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SURFACE MODIFYING COMPOSITION

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21 Claims. (Cl. 252—357)

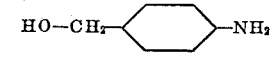
My invention relates to compositions having surface active properties or surface modifying properties and is particularly concerned with such preparations containing so-called cation-active or cationic surface modifying agents.

The prior art has known and utilized for some time past cation-active or cationic surface active agents in various arts dealing with the treatment of textiles, leather, furs, problems in ore flotation and the like. Numerous agents of this type have been developed during the past several years.

In general, my invention relates to enhancing the surface active properties and characteristics, such as the wetting-out properties, of these cation-active or cationic agents. These latter agents, while having many desirable properties and characteristics which adapt them for various uses in the industrial and related arts, nevertheless, in contrast to many anionic surface active agents, have poor wetting-out properties. I have made the surprising discovery that the addition of certain materials, hereinafter described, many of which, in themselves, have very poor wetting-out properties, to aqueous-containing baths markedly enhances the surface active properties, particularly the wetting-out power, of the cation-active or cationic agents. These addition or enhancing agents not only enhance the wetting-out properties of the said cation-active or cationic agents but, as indicated, also serve definitely to improve many of the other valuable colloidal properties of said cation-active agents.

These addition or enhancing agents are, in general, amides of carboxylic acids containing at least six and, preferably, from 8 to 14 carbon atoms. Of particular utility are the lauric acid or coconut oil mixed fatty acid amides of hydroxy-alkyl primary or secondary amines. Representative examples of enhancing agents which may be utilized in accordance with my present invention are, for example, the lauric acid amide of diethanolamine, the lauric acid amide of monoethanolamine, the caprylic acid amide of monoethanolamine, the lauric acid amide of morpholine, the coconut oil mixed fatty acid amides of glycerol mono-amine, the myristic acid amide of di-methylol ethyl amino methane, the myristic acid amide of propanolamine, and caprylic and capric acid amides of diethanolamine.

In general, the amides which are utilized as enhancing agents are of non-ionic character and may be prepared by reacting ammonia or primary or secondary amines such as ethyl amine, di-ethyl amine, propyl amine, di-propyl amine, butyl amine, or hydroxy primary and secondary amines, with carboxylic acids containing at least six carbon atoms and, for best results, preferably not more than about fourteen carbons. The hydroxy primary and secondary amines, or, in other words, hydroxy non-tertiary amines, which may be utilized in the preparation of the amide addition or enhancing agents employed in accordance with the present invention include, among others, symmetrical, unsymmetrical, normal and iso-derivatives, such as monoethanolamine, diethanolamine, monopropanolamine, dipropanolamine, isopropanolamine, monobutanolamine, mono-isobutanolamine, dibutanolamine, monopentanolamine, dipentanolamine, monohexanolamine, dihexanolamine, mono-octanolamine, dioctanolamine, monodecylolamine, mono-laurylolamine, mono-hexadecylolamine, mono-octalecylolamine; arylolamines such as p - amino phenol and



mono-ethyl, mono-ethanolamine; mono-butyl, mono-ethanol amine; monocyclohexyl, monoethanol amine; alkylol polyamines such as alkylol derivatives of ethylene diamine, diethylene triamine, and triethylene tetra-amine as for example, hydroxy-ethyl ethylene diamine; diglycerol mono-amine; diglycerol di-amine; hydroxy-amines derived from other polyhydric alcohols, including glycols, sugars and sugar alcohols such as ethylene glycol, diethylene glycol,

dextrose, sucrose, sorbitol, mannitol and dulcitol; 1 - amino - 2,3-propanediol; 2 - amino-1,3-propanediol; 2-amino-2-methyl-1,3-propanediol; 2-amino-2-n-propyl-1,3-propanediol; 2-amino-2-isopropyl - 1,3-propanediol; 2-amino-2-methyl-1,4 - butanediol; 2 - amino-2-methyl-1,5-pentanediol; 2-amino-2-ethyl-1,3-propanediol; 2-amino - 2 - ethylol-1,3-propanediol; 2-amino-2-methyl - 1,6-hexanediol; and 1-amino-1,1-dimethyl ethanol. The glycerol mono-amines and the related hydroxy amines such as various of those disclosed hereinabove may be prepared by various procedures and in different ways. Many of them are conveniently produced by nitrating paraffin hydrocarbons, substituting methylol groups for hydrogen on the carbons to which the nitro groups are attached, and then reducing the nitro groups to amine groups. Polymerized hydroxy non-tertiary amines prepared, for example, by polymerizing monoethanolamine, diethanolamine, or other hydroxy non-tertiary amines, such as those mentioned hereinabove, particularly in the presence of a catalyst such as sodium hydroxide or the like, may also be employed. The preparation of polymerized hydroxy amines is disclosed, for example, in United States Patent No. 2,178,173. Homologues and substitution derivatives of the above-mentioned hydroxy amines may also be utilized. Because of commercial and other considerations, monoethanolamine and diethanolamine are especially desirable. It will be understood that the hydroxy non-tertiary amines may be utiilzed in pure, impure or commercial form.

