

PATENT SPECIFICATION

NO DRAWINGS

Inventor: HARRY CLARENCE de VROOME

1.195.796

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Date of filing Complete Specification: 5 Nov., 1968.

Application Date: 14 Aug., 1968.

No. 38797/68.

Complete Specification Published: 24 June, 1970.

Index at acceptance: —C5 D(3A1X, 3B1, 3B2, 3X)

International Classification: —C 11 d 1/38, 3/20, 3/44

COMPLETE SPECIFICATION

Improvements in or relating to Cleaning Compositions

We, AYRODEV PROCESSES LIMITED, a British Company of Prestons Road, Poplar, London E.14., do hereby declare the invention for which we pray that a Patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to cleaning compositions capable of both cleansing insulated surfaces which have become defective and contaminated with carbonaceous matter, salts, water and other contaminants, and providing a priming coat for subsequent re-insulation. Such compositions are intended to be employed for instance in the cleansing of rotating electrical machinery in which electrical resistance has been impaired by exposure to adverse conditions, including such machinery in marine service, the compositions also serving to prime the machinery for the re-application of insulating varnish or other coating media.

When electrical machinery has been adversely affected by exposure to conditions causing deterioration of the insulation of such items as generator coils, it has been the practice to remove dirt and accumulated carbon deposits by means of cleansing solvents. Frequently such cleansers incorporate materials of an oily nature to assist preferential wetting of moist surfaces by the cleansers, and to afford a degree of protection of exposed metallic surfaces against atmospheric corrosion, re-adsorption of moisture or other adverse influences. The oil deposits remaining from such cleansers frequently interfere with the drying and curing characteristics of subsequently applied insulating varnishes.

It is known that most solid surfaces possess electronegative charges which are strongly attractive to the electropositive groups in

cationic surfactants. Although such cationic surfactants are not ionised in non-polar solvents, these attractive forces are nevertheless operative under these conditions, for example in hydrocarbon solvents. This phenomenon is exploited in many applications, particularly in the dispersion of pigment aggregates and preferential wetting of surfaces by non-polar solvents under moist conditions. Furthermore, it is known that cationic surfactants, particularly those which are substantially insoluble in water but highly soluble in non-polar solvents, are more strongly adherent to solid surfaces under moist conditions. The non-polar moieties of the adherent cationic surfactants being directed away from the substrate surface for a moisture-repellent, non-polar covering over the substrate surface.

According to one aspect of this invention, we provide a substantially non-aqueous cleaning composition containing a cationic surfactant comprising an organic acid salt of a primary, secondary, tertiary or quaternary amine containing a hydrocarbon moiety of not less than 12 carbon atoms; hydroxy aromatic acid or ester thereof; and at least one organic hydrocarbon solvent but excluding any halogenated hydrocarbon solvent. The proportions of the said surfactant to the said hydroxy aromatic acid or ester thereof may vary over a wide range for instance from 10% by weight to 90% by weight of the said surfactant to the said hydroxy aromatic acid or ester thereof. Expediently, the proportion of the said surfactant to the said hydroxy aromatic acid or ester thereof may be from 35% by weight to 65% by weight. It is preferred that the cationic moiety of the surfactant should contain at least two like or unlike amino groups.

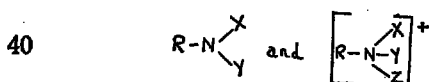
According to another aspect of this inven-

[Price 5s. 0d.]

tion, we provide a method of cleaning a contaminated electrically insulated surface comprising applying to the said surface the composition of this invention and after all contaminating material has been removed allowing the solvent(s) to volatilise from the residual cleaning composition thereby cleaning the surface and forming a protective film thereon. The preferred method of application is by spraying. An insulating varnish or other coating may then be applied, e.g. by spraying, to the said protective film.

