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COLORATION OF MATERIALS COMPRISING CELLULOSE DERIVATIVES

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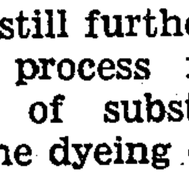
This invention relates to the dyeing, printing, or stencilling of artificial threads, yarns, fabrics, films or other products made with or containing cellulose acetate or other organic esters of cellulose or made with or containing cellulose ethers. This invention relates more particularly to the dispersion of relatively water insoluble coloring matter or dyes.

It is an object of this invention to produce superior dispersions of substantially insoluble coloring matters and organic compounds. A further object is to devise a process whereby cellulose derivatives may be colored readily and efficiently. A still further object is to produce a more satisfactory process for imparting substantially insoluble coloring materials and organic compounds to textile materials containing cellulose derivatives, and in particular containing cellulose ethers or esters. A still further object is to provide an improved process for producing an aqueous dispersion of substantially insoluble dyes to be used in the dyeing of cellulose acetate textile materials.

These objects are attained according to the herein described invention wherein cellulose derivatives are colored by treating with a dispersion of a substantially insoluble coloring material or organic compound and a compound which upon dissociation gives a positively charged surface active ion. In a more restricted sense it pertains to the coloring of textile materials containing a cellulose derivative by immersion in an aqueous dispersion of a substantially insoluble dye and a compound which upon dissociation gives a positively charged surface active ion, in particular a quaternary ammonium, quaternary phosphonium, or tertiary sulfonium compound containing at least 10 carbon atoms. In its preferred embodiment this invention pertains to the coloring of cellulose acetate textiles by immersing said textiles in an aqueous dispersion of a substantially insoluble dye and a quaternary ammonium derivative having the following general formula:

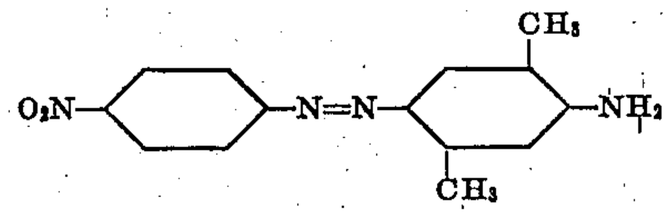


wherein R_1 represents a hydrocarbon radical of at least 6 carbon atoms, R_2, R_3 and R_4 represent hydrocarbon radicals which may be externally joined to form a heterocyclic ring, and X represents an anion usually possessing practically negligible surface active properties.

The invention may be more readily understood by a consideration of the following illustrative examples in which the quantities are stated in parts by weight:

Example 1

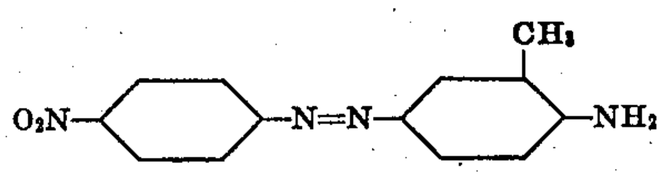
One part of the combination: p-nitro-aniline→xylidine having the following formula:



is dispersed (apparently dissolved) by stirring in 100 parts of a 10% water solution of cetyl trimethyl ammonium bromide heated to the boiling point. Boiling water is then added to make the liquor to a total of 30,000 parts. The dyebath is raised to 40–50° C. and 100 parts of cellulose acetate silk yarn in hank form are entered, the dyeing temperature being raised to 65–75° C. during half an hour and maintained at that temperature for one hour. The goods dyed an orange shade are lifted, rinsed and dried or otherwise finished as desired.