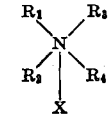
The carboxylic acids containing at least six carbon atoms which are utilized with the aforementioned amines to form the amide addition or enhancing agents include, among others, straight chain and branched chain, saturated and unsaturated, carboxylic, aliphatic (including cycloaliphatic), fatty, aromatic, hydroaromatic, and araliphatic acids including caproic acid, caprylic acid, pelargonic acid, capric acid, sebacic acid, oleic acid, ricinoleic acid, ricinelaidic acid, ricinostearolic acid, linoleic acid, linolenic acid, lauric acid, myristic acid, palmitic acid, mixtures of any two or more of the above mentioned acids or other acids, mixed higher fatty acids derived from animal or vegetable sources, for example, lard, coconut oil, rapeseed oil, sesame oil, palm kernel oil, palm oil, olive oil, corn oil, cottonseed oil, sardine oil, tallow, soya bean oil, peanut oil, castor oil, seal oils, whale oil, shark oil and other fish oils, partially or completely hydrogenated animal and vegetable oils such as those mentioned; oxidized hydroxy and alpha-hydroxy higher carboxylic, aliphatic and fatty and/or polymerized higher fatty acids or higher fatty acids derived from oxidized and/or polymerized triglyceride oils; hydroxy acids such as alpha-hydroxy capric acid, alpha-hydroxy lauric acid, alpha-hydroxy myristic acid, alpha-hydroxy coconut oil mixed fatty acids, and the like; naphthenic acid; araliphatic and aromatic acids such as phthalic acid, benzoic acid, Twitchell fatty acids, naphthoic acid, pyridine carboxylic acid; hydroxy aromatic acids such as salicylic acid, hydroxy benzoic and naphthoic acids, and the like. It will be understood that mixtures of any two or more of said acids may be employed if desired and it will also be appreciated that said acids may contain substituent groups such as halogen, ketone and other groups.

Other amides which may be utilized are those derived from polyamines, illustrative examples of which are the lauric acid mono-amide of ethylene diamine and the caprylic acid mono-amide of diethylene triamine; the acetic, propionic, butyric, chloracetic, and maleic acid amides of higher molecular weight fatty acid esters of monoethanolamine or diethanolamine or similar hydroxy-alkyl primary and secondary amines; higher molecular weight alkyl urea derivatives; and the like.

The cation-active or cationic surface active modifying agents whose surface active properties are enhanced by the addition thereto of the amide enhancing agents disclosed hereinabove may be of aliphatic, carbocyclic, or heterocyclic character and, as will be understood, comprise substances in which the surface activity is due to a group or radical present in the cationic portion of the molecule. Among the cation-active compounds which may be employed in accordance with the present invention are the bases or their salts, such as may be derived from pentavalent nitrogen, and further the sulphonium, phosphonium and arsonium, etc. bases and their salts. The quaternary ammonium compounds are examples of such compounds, the pyridonium or pyridinium compounds being specific examples thereof. In the bases or their salts, the innocuous anions may be hydroxide, chloride, sulphate, bromide, iodide, acetate, etc. The groups inducing cation activity comprise long chain groupings such as aliphatic hydrocarbon chains having at least six and preferably from twelve to eighteen carbon atoms. The long chain groupings may be composed of two or more benzene nuclei or other cyclic radicals, either combined directly or, for example, through carbon or nitrogen or other linkages, with or without aliphatic chains substituted for the hydrogen in rings.