According to a further aspect of this invention, we provide a method of cleaning a contaminated electrically insulated surface comprising applying to the said surface components which will react in the presence of organic solvent *in situ* to form a cationic surfactant comprising an organic acid salt of a primary, secondary, tertiary or quaternary amine containing a hydrocarbon moiety of not less than 12 carbon atoms; a hydroxy aromatic acid or ester thereof; and at least one organic hydrocarbon solvent; but excluding any halogenated hydrocarbon solvent and allowing the solvent(s) to volatilise from the residual cleaning composition thereby cleaning the surface and forming a protective film thereon. The said cationic surfactant-forming components may be the said amine or a salt thereof with an inorganic acid, and an organic acid or a salt thereof. Here also, the preferred method of application is by spraying. As above, an insulating varnish or other coating may then be applied, e.g. by spraying, to the said protective film. The said cationic surfactant may be derived from the following amines:—

Aliphatic amines of the type:



wherein R=an aliphatic hydrocarbon group of C₁₂₋₂₂ and X,Y,Z=hydrogen or a C₁₋₃ aliphatic radical.

45 Diamines of the type:
R.NH.(CH₂)_xNH₂ wherein x can vary from 1 to 6 and R is as above.

Higher alkyl amines of the type:
50 R.NH(CH₂H₄NH)_xC₆H₄OH wherein x and R are as above, which are synthesised, for example by the reaction of ethanolamine sulphuric esters with fatty amine salts in the presence of strong alkalis, and alkyl polyamines formed by the reaction of C₁₂₋₂₂ alkyl halides with triethylene tetramine. Ester linked polyamines formed by the reaction of fatty esters of ethylene chlorohydrin with diethylene-tetramine or triethylenetetramine.

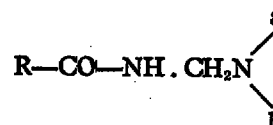
Ether linked amines of the type:

60 R—O—(CH₂)₃.NH₂ wherein R is as above, formed by reacting fatty alcohols with acrylonitrile and hydrogenating the resulting cyanoalkyl ethane.

Amide linked amines of the type:

65 R—CO—NH(CH₂)₂NH₂ wherein R is as above.

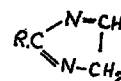
Aminomethyleneamides of the type:



wherein a and b are lower alkyl and/or hydroxy alkyl, and R is as above.

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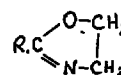
Imidazolines of the type:



wherein R is as above, and which form complex fatty acids.—not true salts.

Quinazolines of the type:

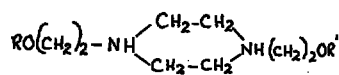
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wherein R is as above, and which form complex fatty acids.—not true salts.

Piperazine Derivatives such as alkyl derivatives of 1,4 - di (β - hydroxyethyl) - piperazine formed by the mono- or di-esterification, etherification of di - (β - hydroxyethyl) piperazine with C₁₂₋₂₂ long chain alkyl carboxylic acids or halides.

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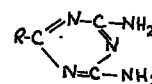
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wherein R is hydrogen or C₁₂₋₂₂ alkyl or alkoxy and R' is C₁₂₋₂₂ alkyl or alkoxy.

Guanidine Derivatives of the type:

80 RNH—NH—NH₂ and lower alkyl, cycloalkyl, aryl, aralkyl substituted derivatives thereof, wherein R is C₁₂₋₂₂ alkyl.

Guanamine Derivatives of the type:

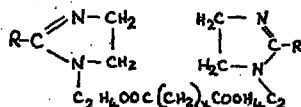


and their secondary and tertiary amino derivatives, wherein R is C₁₂₋₂₂ alkyl.

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Bi-cyclic Compounds.

Bis-imidazoline compounds, formed from the reaction of dibasic carboxylic acids with higher alkyl substituted 2 - Hydroxyethyl-imidazoline.