Example 2

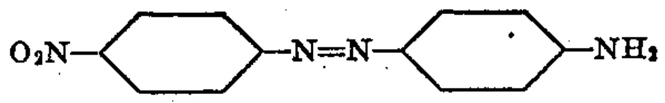
One part of the combination: p-nitro-aniline→toluidine having the following formula:



is pasted with one part of hexadecyl betaine and one part of water. The paste is diluted with 200 parts of boiling water and added, through a sieve if necessary, to 2500 parts of cold water. 100 parts of cellulose acetate silk are entered at about 60° C. and the temperature slowly raised to 75° C. and the dyeing being continued until the requisite shade of orange is obtained. The goods are then rinsed and dried.

Example 3

5 parts of the combination: p-nitro-aniline→aniline having the following formula:



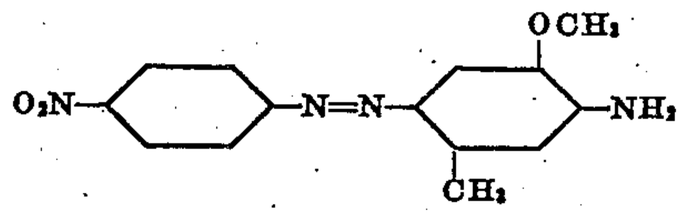
are ground with 1 part of cetyl trimethyl ammonium bromide. This mixture is pasted with 1 part of water and then 3000 parts of water are added. The dyeing of the cellulose acetate (100 parts) is carried out in the usual manner. An orange shade is obtained.

Example 4

One part of a 50% paste of the combination: 4'-nitro-2'-methoxy-4-(dimethylamino) azo benzene is pasted with one part of cetyl pyridinium bromide. 3000 parts of warm water are added and the dye bath heated to 60° C. 200 parts of cellulose acetate silk are dyed a red shade.

Example 5

2 parts of the combination: p-nitro-aniline→ cresidine having the following formula:



is ground with 1 part of N-stenyl betaine. This mixture is pasted with 1 part of water and then diluted with 3000 parts water. When the bath is raised to 60° C. 200 parts of cellulose acetate silk in hank form are entered and dyed in the customary manner to obtain a scarlet shade.

Example 6

One part of 1,4-diamino anthraquinone is milled with 1 part of cetyl trimethyl ammonium bromide. This mixture is pasted with 5 parts of water and then 3000 parts of water are added. 300 parts of cellulose acetate are dyed a violet shade.

Example 7

One part of 1,4,5,8-tetra amino anthraquinone is treated in the same manner as Example 6. 300 parts of cellulose acetate are dyed a blue shade.

Exdmple 8

2 parts of amino azo toluene are milled with 1 part of cetyl trimethyl ammonium bromide and 14 parts of dextrin. This mixture is pasted with 10 parts of water and then diluted to 6000 parts with water. 200 parts of cellulose acetate are dyed a bright yellow shade.

Example 9

40 parts of dianisidine, 9 parts of dextrin and 1 part of cetyl trimethyl ammonium bromide are milled together and then warmed to 60° C. with 450 parts of water. One part of this mixture, diluted with 500 parts of water is suitable for the treatment of 200 parts of cellulose acetate to be followed by development methods.

It is to be understood that the aforementioned examples are illustrative merely of a few of the many processes of carrying into practical operation the present invention. The materials treated, the treating agents, the dispersing agents, the proportions of the various agents and the conditions of treatment may be varied within wide limits without departing from the scope hereof.

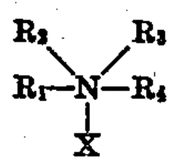
In place of cellulose acetate silk other fibers composed of cellulose derivatives may be selected. For example, cellulose esters and ethers and cellulose derivatives generally such as cellulose propionate, cellulose butyrate, benzyl cellulose, amino cellulose and the numerous cellulose derivatives heretofore used in place of or in combination with cellulose acetate are contemplated. These cellulose derivatives may be in the form of artificial threads, yarns, fabrics, films, and the like. They may be used alone, in conjunction with one another, and/or in combination with natural silk, cotton, wool and the various materials with which cellulose acetate and related substances are combined in the industrial arts.