Examples of cation-active substances which may be used in accordance with my invention include octyl pyridinium iodide, dodecyl pyridinium bromide, hexadecyl pyridinium iodide, octadecyl pyridinium bromide, dodecyl pyridinium iodide, dodecyl pyridinium chloride, dodecyl-triethyl ammonium iodide, octyl-triethyl ammonium iodide, decyl-triethyl ammonium iodide, dodecyl-triethyl ammonium iodide, hexadecyl-triethyl ammonium iodide, lauryl amine hydrochloride, cetyl amine hydrochloride, heptadecyl amine hydrochloride, octa-decyl amine hydrochloride, octyl amine hydrobromide, octyl amine hydrochloride, toluene azophenyl-trimethyl ammonium iodide, benzene azophenyl-tri-methyl ammonium iodide, diphenyl-azophenyl-trimethyl-ammonium methylsulphate, isopropyl-naphthyl-trimethyl ammonium iodide, diethyl-dodecyl sulphonium hydroxide, triethyl-dodecyl phosphonium hydroxide, trimethyl-dodecyl phosphonium iodide, and trimethyl-dodecyl phosphonium bromide.

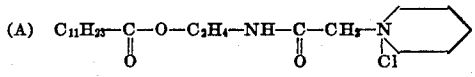
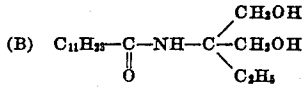
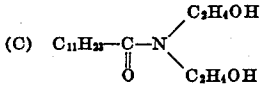
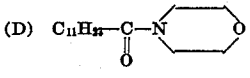
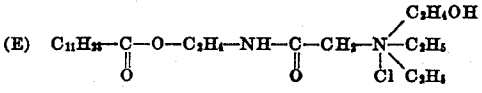
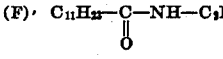
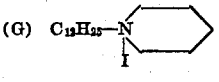
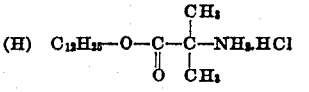
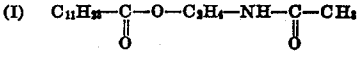
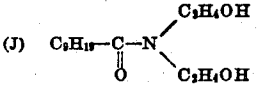
Various of the cation active substances, listed hereinabove, may be represented by the general formula



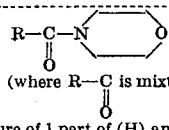
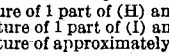
wherein R_1 represents an aliphatic radical, such as a hydrocarbon radical, or the radical of a polyhydric alcohol linked to an alkyl or acyl

group in the form of an ester or an ether, in each case said aliphatic radical containing at least eight carbon atoms, R_2, R_3, and R_4 are hydrogen or hydrocarbon groups which may be components of a heterocyclic ring, and X represents halogen or other anions such as OH^-, HSO_4^-, RSO_4^-, $C_6H_5SO_3^-$, borate, phosphate, nitrate, acetate, etc. Among the specific substances falling within this general class, some of which have been mentioned hereinabove, are cetyl trimethyl ammonium bromide or chloride, dodecyl pyridinium bromide, cetyl pyridinium iodide, lauryl trimethyl ammonium chloride or iodide, monooleic acid ester of diethylene glycol pyridinium chloride, octa-decyl pyridinium bromide, octyl pyridinium chloride; 4 dodecyl, N-methyl-quinaldinium-methylsulphate; N-ethyl triethanolamine mono-oleate-bromide, salts of higher molecular weight betaine esters, etc.

In order to show the marked enhancing effect upon the surface active properties of various cation-active agents, by reason of the addition thereto of the previously disclosed enhancing agents, I have utilized the wetting-out properties as a criterion and have employed the so-called Draves test as a measure of the wetting-out properties. This test comprises suspending a skein of unscoured cotton of predetermined character and weight in a cylinder of water, a small weight attached to a string being affixed to the bottom of said skein. The length of time required for the skein to sink is taken as a measure of the potency of the surface active agents, so far as their wetting-out properties are concerned, which have been previously dissolved or dispersed in the water in the cylinder, the shorter the length of time the more potent the wetting-out effect. The following table sets forth graphically the effect of the enhancing agents upon the wetting-out properties of the cationic surface active agents as determined by the Draves test. In each case, a stated quantity, as indicated, of the cation-active surface modifying agents was dispersed in the water and the time required for the sinking of the skein of cotton was determined. Then another test was performed using the same cation-active surface modifying agent in combination with the enhancing agent, and again the time for sinking of the cotton skein was determined. In most cases the total weight of the mixture of the cation-active surface modifying agent and the enhancing agent was the same as the weight of the cation-active surface modifying agent itself in the previously conducted comparative test. In all of the tests indicated below, tap water was employed.