In the above list of amines, it should be mentioned that R may include substituted alkyl ($\text{C}_{12}-\text{C}_{22}$) groups including a hydrophobic group, e.g. tertiary substituted phenol groups (e.g. a tertiary octyl phenol group), a dodecylbenzene group or an abietinyl or a dehydroabietinyl group.

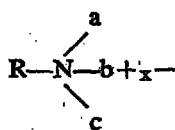
The said cationic surfactant may be derived from the following quaternary amines:

1. Mono and poly quaternised analogues of the primary, secondary and tertiary amino groups mentioned above.

When the compounds listed involve, for example, primary and secondary amino groups in addition to the amino group containing the hydrophobic group, it is to be understood that their secondary and tertiary analogues are also included.

2. Principal Commercially Available Quaternaries.

Single Quaternaries.



wherein R is the $\text{C}_{12}-\text{C}_{22}$ alkyl hydrophobic group, a, b and c are mainly lower alkyl groups but can also include as single substituents:

Aryl oxy ether group, e.g. $\text{Ar}-\text{O}-\text{C}_2\text{H}_5$
Hydroxybutyryl groups, particularly where R is a higher alkylbenzyl radical.

X, normally a halide ion, would become an organic anion by double decomposition.

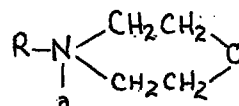
Cyclic Quaternaries.

Alkyl pyridinium salts, e.g. cetyl pyridinium salts.

And analogous substituted pyridines, analogous tetrahydroquinolines and isoquinolines.

Pyridinium derivatives of halogen amines with two quaternary N functions but with only one hydrophobic group, e.g. the reaction product of 2 - chloroethyldimethyldodecylammonium chloride with pyridine.

N-Alkyl Morpholines.



and piperidine analogues, wherein R is $\text{C}_{12}-\text{C}_{22}$ alkyl, and where a is a lower alkyl.

Analogously alkylbenzyl dimethylamines may be quaternized with dihalo compounds of the type



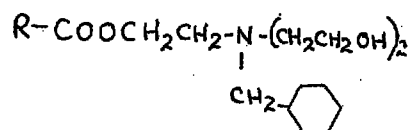
and higher alkaryl ethers may be chloromethylated then quaternized with tertiary amines, including for example, benzyldimethylamine and pyridine.

Ether linked Quaternaries.

For example, by reacting epoxyethers such as 3 - octyloxy - 1,2 - epoxypropane with tertiary amines such as pyridine.

Ester linked Quaternaries.

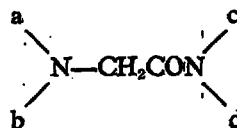
Such as



(R is $\text{C}_{12}-\text{C}_{22}$ alkyl) by quaternising esters of triethanolamine, with for example, benzyl halides.

Amide linked Quaternaries.

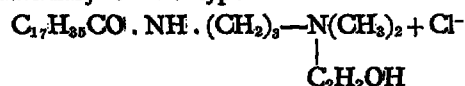
Formed by quaternising tertiary amines of the type:



with, for example, chloromethylstearamide a, b, c and d may be lower alkyl or in cyclic structures.

"Zelan" is of this type.

"Aerosol S E" is an amide linked quaternary of the type:



Organic acids from which the said cationic surfactant salts may be derived may be selected from:

$\text{C}_{12}-\text{C}_{22}$, Aliphatic, straight-chain saturated or ethylenically unsaturated monobasic carboxylic acids, preferably $\text{C}_{18}-\text{C}_{20}$, such as oleic acid, stearic acid, linoleic acid, oleostearic acid, caproic acid, dodecanoic acid.

C₃₋₂₂, preferably C₆₋₂₀, branched-chain saturated or ethylenically unsaturated mono-basic carboxylic acids.

- 5 C₇₋₂₂, Cyclo aliphatic, aromatic carboxylic acids and substituted derivatives thereof, such as: salicylic acid, abietic acid, hydrogenated abietic acid and dehydroabietic acid, benzoic acid, hexahydrobenzoic acid and substituted derivatives thereof.

