

1

3,367,878

ALKALINE WATER-BASED CLEANER

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The invention described herein may be manufactured and used by or for the Government for governmental purposes, without the payment to me of any royalty thereon.

This invention relates to compositions of matter for use as alkaline cleaners of asphalt, sodium and/or metallic soap greases, road dirt, forming oils, cutting oils, and aviation dirt from ferrous and non-ferrous metal surfaces.

Specifically it deals with stable, single phase alkaline water-based cleaners containing an organic solvent and is designed to clean aircraft surfaces by immersion, spraying, brushing or preferably by a hydrosteam cleaning machine. Hydrosteam cleaning machines are of the injection type which use existing plant steam supplies and contain no tubular coils.

The alkaline water-based cleaners comprise specific alkaline salt detergents and specific anionic-nonionic surfactant mixtures combined with specific organic sequestrants. These alkaline salt detergents are inorganic salts or mixtures thereof which, when dissolved in the systems referred to herein, produce a pH not exceeding 12.1 and contain anionic groups (silicate) that act as corrosion inhibitors for nonferrous (aluminum) base metals. The glycols hereinafter referred to, form stable, single phase solutions with aqueous solutions of the other ingredients comprising this invention.

This application is an improvement on the Paint Remover for Missile Component Parts covered in application filed by A. Mankowich, Ser. No. 215,465 on Aug. 7, 1962.

The prior art as it relates to alkaline water-based cleaners is typified by the comparison formula of Military Specification Mil-C-25769B, Cleaning Compound, Aircraft Surface, Alkaline Waterbase with the composition as follows:

Component:	Percent by weight
Na ₂ PO ₄ ·12H ₂ O	10
9-10 ethylene oxide adduct of octylphenol	2
Ethylene glycol monoethyl ether	6
Water	82

The 9-10 ethylene oxide adduct of octylphenol is the nonionic surfactant, Triton X. 100 (Rohm & Haas Company, Phila., Pa.), and ethylene glycol monoethyl ether is Cellosolve (Union Carbide Corp.).

Another example of the prior art contains a high concentration of aromatic petroleum hydrocarbon solvent and is typified by the control formula of Military Specification Mil-C-22543, Cleaning Compound, Water-Emulsion with a composition as follows:

Component:	Percent by weight
Water	20.2
Sodium xylene sulphonate	1.8
9-10 ethylene oxide adduct of octylphenol	4.3
Triethanolamine	4.0
Ethylene glycol monobutyl ether (butyl Cellosolve)	9.2
Petroleum solvent, 95% aromatic	36.7
Oleic acid	12.8
Pine oil	1.0
Hexylene glycol	10.0

2

The following tests show that each of these conventional cleaners is deficient or borderline in the deterging of one or more of the common soils, mineral oil (non-detergent, SAE 30 grade), petroleum asphalt (Federal Specification SS-A-706, grade 85-100, designation AP-3) and calcium soap-grease (Federal Specification VV-G-632, Type A, Grade 1). The test panels were 2½ by 2½ inches, 18-20 gage, cold rolled SAE 1020 steel, polished with No. 1 emery cloth and cleaned prior to soil application. Mineral oil was supplied by dipping the panel into a beaker of oil, removing and draining thirty minutes; 320 to 340 mg. asphalt was spread over one face of the panel with a steel spatula; 290 to 310 mg. grease was spread over one face of the panel with finger tips. The cleaning tests were carried out in 2-liter beakers, using 1600 ml. cleaning solution in every case. The Mil-C-25769B tests were run at a boil, one series on the concentrate as given above and one series on the concentrate diluted with three parts water by volume. The Mil-C-22543 tests were run at 130° F. on the concentrate given above diluted with four parts water by volume. The results obtained were as follows:

Cleaner	Mineral Oil (3 minute cycle)	Calcium Soap-Grease (5 minute cycle)	Asphalt (21 minute cycle)
MIL-C-22543: 1-4 dilution.	60 mg. residue...	106 mg. residue...	193 mg. residue.
MIL-C-25769B: Concentrate.	Zero residue....	246 mg. residue... to 3.6 mg.	297 mg. residue to 120 mg.
1-3 dilution.	Water breaks..		

These conventional cleaners are also deficient in certain physical properties. The Mil-C-25769B type when used in the concentrate form exhibits separation of the nonionic surfactant, Triton X. 100 at elevated temperatures. Mil-C-22543 compositions are limited by safety considerations to operation at temperatures not exceeding 130° F. because of the low flash point of their petroleum solvent.

The object of the present invention is, therefore, the development of stable, single phase compositions of matter of the alkaline water-based cleaner type containing a high boiling point, high flash organic solvent of co-solvent characteristics, the said compositions of matter possessing improved detergent efficiency.

The above objective can be obtained by the addition to an aqueous solution of alkaline salt detergents, neutral builders and anionic-nonionic surfactants of suitable quantities of specific glycols. These glycols are high boiling point, high flash point solvents of powerful co-solvent characteristics, which form stable, single phase solutions with the other ingredients of the developed compositions even at boiling temperatures. The alkaline salt detergents are inorganic salts or mixtures thereof which impart a pH not exceeding 12.1 to the developed cleaners, and which contain anionic groups such as silicate that act as corrosion inhibitors for non-ferrous base metals like aluminum.

