example 3

A paste is prepared from 0.1 g. of the dye which is the mixed sodium-ammonium salt of the 2:1 chromium complex of the azo compound obtained by coupling 2-aminophenol-4-sulfonamide diazo to p-cresol, and containing 2.5 g. tetraethylurea, 4 g. methylcellulose, enough water to bring the volume to 100 ml., and enough tartaric acid to bring the pH to 3. When this dyeing composition is applied to normal gray hair, permanent-waved hair, or bleached hair, and allowed to impregnate the hair for 20 minutes at room temperature, all of the hair is dyed in strong level shades of brown, fast to rubbing and shampooing. A similar experiment with the omission of the tetraethylurea shows no dyeing of the normal gray hair, and weak tints on the other hair.

If in place of the dye of the above paragraph there is used a salt of the 1:2 chromium complex of the azo coupling product obtained from 2-aminophenol-4-sulfonamide diazo and 1-p-tolyl-3-methyl-5-pyrazolone, there is observed a strong orange dyeing of the hair.

Example 4

The procedure of Example 1 is followed, except that in place of the 3 g. of tetraethylurea of that example, there is used 1 g. tetrapropylurea. A strong violet dyeing of gray hair is obtained which is fast to rubbing and washing. Similar results are obtained by using 1 g. of 1,1-diethyl-3,3-dipropylurea in place of the tetrapropylurea.

Example 5

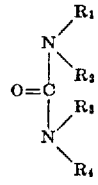
A paste consisting of 0.2 g. of the dye, C.I. Disperse Orange 5 (C.I. 11100), which is the azo dye obtained by coupling diazotized 2,6 - dichloro - 4 - nitroaniline onto N-phenyl-N-methylethanolamine, 3 g. tetraethylurea and 4 g. methylcellulose, made up to 100 ml. with water, and having a pH of 6.5 is poured on human gray hair and allowed to remain on the hair for 20 minutes at room

temperature. The hair is shampooed, rinsed and dried, and shows a strong orange coloration, very much stronger than similar hair dyed in the absence of tetraethylurea. Substitution, as the dye component, of C.I. Disperse Blue 7 (C.I. 62500), or C.I. Disperse Red 17 (C.I. 11210) for the C.I. Disperse Orange 5 in the composition and process of this example produces the corresponding shades on gray hair in high strength when tetraethylurea is present in the dye bath.

It is to be understood that the foregoing examples are intended only to illustrate the invention. The invention can be practiced broadly within the description set forth hereinabove, and it is to be understood that any modifications or equivalents that would occur to one skilled in the art are to be considered as lying within the scope of this invention.

What is claimed is:

1. An aqueous dyeing composition containing: (a) from about 0.1% to 10% of a urea derivative having a melting point less than 40° C. and having the formula:



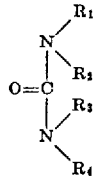
wherein R_1, R_2, R_3 and R_4 are alkyl having from 1 to 5 carbon atoms; and (b) from about 0.001% to about 5% of an organic dye of low water solubility selected from the group consisting of a disperse dye, and neutral dyeing metallized azo dye.

2. The dyeing composition of claim 1 wherein the dye is a disperse dye.

3. The dyeing composition of claim 1 wherein the dye is a neutral dyeing metallized azo dye and the composition has a pH of about 3 to 6.

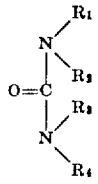
4. The dyeing composition of claim 1 wherein each of R_1, R_2, R_3, and R_4 is alkyl having from 2 to 3 carbon atoms.

5. A method for dyeing living human hair on the head which comprises applying thereto an aqueous dyeing composition containing: (a) a urea derivative having a melting point less than 40° C. and having the formula:



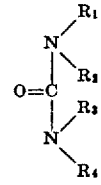
wherein R_1, R_2, R_3 and R_4 are alkyl having from 1 to 5 carbon atoms; and (b) an organic dye of low water solubility selected from the group consisting of a disperse dye, and a neutral dyeing metallized azo dye.

6. A method for dyeing living human hair on the head which comprises applying thereto at a temperature below 40° C. an aqueous dyeing composition containing: (a) a urea derivative having a melting point less than 40° C. and having the formula:



wherein R_1, R_2, R_3 and R_4 are alkyl having from 1 to 5 carbon atoms; and (b) an organic dye of low water solubility selected from the group consisting of a disperse dye, and a neutral dyeing metallized azo dye, said urea derivative being a solvent for said dye.