- 10 Polybasic carboxylic acids (C₆₋₂₂) such as adipic acid, isophthalic acid, hexane dicarboxylic acid.

- 15 The said hydroxy aromatic acids and esters thereof may include: Salicylic acid, -m-hydroxybenzoic acid, -p-hydroxybenzoic acid, the dihydroxy isomers of benzoic acid, the mono-, di- and tri-hydroxy isomers of the naphthoic acids, and their esters with C₁₋₄ mono or dihydric alcohols.

- 20 Solvent Basis.

- Whereas the normal commercially available aliphatic hydrocarbon solvents, such as white spirit, S.P.B.3 are satisfactory for the purpose of this invention, there performance may be improved by the introduction of aromatic solvents such as toluene or xylene, and/or terpene based solvents, such as turpentine and dipentene. The use of halogenated hydrocarbon solvents is excluded.
- 30 piate volatility and solvent power as required and, according to the severity of the cleansing operation and its environment.

EXAMPLE:

- 35 A 600kW., D.C. armature, 3½ tons in weight coupled to a commutator 1'6" long and 2'6" diameter, installed on a ship had become heavily encrusted with oil, salts and a carbon deposit. It was ascertained that the electrical resistance of the winding had fallen to a value of 100,000 ohms. at 87 volts.

- 40 After spraying with the following composition, which rapidly dispersed the encrusted deposit, the insulation resistance, when measured four hours after the commencement of application, had risen to a value of 20 megohms.

- | | | |
|----|--|-----|
| 50 | Diolate salt of - N - stearyl - propylene - 1,3 - diamine (marketed under the Registered Trade Name "Duomeen TDO") | 22 |
| | Methyl salicylate | 15 |
| 55 | White spirit | 250 |
| | Dipentene | 75 |

This value for insulation resistance was maintained on standing for 24 hours.

- 60 Subsequent spray application of two coats of an insulating varnish, based upon an oil modified pentaerythritol alkyl, resulted in a

maintained insulation resistance of 20 megohms at 500 volts and enabled the ship to return to intermediate service.

We have found that the cleaning composition exemplified above is most efficacious in removing dirt, moisture and carbon scale from electrical machinery while forming a protective barrier on evaporation of the solvent which affords a tough adherent priming coat for subsequent application of insulating varnish media. By the use of such a composition it becomes possible to effect repairs of rotating electrical equipment *in situ* without having to resort to removal and a prolonged drying operation. This is particularly valuable when repairing such equipment as electrical generators in marine installations, and considerably facilitates the retrieval and renovation of such equipment from sunken vessels.

WHAT WE CLAIM IS:—

1. A substantially non-aqueous cleaning composition containing a cationic surfactant comprising an organic acid salt of a primary, secondary, tertiary or quaternary amine containing a hydrocarbon moiety of not less than 12 carbon atoms; a hydroxy aromatic acid or ester thereof; and at least one organic hydrocarbon solvent but excluding any halogenated hydrocarbon solvent.

2. Composition according to Claim 1, wherein the proportion of the said surfactant to the said hydroxy aromatic acid or ester thereof is 10% by weight to 90% by weight.

3. Composition according to Claim 1, wherein the proportion of the said surfactant to the said hydroxy aromatic acid or ester thereof is 35% by weight to 65% by weight.

4. Composition according to any preceding Claim, wherein the cationic moiety contains at least two like or unlike amino groups.

5. A cleaning composition according to Claim 1, substantially as herein described.

6. A method for cleaning a contaminated electrically insulated surface comprising applying to the said surface the cleaning composition claimed in Claim 1 and after all contaminating material has been removed allowing the solvent(s) to volatilise from the residual cleaning composition, thereby cleaning the surface and forming a protective film thereon.