Organic compounds or coloring materials which are contemplated herein are understood to include those organic compounds and coloring materials which have been used or are capable of use in the treatment of the aforementioned cellulose derivatives or products containing such cellulose derivatives. These materials are ordinarily either dyes or dye intermediates. They are insoluble or practically insoluble in water, and are referred to in the present description and claims as substantially insoluble. In their practical application they may be used for dyeing, printing or stenciling of the materials comprised herein. In general, dyes or dye intermediates for the coloring of cellulose acetate silk are preferred. A few representative classes of materials from this group are: substantially insoluble azo dyes, such as diazotized nitro amines coupled with amines, N-dialkylamines, N-alkyl-(hydroxy-alkyl)-amines, N-di-(hydroxy-alkyl)-amines and the reduction products of such combinations; basic derivatives of the anthraquinone series, such as amino-anthraquinones, aminohydroxy-anthraquinones, or their derivatives such as 1-hydroxy-4-para-tolylamino-anthraquinone, and the like; nitro-diphenylamine derivatives; simple amino bases for use in the production of azo dyes such as dianisidine, etc. It is, of course, to be understood that the aforementioned dyes and intermediates are illustrative merely of the compounds which are to be used in the treatment of cellulose derivatives as defined herein. Other compounds related thereto or widely differing therefrom but which are capable of use in this connection are also contemplated.

The aforementioned dyes, intermediates and related materials may be dispersed by mixing them in finely divided form with the dispersing agent or agents described herein. Mixing may be accomplished in the dry phase or before drying. The mixture may be heated under atmospheric pressure or under either superatmospheric or subatmospheric pressure, in the presence or absence of water. Where the coloring agents are azo dyes, they may be coupled in the presence of a dispersing agent or mixture thereof and the resulting mixture subsequently dried. Moreover, the dye may be dissolved in a solvent and the resulting solution poured into an aqueous solution of the dispersing agent or mixture thereof. This aqueous solution may or may not contain protective colloids. The substantially insoluble dye may be treated with a combination of the dispersing agent and an auxiliary solvent. The dispersed modification of the coloring material may be utilized for the dyeing of cellulose derivatives generally and cellulose acetate in particular by simply treating such dispersed modification with hot or cold water, filtering or pouring into the dye bath, which bath may be acid, neutral or alkaline, and conducting the dyeing in the customary manner.

Dispersing agents contemplated herein are those compounds which upon dissociation give a positively charged surface active ion. Compounds which are particularly adapted for this purpose are quaternary ammonium, quaternary phosphonium, and tertiary sulfonium compounds containing a positively charged surface active ion. Those compounds are preferable which contain at least 10 carbon atoms. Where the aforementioned or related compounds contain a hydrocarbon chain of at least 6 carbon atoms, and preferably from 12 to 18 carbon atoms, they have been found to be quite satisfactory. In the case

of the quaternary ammonium compounds, they may be represented by the following general formula:



wherein R_1 represents a hydrocarbon radical of at least 6 carbon atoms, R_2, R_3 and R_4 represent hydrocarbon radicals which may be externally joined to form a heterocyclic ring, and X represents an anion possessing practically negligible surface active properties. In the above formula X is preferably chlorine or bromine; R_1 is preferably an aliphatic hydrocarbon radical containing at least 6 carbon atoms and in particular a straight chain aliphatic hydrocarbon radical containing from 12 to 18 carbon atoms; R_2, R_3 and R_4 are preferably hydrocarbon radicals of open chain or cyclic derivation, for example, R_2, R_3 and R_4 may represent methyl or ethyl groups or their higher homologues, or they may be externally joined to form a heterocyclic ring in which the nitrogen nucleus is a hetero atom. The aforementioned heterocyclic ring may represent pyridine, quinoline, isoquinoline, partially or completely reduced quinoline, piperidine, morpholine, and the like. Where R_1, R_2, R_3 or R_4 contains a salt forming group such as the carboxylic acid or sulfonic acid group it is contemplated that inner salts analogous to the betaine type may be produced therefrom, for instance by treatment with an alkali. Compounds of the betaine type are described in considerable detail in a copending application, Serial No. 13,664, filed by Downing and Johnson of even date herewith. The instructions of said application when modified in accordance with the present invention are to be considered as a part hereof in the same manner as if they were incorporated herein.