Agent	Agent alone	
	Concentration (by weight on water employed)	Time
(A) 	*Per cent* 0.2	1020 seconds
(B) 	0.067	>1800 seconds
(C)  (condensation product of diethanolamine and lauric acid)	0.033	104 seconds
(D) 	0.2	>1800 seconds
(E) 	0.2	>1800 seconds
(F) 	0.067	>1800 seconds
(G) 	0.2	690 seconds
(H) 	0.2	>1000 seconds
(I) 	0.2	>24 hours
(J) 	0.2	90 seconds

Ratio of cation-active surface modifying agent to enhancing agent. Total of cation-active surface modifying agent and enhancing agent

Concentration by weight on water employed	Time
	Seconds
(1) 0.2% of a mixture of 2 parts of (A) and 1 part of B	57
(2) 0.1% of a mixture of 2 parts of (A) and 1 part of B	270
(3) 0.1% of a mixture of 2 parts of (A) and 1 part of (C)	80
(4) 0.2% of a mixture of 2 parts of (A) and 1 part of (D)	170
(5) 0.2% of a mixture of 2 parts of (E) and 1 part of (F)	130
(6) 0.2% of a mixture of 2 parts of (E) and 1 part of (C)	39
(7) 0.2% of a mixture of 2 parts of (G) and 1 part of (D)	200
(8) 0.2% of a mixture of 3 parts of (G) and 2 parts of a mixture of  (where R—C is mixture of C_8 and C_{10}) 	42
(9) 0.2% of a mixture of 1 part of (H) and 2 parts of (I)	39
(10) 0.2% of a mixture of 1 part of (I) and 2 parts of (E)	74
(11) 0.2% of a mixture of approximately equal parts of (G) and (I)	36
(12) 0.2% of a mixture of 2 parts of (G) and 1 part of (J)	39

It will be seen that, by combining one of the cation-active surface modifying agents together with one of the enhancing agents, very much better wetting-out action was obtained than by the use of the cation-active surface modifying agent per se. Surprisingly enough, as I have previously pointed out hereinabove, while many of the enhancing agents in themselves have very poor wetting-out properties, as the foregoing table shows, they act to markedly increase the wetting-out action of the cation-active surface modifying agents, notwithstanding the fact that the concentration or amount of the cation-active surface modifying agents is diminished.

While I have chosen the Draves test as a convenient means of illustrating the effect of the enhancing agents, the fact is that said enhancing agents also radically influence other valuable colloidal characteristics of the cation-active surface modifying agents and of the medium into which they are introduced.

It will be apparent that neither the cation-active surface modifying agents nor the enhancing agents need be employed in a pure state and it will also be clear that admixtures of the cation-active surface modifying agents and different enhancing agents may likewise be utilized without departing from the spirit of my invention. In general, I prefer to employ the enhancing agents in amounts less than the amounts of the cation-active surface modifying agents in any particular environment in which the mixture may be employed.

The enhancement of the surface active properties of the cation-active surface modifying agents may be taken advantage of in treating baths containing an aqueous medium, with or without additional substances such as, for example, alkalies, mordants, dyes, color discharging agents, soaps and synthetic detergents, hydrogen peroxide, color reducing agents, and other like agents or substances commonly used in treating baths, and the treating bath so formed may be employed with improved results in many of the arts in which surface modification is desired. For example, dyeing, bleaching, scouring, and otherwise treating fabrics and fibers and other materials in treatment baths of this character are productive of excellent results. Also, in the stuffing of leather, dyeing and otherwise treating furs, and in many other arts, where treating baths are employed, the materials of my invention may be used. A further illustration is in connection with the flotation of ores where the teachings of my present invention may be utilized in connection with modifying the interface between the finely divided ore and the aqueous medium.

What I claim as new and desire to protect by Letters Patent of the United States:

1. A method of enhancing the surface modifying properties, in water-containing media, of cation-active surface modifying agents which comprises admixing therewith an amide of a carboxylic acid, said amide containing a chain of at least 6 carbon atoms.

2. A method of enhancing the surface modifying properties, in water-containing media, of cation-active surface modifying agents which comprises admixing therewith a non-ionic amide of an aliphatic carboxylic acid containing at least 6 carbon atoms.

3. A method of enhancing the surface modifying properties, in water-containing media, of cation-active nitrogenous surface modifying agents which comprises admixing therewith an amide of a fatty acid containing from 8 to 14 carbon atoms.