7. Method according to Claim 6, wherein the said cleaning composition is applied to the said surface by applying to the said surface components which will react in the presence of organic solvent *in situ* to form a cationic surfactant comprising an organic acid salt of a primary, secondary, tertiary or quaternary amine containing a hydrocarbon moiety of not less than 12 carbon atoms; a hydroxy aromatic acid ester thereof; and at least one organic hydrocarbon

C_{3-22} , preferably C_{8-20} branched-chain saturated or ethylenically unsaturated mono-basic carboxylic acids.

- 5 C_{7-22} Cyclo aliphatic, aromatic carboxylic acids and substituted derivatives thereof, such as: salicylic acid, abietic acid, hydrogenated abietic acid and dehydroabietic acid, benzoic acid, hexahydrobenzoic acid and substituted derivatives thereof.

- 10 Polybasic carboxylic acids (C_{8-22}) such as adipic acid, isophthalic acid, hexane dicarboxylic acid.

- 15 The said hydroxy aromatic acids and esters thereof may include: Salicylic acid, -m-hydroxybenzoic acid, -p-hydroxybenzoic acid, the dihydroxy isomers of benzoic acid, the mono-, di- and tri-hydroxy isomers of the naphthoic acids, and their esters with C_{1-4} mono or dihydric alcohols.

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- Whereas the normal commercially available aliphatic hydrocarbon solvents, such as white spirit, S.P.B.3 are satisfactory for the purpose of this invention, there performance may be improved by the introduction of aromatic solvents such as toluene or xylene, and/or terpene based solvents, such as turpentine and dipentene. The use of halogenated hydrocarbon solvents is excluded. appropriate volatility and solvent power as required and, according to the severity of the cleansing operation and its environment.

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- | | parts by weight. |
|--|------------------|
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WHAT WE CLAIM IS:—

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2. Composition according to Claim 1, wherein the proportion of the said surfactant to the said hydroxy aromatic acid or ester thereof is 10% by weight to 90% by weight.

3. Composition according to Claim 1, wherein the proportion of the said surfactant to the said hydroxy aromatic acid or ester thereof is 35% by weight to 65% by weight.

4. Composition according to any preceding Claim, wherein the cationic moiety contains at least two like or unlike amino groups.

5. A cleaning composition according to Claim 1, substantially as herein described.

6. A method for cleaning a contaminated electrically insulated surface comprising applying to the said surface the cleaning composition claimed in Claim 1 and after all contaminating material has been removed allowing the solvent(s) to volatilise from the residual cleaning composition, thereby cleaning the surface and forming a protective film thereon.

7. Method according to Claim 6, wherein the said cleaning composition is applied to the said surface by applying to the said surface components which will react in the presence of organic solvent *in situ* to form a cationic surfactant comprising an organic acid salt of a primary, secondary, tertiary or quaternary amine containing a hydrocarbon moiety of not less than 12 carbon atoms; a hydroxy aromatic acid ester thereof; and at least one organic hydrocarbon



solvent, but excluding any halogenated hydrocarbon solvent.

- 5 8. Method according to Claim 7, wherein the said cationic surfactant-forming components are the said amine or a salt thereof with an inorganic acid, and an organic acid or a salt thereof.

- 10 9. Method according to any one of Claims 6 to 8, wherein the cleaning composition is applied to the said surface by spraying.

- 10 10. Method according to any one of Claims 6 to 9, wherein an insulating varnish or other coating is subsequently applied to the said protective film.

11. Method according to Claim 10, where- 15 in the insulating varnish or other coating is applied by spraying.

12. Method according to Claim 6 or Claim 7 substantially as herein described.

13. An article provided with a protective 20 film by the method claimed in any one of Claims 6 to 12.

HERBERT J. W. WILDBORE,
101 Leadenhall Street,
London E.C.3.
Agent for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1970.
Published by The Patent Office, 25 Southampton Buildings London WC2A 1AY, from which copies may be obtained.



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