

UNITED STATES PATENT OFFICE

2,310,074

TREATMENT BATH

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No Drawing. Application May 4, 1939, Serial No.
271,712. In Germany May 5, 1938

9 Claims. (Cl. 8—54)

This invention relates to a method for preventing the dissipation or loss of strength of agents which are both anion active and capillary active in baths during their use for the treatment of various types of nitrogenous materials. It also relates to the treatment baths themselves containing anion active and capillary active agents which maintain their original efficiency throughout the period of treatment.

It is a known fact that the effectiveness of acid baths and neutral baths as ordinarily employed in the treatment of nitrogen-containing materials such as textiles, furs, fibrous materials and the like, which include agents which are both anion active and capillary active, decreases during the course of the treatment period unless the operator continually adds further quantities of such agents to the baths. This fact is easily verified by a consideration of the readily observed characteristic decrease in the foaming properties of these baths in the course of treatment. Closer examination of the treated materials has shown that a considerable portion of these anion and capillary active substances is absorbed by the materials treated, thereby decreasing the concentration of these substances in the baths to a point where their effectiveness is practically lost. This absorption results in needless interruption in the continuity of the process and in a dissipation of expensive raw materials and frequently without a compensatory improvement in the ultimate product.

It is a principal object of this invention to provide a method which stabilizes anion active and capillary active agents in treatment baths for nitrogen-containing materials. Another object of the invention is to provide treatment baths for nitrogen-containing materials the effectiveness of which does not diminish during use with respect to anion active and capillary active agents contained therein. Other objects of the invention will be apparent from the examples and specific illustrations hereinafter set out.

In accordance with the process of the present invention the absorption of anion active and capillary active substances is prevented by adding capillary active compounds which do not dissociate electrolytically in aqueous solutions, to such baths before or during the treatment of the nitrogenous materials. No loss of the anion active substances occurs through absorption by the nitrogenous materials being treated, and hence the effectiveness of the treatment baths is maintained throughout the treatment process. This invention, therefore, makes it possible to overcome

a disadvantage inherent in the prior compositions and processes.

The anion active and capillary active substances suitable for use in this invention, broadly considered, include all those capillary active substances which ionize negatively in aqueous solutions. In general, these anion active and capillary active compounds are characterized by having a lipophile group and a hydrophile group, and by having the general formula: $R.X.R'G$. In this formula, R represents any one of a number of types or organic radicals, but primarily higher molecular aliphatic, cyclo-aliphatic, mixed aliphatic aromatic or aliphatic hydro-aromatic hydrocarbon radicals; R' represents a divalent acyclic or cyclic hydrocarbon radical which may also contain hetero-atoms or hetero-atomic radicals, such as, oxygen, sulfur, nitrogen, halogen, hydroxyl, ether radicals, and the like; X represents a hetero-atom or a hetero-atomic group, such as, for instance, oxygen, sulfur, nitrogen, sulfonyl, carbonyl, ester, acid amide and like radicals, or X may be omitted; and G represents an acid radical, preferably an inorganic salt-forming acid radical capable of being later neutralized with a base to form water-soluble salts, examples of suitable acids being, for instance, the sulfuric acid ester radical, the sulfonic acid radical, the thio-sulfuric acid ester radical, the phosphoric acid ester radical, the pyro-phosphoric acid ester radical, the boric acid ester radical, and where the treatments are in neutral baths the carboxylic radical. Suitable salts are those formed, for instance, with an alkali metal, ammonia, or amine radical. Such substances include, for instance, water-soluble salts of higher molecular fatty alcohol sulfonates and of higher molecular sulfonic acids, and also water-soluble salts of the sulfonates of glycerine and poly-glycerine esters of ethers. Other such substances are water-soluble salts of taurine, taurine substituted on the nitrogen atom by higher molecular fatty acid groups, N-methyl taurine, and other amino alkyl sulfonic acids, as well as the water-soluble salts of isothionic acid and other hydroxy alkyl sulfonic acids esterified with higher molecular fatty acids.

Specific capillary active and anion active compounds suitable for use in the treatment baths of this invention and conforming to the aforementioned formula are dodecyl sulfuric acid ester, mixtures of sulfuric acid esters of fatty alcohols obtained by catalytic reduction from coconut oil, oleyl sulfuric acid ester, sulfuric acid ester of ethylene glycol mono-octyl ether, mono- or disulfuric acid esters of glycerine