4. A method of enhancing the surface modifying properties, in water-containing media, of cation-active surface modifying agents, which comprises admixing therewith an amide of an hydroxy-alkyl non-tertiary amine with a fatty acid containing from 8 to 14 carbon atoms.

5. A method of enhancing the surface modifying properties, in water-containing media, of cation-active nitrogenous surface modifying agents, which comprises admixing therewith an amide of monoethanolamine with a fatty acid containing from 8 to 14 carbon atoms.

6. A method of enhancing the surface modifying properties, in water-containing media, of cation-active surface modifying agents, which comprises admixing therewith an amide of diethanolamine with a fatty acid containing from 8 to 14 carbon atoms.

7. A treating bath containing water and having dispersed therein a cation-active surface modifying agent and a non-ionic amide of a carboxylic acid, said amide having a chain of at least 6 carbon atoms.

8. A treating bath containing water and having dispersed therein a cation-active surface modifying agent and a non-ionic amide of an aliphatic carboxylic acid having at least 6 carbon atoms.

9. A treating bath containing water and having dispersed therein a cation-active nitrogenous surface modifying agent and an amide of a fatty acid having from 8 to 14 carbon atoms.

10. A treating bath containing water and having dispersed therein a cation-active nitrogenous surface modifying agent and an amide of an hydroxy-alkyl non-tertiary amine with a fatty acid containing from 8 to 14 carbon atoms, the amide being present in amounts less than the amount of the cation-active nitrogenous surface modifying agent.

11. A treating bath containing water and having dispersed therein a cation-active nitrogenous surface modifying agent and an amide of monoethanolamine with a fatty acid containing from 8 to 14 carbon atoms, the amide being present in amounts less than the amount of the cation-active nitrogenous surface modifying agent.

12. A treating bath containing water and having dispersed therein a cation-active nitrogeneous surface modifying agent and an amide of di-

ethanolamine with a fatty acid containing from 8 to 14 carbon atoms, the amide being present in amounts less than the amount of the cation-active nitrogenous surface modifying agent.

13. A composition comprising a cation-active surface modifying agent and an amide of a carboxylic acid, said amide containing a chain of at least 6 carbon atoms.

14. A composition comprising a cation-active nitrogenous surface modifying agent and an amide of a fatty acid containing from 8 to 14 carbon atoms.

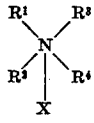
15. A composition comprising a cation-active nitrogenous surface modifying agent and an amide of lauric acid.

16. A composition comprising a cation-active nitrogenous surface modifying agent and an amide of an hydroxyalkyl non-tertiary amine with a fatty acid containing from 8 to 14 carbon atoms.

17. A composition comprising a cation-active nitrogenous surface modifying agent and an amide of monoethanolamine with a fatty acid containing from 8 to 14 carbon atoms.

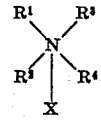
18. A composition comprising a cation-active nitrogenous surface modifying agent and an amide of diethanolamine with a fatty acid containing from 8 to 14 carbon atoms.

19. A composition comprising a cation-active quaternary ammonium compound corresponding to the general formula



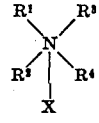
where R^1 represents an aliphatic radical containing at least 6 carbon atoms, R^2, R^3 and R^4 are hydrogen or hydrocarbon groups which may be components of a heterocyclic ring, and X represents an anion; admixed with a proportion of an amide of an aliphatic carboxylic acid having from 8 to 14 carbon atoms.

20. A composition comprising a cation-active quaternary ammonium compound corresponding to the general formula



where R^1 represents an aliphatic radical containing from 8 to 14 carbon atoms, R^2, R^3 and R^4 are hydrogen or hydrocarbon groups which may be components of a heterocyclic ring, and X represents halogen; admixed with a proportion of an amide of a hydroxy-alkyl primary amine with a fatty acid having from 8 to 14 carbon atoms.

21. A composition comprising a cation-active quaternary ammonium compound corresponding to the general formula



where R^1 represents an aliphatic radical containing 12 carbon atoms, R^2, R^3 and R^4 are hydrogen or hydrocarbon groups which may be components of a heterocyclic ring, and X represents chlorine; admixed with a lesser proportion of an amide of a hydroxy-alkyl secondary amine with a fatty acid having from 8 to 14 carbon atoms.

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