In place of the above described quaternary ammonium compounds or in addition thereto quaternary phosphonium compounds may be used.

A few of the many compounds which are contemplated for use herein as dispersing agents will now be given. These compounds are principally quaternary ammonium compounds and tertiary sulfonium compounds. However, attention is called to the fact that several of the compounds contain hydrogen in place of the alkyl groups of a quaternary ammonium compound.

Cetyl trimethyl ammonium bromide
Octadecyl trimethyl ammonium chloride
Distearyl dimethyl ammonium bromide
Cetyl pyridinium bromide
Hexadecyl betaine (from alpha halogenated stearic acid+trimethylamine)
N-stearyl alpha betaine (from stearyl dimethylamine+chloracetic acid)
N-dimethyl stearyl alanine
Octadecyl cyclohexyl dimethyl ammonium bromide
Condensation product of 2 moles of stearyl dimethyl-amine+1 mole of 1,3-dichloro propanol-2
N-lauryl alpha betaine
N-stearyl methyl alpha betaine
N-stearyl beta betaine sulfate (inner salt of N-stearyl choline sulfate)
N-lauryl beta betaine sulfate (inner salt of N-lauryl choline sulfate)
N-stearyl beta betaine
N-stearyl beta hydroxy gamma betaine sulfonate
N-stearyl beta hydroxy gamma betaine sulfate
Cetyl trimethyl ammonium chloride
Beta diethyl amino ethyl oleyl amide acetate
Beta diethyl amino ethyl oleyl amide hydrochloride
Trimethyl ammonium methyl sulfate of amino oleyl ethylene diamine
Trimethyl eicosyl ammonium iodide
Octadecyl pyridinium bromide
Trimethyl dodecyl ammonium bromide
Trimethyl dodecyl ammonium iodide
Octadecyl beta hydroxyethyl morpholinium bromide
Cetyl beta hydroxyethyl morpholinium bromide
Triethyl octadecyl ammonium bromide
Triethyl cetyl ammonium bromide
Stearamido phenyl trimethyl ammonium methyl sulfate
Octadecyl pyridinium chloride
Octadecyl pyridinium iodide
Octadecyl alpha picolinium bromide
Octadecyl quinolinium bromide
Dodecyl pyridinium bromide
Heptadecylamine hydrochloride
Hexadecylamine hydrochloride
Dodecylamine hydrochloride
Octadecyl diethyl amine hydrochloride
Methyl butyl hexadecyl sulfonium chloride
Methyl butyl hexadecyl sulfonium methyl sulfate
Methyl benzyl hexadecyl sulfonium chloride
Methyl cyclohexyl hexadecyl sulfonium chloride
Benzothiazole - 2 - cetyl methyl sulfonium methyl sulfate
4-Methyl benzothiazole-2-cetyl methyl sulfonium methyl sulfate
Para cetyl phenyl dimethyl sulfonium methyl sulfate
Hexadecyl trimethyl phosphonium chloride

The aforementioned dispersing agents may be used either alone or in admixture with one another. They may also be used in admixture with prior art wetting, detergent, emulsifying and dispersing agents or assistants therefor. In this connection it may be stated that since the dispersing agents referred to herein are capable of dissociating into positively charged surface active ions it is in general advisable to mix therewith only compounds which are likewise capable of dissociating with the production of positively charged surface active ions.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

We claim:

1. A process for coloring materials comprising organic substitution derivatives of cellulose which comprises applying thereto a substantially insoluble coloring compound capable of coloring cellulose acetate in the form of an aqueous dispersion obtained with the aid of a surface active compound selected from the group consisting of ammonium, sulfonium, and phosphonium compounds which contain a positively charged ion that contains an aliphatic hydrocarbon group having at least six carbon atoms.