monostearic acid ester, omega-butyl ether of decyl sulfuric acid ester, phosphoric acid esters of the pentanediol monoacetates, omega-hexyl thioethers of octyl thiosulfuric acid esters, N-butyl amino dodecyl sulfuric acid ester, sulfuric acid ester of beta-hydroxy, gamma-(sec. octyl-cresoxy) propanes, sec. octyl phenoxy ethane sulfuric acid ester, dodecoxy acetic acid, N-oleoyl methyl beta-amino ethane sulfonic acid, stearoyl beta-oxyethane sulfonic acid, N-cetyl sulfone sulfanilic acid, omega-cyclo hexyl ether of decane sulfonic acid, sec. octyl phenyl benzyl ether 4'-sulfonic acid, mixtures of isomeric 2-iso alkyl cresoxy benzoic acid sulfonic acids (5) (alkyl groups with 5-11 carbon atoms), 1-sec. octyl phenoxy benzene 2,4-disulfonic acid, 1-sec. hexyl phenoxy 2-(acetyl amino) benzene 4-sulfonic acid, the sulfuric reaction product of sec. octyl ortho-cresyl benzyl ether, sulfuric reaction product of the cresoxy acetic acid dodecyl amide and similar compounds, and the water-soluble salts of these compounds, as with alkali metals, ammonia, organic bases and the like.

Baths containing these anion active and capillary active substances may be used in known manner for the treatment of nitrogen-containing materials, such as textiles, furs, leathers, skins, hairs, especially living hair, feathers, and the like. For instance, wool, artificial wool, natural silk, nitrogen-containing cellulosic substances, and the like are treated in various forms, such as in the form of flakes, threads, ribbons, strands as well as in the form of spun and woven fabrics. Animal hides, leathers, skins, hairs, feathers, furs and their dressed products are likewise treated in such baths. These anion active and capillary active substances are used therein for various purposes including the generation of foam, or for emulsifying, dispersing, wetting, peptizing, stabilizing, equalizing, dividing, dissolving, or like purposes in processes involving washing, cleaning, dyeing, coloring, and the like. These anion active and capillary active agents may amount to from 0.01% to 20% of the bath but usually constitute from 0.05% to 3% of such baths.

The capillary active agents which are stable against electrolytic dissociation and which are suitable as stabilizing agents in the practice of the instant invention include such compounds, for instance, as polyethers, polyether alcohols and polyalcohols which in part are derived from higher molecular organic compounds, and higher molecular amino oxides.

Polyethers of higher molecular organic compounds of satisfactory structure are already known per se. Such compounds may be obtained by the action of alkylene oxides on higher molecular organic acyclic and cyclic compounds having at least one hydrogen atom in the molecule capable of reacting with the alkylene oxide whereby as many moles of alkylene oxide, as a rule at least 4 moles, are added as are required to make the condensation product water soluble. Compounds containing hydrogen atoms capable of reaction are, for instance, compounds with hydroxyl, mercapto, sulfine, amino, substituted amino, carboxyl and like radicals. Suitable alkylene oxides include such oxides as ethylene oxide, propylene oxide and the like. Similar products can be produced by forming addition products with several moles of glycols, for instance, ethylene glycol, propylene glycol and the like.

Polyether compounds of the type described as

useful in the practice of the invention are, for instance, the condensation products from one mole of octanol, decanol or dodecanol and about 8 to 15 moles of ethylene oxide, or from one mole of cetyl alcohol and about 15 moles of ethylene oxide, or from one mole of octadecyl alcohol and about 15 to 20 moles of ethylene oxide and the like. Suitable polyether condensation products also include condensation products of alkylated and cyclo-alkylated aromatic and hydro-aromatic compounds, such as, for instance, isopropyl phenol, di- or tri-iso butyl phenol, sec. octyl cresol, di-hydroxy-di-phenyl methane, alpha alpha-bis-(hydroxy-phenyl) beta-ethyl hexane, and the like or their corresponding hydrogenation product with about 10 or more moles of ethylene oxide per hydroxyl group.

Polyether alcohols of higher molecular organic compounds suitable for addition to the treatment baths of this invention are also known per se and include the water-soluble condensation products of polyglycerine, and the like, with higher molecular organic compounds, such as fatty acids; mineral acid esters of higher molecular alcohols and the like. Similar products are likewise obtained by the reaction of glycidide with higher molecular hydrocarbons having at least one hydrogen atom capable of reaction with glycidide, such as, for instance, higher molecular hydroxyl-, mercapto-, and amino-compounds and the like. Polyether alcohols of this nature are, for instance, octyl polyglycerine ether, dodecyl polyglycerine ether, palmitic acid polyglycerine ester, oleic acid polyglycerine ester, the condensation product obtained from one mole of stearic acid amide and 10 moles of glycidide and the like.

Polyalcohol condensation products derived from higher molecular organic compounds and used in the treatment baths of this invention are known per se and include the condensation products of higher molecular acyclic and cyclic hydroxyl, carboxyl, amino and like compounds with polyalcohols; such as, for instance, the lauric acid and ricinoleic acid esters of the sorbites, dulcites or mannites, the higher molecular alkyl or alkyl aryl ethers of these polyalcohols; the hydrogenated condensation products of higher molecular amines with glucose, mannose, fructose and the like, such as, for instance, octyl glucamine, dodecyl glucamine, and the like.