7. A method for dyeing living human hair on the head which comprises applying thereto at a temperature below 40° C. an aqueous dyeing composition containing: (a) a urea derivative having a melting point less than 40° C. and having the formula:

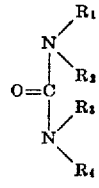


wherein R_1, R_2, R_3 and R_4 are alkyl having from 1 to 5 carbon atoms; and (b) a low water-soluble disperse dye; said composition containing at least 50% of water and said urea derivative being a solvent for said dye.

8. The method of claim 7 wherein each of R_1, R_2, R_3, and R_4 of the urea derivative is alkyl having from 2 to 3 carbon atoms.

9. The method of claim 8 wherein R_1, R_2, R_3 and R_4 are ethyl.

10. A method for dyeing living human hair on the head which comprises applying thereto at a temperature below 40° C. an aqueous dyeing composition containing: (a) a urea derivative having a melting point less than 40° C. and having the formula:



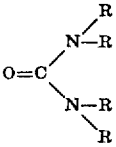
wherein R_1, R_2, R_3 and R_4 are alkyl having from 1 to 5 carbon atoms; and (b) a low water-soluble neutral dyeing metallized azo dye; said composition containing at least 50% of water and said urea derivative being a solvent for said dye.

11. The method of claim 10 wherein each of R_1, R_2, R_3, and R_4 of the urea derivative is alkyl having from 2 to 3 carbon atoms and the composition has a pH of about 3 to 6.

12. The method of claim 11 wherein the urea derivative is tetraethylurea.

13. A composition according to claim 1 wherein said urea derivative is tetraethylurea.

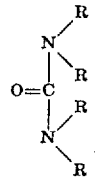
14. An aqueous dyeing composition containing (a) from 0.1% to 10% of a tetraalkylurea derivative having a melting point less than 40° C. and a water solubility of less than about 10% at 25° C. and having the formula:



wherein R is alkyl having from 1 to 5 carbon atoms and (b) from .001% to 5% of a low water soluble organic dye having a solubility in water of less than about .5% at 25° C. and selected from the group consisting of disperse dyes and neutral dyeing metallized azo dye, said tetraalkylurea derivative being a solvent for said dye.

15. A method for dyeing living human hair on the head which comprises applying thereto an aqueous dyeing composition containing (a) a tetraalkylurea derivative having

a melting point less than 40° C. and a water solubility of less than 10% at 25° C. and having the formula:



wherein R is alkyl having from 1 to 5 carbon atoms and (b) a low water soluble organic dye having a solubility in water of less than about .5% at 25° C. and selected from the group consisting of disperse dyes and neutral dyeing metallized azo dye, said tetraalkylurea derivative being a solvent for said dye.

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2,163,043	6/39	Kritchevsky	167—88
2,551,056	5/51	Schetty	260—149
3,098,013	7/63	Austin et al.	167—88

OTHER REFERENCES

Colour Index, 2nd Ed., vol. I, The Society of Dyers and Colourists, and The American Association of Textile Chemists and Colourists, Lowell, Mass. (1956), pp. 1655–1656, 1679, 1684, 1695, 1706, and 1716.

JULIAN S. LEVITT, *Primary Examiner.*

LEWIS GOTTS, *Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

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Hans Z. Lecher et al.

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

Column 3, lines 16 to 18, strike out "1-ethyl-1-propyl-ethyl-3,1 methyl-3-ethyl-3-methylurea; 1-ethyl-1-propyl-3 propylurea" and insert instead -- 1-ethyl-1-propyl-3-ethyl-3-propylurea --.

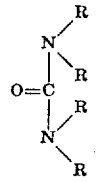
Signed and sealed this 19th day of April 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents

a melting point less than 40° C. and a water solubility of less than 10% at 25° C. and having the formula:



wherein R is alkyl having from 1 to 5 carbon atoms and (b) a low water soluble organic dye having a solubility in water of less than about .5% at 25° C. and selected from the group consisting of disperse dyes and neutral dyeing metallized azo dye, said tetraalkylurea derivative being a solvent for said dye.

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