2. A process for coloring materials comprising cellulose acetate which comprises applying thereto a substantially insoluble coloring compound

capable of coloring cellulose acetate in the form of an aqueous dispersion obtained with the aid of a surface active compound selected from the group consisting of ammonium, sulfonium, and phosphonium compounds which contain a positively charged ion that contains an aliphatic hydrocarbon group having at least six carbon atoms.

3. A composition of matter applicable for the dyeing of cellulose acetate comprising a substantially insoluble coloring compound capable of coloring cellulose acetate and a surface active compound selected from the group consisting of ammonium, sulfonium, and phosphonium compounds which contain a positively charged ion that contains an aliphatic hydrocarbon group having at least six carbon atoms, said surface active compound being present in such a proportion that said composition of matter can be dispersed in water.

4. A process for the dyeing of materials comprising cellulose acetate which comprises treating said materials with an aqueous dispersion of a substantially insoluble dye capable of coloring cellulose acetate, said dispersion having been obtained with the aid of a surface active compound selected from the group consisting of ammonium, sulfonium, and phosphonium compounds which contain a positively charged ion that contains an aliphatic hydrocarbon group having from twelve to eighteen carbon atoms.

5. A composition of matter applicable for the dyeing of cellulose acetate comprising a substantially insoluble dye capable of coloring cellulose acetate and a surface active compound selected from the group consisting of ammonium, sulfonium, and phosphonium compounds which contain a positively charged ion that contains an aliphatic hydrocarbon group having from twelve to eighteen carbon atoms, said surface active compound being present in such a proportion that said composition of matter can be dispersed in water.

6. A process for the dyeing of textile materials comprising cellulose acetate which comprises applying thereto an aqueous dispersion of a relatively water-insoluble organic compound capable of coloring cellulose acetate wherein the dispersing agent is solely a quarternary ammonium compound, the positive ion of which contains a straight chain aliphatic hydrocarbon group having from twelve to eighteen carbon atoms.

7. A dyeing preparation containing no protective colloid comprising a relatively water-insoluble organic compound capable of coloring cellulose acetate and a quaternary ammonium compound, the positive ion of which contains a straight chain alkyl group having from twelve to eighteen carbon atoms, said quarternary ammonium compound being present in such a proportion that said dyeing preparation is dispersible in water.

8. A process of dyeing textile materials comprising cellulose acetate which comprises applying thereto a relatively water insoluble organic compound capable of coloring cellulose acetate in the form of an aqueous dispersion prepared by using a tetra-alkyl ammonium halide containing one alkyl group having from twelve to eighteen carbon atoms in a straight chain as the dispersing agent.

9. A dyeing preparation which is dispersible in water comprising a relatively water-insoluble organic compound capable of coloring cellulose acetate and a tetra-alkyl ammonium halide in which one of the alkyl groups contains from twelve to eighteen carbon atoms in a straight chain.

10. A process of dyeing textile materials comprising cellulose acetate which comprises applying thereto an aqueous dispersion of a substantially water-insoluble organic compound capable of coloring cellulose acetate, said dispersion having been prepared by using as a dispersing agent an alkyl pyridinium halide wherein the alkyl group contains a straight chain having from twelve to eighteen carbon atoms.

11. A process for the coloration of textile materials comprising cellulose acetate which comprises applying thereto a relatively insoluble coloring compound capable of coloring cellulose acetate in the form of an aqueous dispersion obtained with the aid of a betaine which contains as one of its substituents an alkyl group having a straight chain containing from twelve to eighteen carbon atoms.

12. A dyeing preparation which is dispersible in water and useful in connection with the dyeing of cellulose acetate comprising a substantially water-insoluble organic compound capable of coloring cellulose acetate and a betaine which contains as one of its substituents an alkyl group having a straight chain containing from twelve to eighteen carbon atoms.

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