Certain higher molecular water-soluble amino oxides have utility in the treatment baths of the invention because they likewise do not dissociate electrolytically in aqueous solutions. They include, for instance, oxides of dodecyl dimethyl amine, dodecyl di-ethyl amine, dodecyl pyridine, lauryl di-ethyl ethylene di-amine and the like.

The surface active compounds mentioned heretofore as being stable against electrolytic dissociation in aqueous solutions may be applied in the baths in various quantities but usually vary from 0.1% to 150%, and preferably from 5% to 50% of the quantity of the anion active and capillary active substances present in the baths.

The combination of these anion active and capillary active agents with the capillary active agents which are stable against electrolytic dissociation do not in any way interfere with the action of other customary addition agents usually found in such treatment baths. For instance, if the baths are to be acid in reaction, there

may be added formic acid, lactic acid, sulfuric acid, or the like, or instead acids of inorganic and organic salts, such as, sodium bisulfate, alum, potassium acid tartrate and the like may be added to give the baths this desirable property.

The following examples are included as illustrations of the methods and the treatment baths used in the practice of the instant invention, but it is to be understood that their specific embodiments are not to be considered as limitations upon the scope of the invention.

Example 1

Dyed woollens are washed at 50° C. in a warm washing bath having a material to bath ratio of 1:50 and containing acetic acid to prevent bleeding out of the dye and also containing per liter, as a foaming, wetting and cleaning agent, 2.5 grams of the sodium salt of a commercial sulfuric acid ester mixture derived from coconut oil fatty alcohols and as a capillary active agent stable against hydrolytic dissociation 1.5 grams of the condensation product obtained from one mole of a commercial mixture of octadecyl and hexadecyl alcohol with about 15 moles of ethylene oxide. Analytical tests and an observation of foaming characteristics of the bath proves that the sodium salt of the mixture of the coconut oil fatty alcohol sulfuric acid esters remained in the bath and was not taken up by the fibers.

If the capillary active agent stable against hydrolytic dissociation is not added as the washing process progresses the bath loses its foaming capacity and thereby part of its effectiveness because the sulfuric acid ester salt is absorbed by the wool.

Example 2

A dye bath for woolen yarns is prepared in a dye vat containing 4% of a slightly equalizing acid wool dye, such as, for instance, acid-fast blue B having the Schultz No. 825, 12% crystallized Glauber's salt, 3% sulfuric acid (66° Bé.), calculated on the material to be dyed and as a wetting and equalizing agent 2 grams of the sodium salt of lauryl sulfuric acid ester per liter of dye liquor. One gram of a perhydrogenated condensation product obtained from a mixture of isomeric sec. alkyl cresols (obtained from condensation of cresol with olefines from benzine synthesis) and about 16 to 17 moles ethylene oxide is added to the dye bath before the dyeing operation. The material to be dyed is introduced at 50° C. (material to bath ratio of 1:40) and the temperature is raised to boiling, whereupon the dyeing is complete. The sodium salt of the sulfuric acid ester of lauryl alcohol remains almost completely intact in the bath upon completion of the dyeing process. It is not necessary to add a portion of this agent when introducing new materials into the freshened dye bath.

In such baths as those just described, the absence of the perhydrogenated ethylene oxide alkyl cresol condensation product or similar products results not only in the absorption of the dye but almost all of the sodium salt of sulfuric acid ester of lauryl alcohol is absorbed by the wool fiber likewise. When replenishing the dye substance in the mother liquor under such circumstances, it is always necessary to add also the sodium salt of the sulfuric acid ester of lauryl alcohol.

Example 3

As in Example 2, woolen yarns are dyed in a bath containing 12% Glauber's salt, 4% acetic acid of 30% strength, 6% Supramine brown (a material to bath ratio of 1:40), and 2 grams of the sodium salt of the N-oleyl methyl beta-amino ethane sulfonic acid per liter of dye liquor as a wetting and equalizing agent. The Schultz number of Supramine brown is not known but the dyestuff is described in Schultz, Farbstofftabellen, Ergänzungsband I (1934), page 135. In order to prevent the wetting and equalizing agent from being almost completely absorbed by the goods in the first batch treatment, there is added 1.2 grams of the condensation product of a mixture of di- and tri-iso-butyl cresol and about 12 moles of ethylene oxide for every liter of the dye liquor.

It should be understood that the present invention is not limited to the specific materials, compositions and processes herein disclosed but that it extends to all equivalents which one skilled in the art would consider within the general purport of the instant disclosure as limited only by the tenor of the specification and the requirements of the appended claims.

I claim:

1. In the treatment of nitrogen-containing fibrous materials with acid-reacting baths containing anion active saponaceous substances composed of a lipophilic group of at least 6 carbon atoms and a hydrophilic inorganic salt-forming acid radical neutralized with a base of the group consisting of alkalies, ammonia and inorganic bases wherein the nitrogen-containing fibrous materials absorb substantial quantities of said saponaceous substances, the step which comprises applying said baths to said materials in the presence of an organic water-soluble surface active agent which is electro-neutral in aqueous solutions in an amount ranging from about 5% to about 50% of the quantity of said anion active substance, said amount substantially completely preventing the absorption of said anion active substance by said fibrous materials.

2. An acid aqueous treating bath for nitrogen containing fibrous materials containing an anion active and capillary active sulfonated aliphatic alcohol and an organic water-soluble surface-active substance which is electro-neutral in aqueous solutions in an amount which substantially completely prevents the absorption of said sulfonated alcohol by said fibrous materials, said amount ranging from about 5% to about 50% of the quantity of said sulfonated alcohol.

3. The process of stabilizing the effectiveness of organic treating agents which are both anion active and capillary active and are composed of a lipophilic group of at least 6 carbon atoms and a hydrophilic inorganic salt-forming acid radical in acidic treatment baths for nitrogen-containing fibrous materials which absorb said anion active treating agents comprising adding to such baths organic water-soluble capillary active substances which are stable against electrolytic dissociation in aqueous solutions in an amount which substantially completely prevents the absorption of said anion active agents by said fibrous materials, said amount ranging from about 5% to about 50% of the anion active substances.

4. In the treatment of a nitrogen-containing fibrous material with an acidic bath containing a water-soluble salt of an organic treating agent which is both anion active and capillary active and is composed of a lipophilic group of at least

six carbon atoms and a hydrophilic inorganic salt-forming acid group, the step which comprises applying said bath to the fibrous material in the presence of a capillary active agent which is stable against electrolytic dissociation in aqueous solutions in an amount which substantially completely prevents the absorption of said anion active agent by said fibrous material, said amount ranging from about 5% to about 50% of the quantity of the anion active agent.

5. In the treatment of nitrogen-containing fibrous materials in acid dye baths which require the presence of an organic treating agent having both anion active and capillary active properties and being composed of a lipophilic group of at least 6 carbon atoms and a hydrophilic inorganic salt-forming acid radical wherein the fibrous materials absorb substantial quantities of the anion active agent, the step which comprises applying said anion active agent to the nitrogen-containing fibrous materials in the presence of other organic water-soluble capillary active agents which are stable against electrolytic dissociation in aqueous solutions in an amount which substantially completely prevents the absorption of said anion active agent by said fibrous materials, said amount being about 50% of the quantity of said anion active substance.

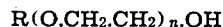
6. An acid dye bath for treating nitrogen-containing fibrous materials comprising a dye component, an organic treating agent which is both anion active and capillary active and is composed of a lipophilic group of at least 6 carbon atoms and a hydrophilic inorganic salt-forming acid radical and an organic water-soluble capillary active agent which is stable against hydrolytic dissociation in aqueous solutions in an amount which substantially completely prevents the absorption of said anion active agent by said fibrous materials, said amount being about 50% of the quantity of said anion active agent.

7. An acidic treatment liquor for nitrogen-

containing fibrous materials containing as wetting, dispersing and cleaning agents the combination of an organic substance which is both anion active and capillary active with an organic water-soluble capillary active agent which is stable against ionic dissociation in aqueous solutions in an amount which substantially completely prevents the absorption of said anion active agent by said fibrous materials, said amount ranging from about 5% to about 50% of the quantity of said anion active substance.

8. In the process of treating wool in an acid bath with an organic treating agent composed of an aliphatic lipophilic group of at least 6 carbon atoms and a hydrophilic sulfonate group wherein the wool absorbs substantial quantities of said treating agent, the step which comprises substantially completely preventing the wool from absorbing said treating agent by incorporating in the acid treating bath from 5% to 50% of a capillary active substance which does not dissociate electrolytically in aqueous solution, the quantity of said capillary active substance being based upon the quantity of said treating agent.

9. In the process of treating wool in an acid dye bath with an organic treating agent composed of an aliphatic lipophilic group of at least 6 carbon atoms and a hydrophilic sulfonate group wherein the wool absorbs substantial quantities of said treating agent, the step which comprises substantially completely preventing the wool from absorbing said treating agent by incorporating in the acid dye bath from 5% to 50% of a compound having the formula



wherein R is a lipophilic hydrocarbon group and n is at least 4, the quantity of said compound being based upon the quantity of said treating agent.

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