The improved compositions described herein possess improved and far superior detergent efficiency than the products described as typical of the prior art. The effectiveness of the deterging action is enhanced by the addition of a specific organic chelating agent, namely, the tetrasodium salt of ethylenediaminetetraacetic acid. Examples of the glycols are hexylene glycol and dipropylene glycol.

Examples of the compositions illustrating this invention are given as follows:

3

EXAMPLE I

Add Solution B to Solution A, and use at a boil.

Solution A

Component:	Grams	
Sodium metasilicate pentahydrate -----	2.59	5
Trisodium phosphate dodecahydrate -----	2.51	
Primary sodium phosphate monohydrate ----	0.90	
Sodium sulphate -----	0.67	
Sodium oleate -----	0.44	10
Nonylphenoxypolyethyleneoxy ethanol having 30 moles of ethylene oxide per mole of nonyl phenol -----	0.39	
Water to make 100 ml.		

Solution B

3.75 ml. hexylene glycol.

EXAMPLE II

Add Solution B to Solution A, and use at a boil.

Solution A

Component:	Grams	
Sodium metasilicate pentahydrate -----	2.76	25
Trisodium phosphate dodecahydrate -----	2.34	
Primary sodium phosphate monohydrate ----	0.90	
Sodium keryl benzene sulphonate (40% ac- tive) -----	1.11	
Polyoxyethylene octyl phenol having 9 to 10 moles of ethylene oxide per mole of octyl phenol -----	0.39	30
Water to make 100 ml.		

Solution B

5 ml. hexylene glycol.

EXAMPLE III

Add Solution B to Solution A, and use at a boil.

Solution A

Component:	Grams	
Sodium metasilicate pentahydrate -----	2.24	
Trisodium phosphate dodecahydrate -----	2.18	
Primary sodium phosphate monohydrate ----	0.78	
Sodium sulphate -----	0.58	45
Sodium dodecyl sulphate -----	0.38	
30 mole ratio ethylene oxide adduct of decyne- 4,7-diol -----	0.34	
Water to make 100 ml.		

Solution B

3.75 ml. hexylene glycol.

EXAMPLE IV

Add Solution B to Solution A, and use at a boil.

Solution A

Component:	Grams	
Sodium metasilicate pentahydrate -----	2.76	60
Trisodium phosphate dodecahydrate -----	2.68	
Primary sodium phosphate monohydrate ----	0.96	
Tetrasodium salt of ethylenediaminetetraacetic acid -----	0.71	
Sodium dodecyl sulphate -----	0.47	65
30 mole ratio ethylene oxide adduct of decyne- 4,7-diol -----	0.42	
Water to make 100 ml.		

Solution B

3.75 ml. hexylene glycol.

The improved detergent efficiency of the improved compositions used in Examples I to IV is illustrated by the following cleaning tests, using the same procedures heretofore in connection with cleaners of the prior art:

4

Cleaner (Examples I to IV):	Residue
Mineral oil, 3 minute cycle -----	0
Calcium Soap-Grease, 3 minute cycle -----	0
Asphalt, 7 minute cycle -----	0

The surfactants used in the above examples are known commercially as follows:

Nonylphenoxypolyethyleneoxy ethanol having 30 moles of ethylene oxide per mole of nonyl phenol is Igepal CO-880, manufactured by Autara Chemicals, General Aniline and Film Corp.

Sodium keryl benzene sulphonate is Naconnol NR, by the National Aniline Division, Allied Chemical and Dye Corp.

15 Polyoxyethylene octyl phenol having 9 to 10 moles of ethylene oxide per mole of octyl phenol is Triton X. 100, by Rohm & Haas Co.

20 30 mole ratio ethylene oxide adduct of decyne-4,7-diol is Surfynol 485, by Air Reduction Chemical and Carbide Co.

It has also been found that certain anionic-nonionic surfactant combinations are to be preferred, because they enhance the removal of asphalt and other bituminous soils. The anionic-nonionic surfactant combinations employed in Examples I to IV provide optimum detergency of such soils. Investigation reveals that the anionic-nonionic combinations sodium dodecyl sulphate-nonylphenoxypolyethyleneoxy ethanol having 30 moles of ethylene oxide per mole of nonyl phenol, sodium oleate-polyoxyethylene octyl phenol having 9 to 10 moles of ethylene oxide per mole of octyl phenol and sodium keryl benzene sulphonate-nonylphenyl decacontaethylene glycol ether possess considerably less surface activity (penetrability, peptization and wetting as judged by asphalt detergency) than the surfactant combinations of Examples I to IV.

It has also been found that specificity exists in the glycol used. Hexylene glycol, for example, provides optimum detergency when used in as small proportions as in Examples I to IV; namely, 3.75 parts hexylene glycol to 100 parts alkaline detergent solution by volume. However, 10 parts dipropylene glycol to 100 parts of the alkaline solution of Example I by volume is necessary for optimum detergency; and if hexanetriol is used, 10 parts by volume of the latter to 100 parts alkaline detergent solution results in a cleaner that cannot deterge calcium soap-grease.

For optimum detergency, the ratio of hexylene glycol to aqueous alkaline detergent solution should be 3.75 to 10 parts hexylene glycol to 100 parts alkaline detergent solution by volume. The concentration of the aqueous alkaline detergent solution should be 7.5%, weight to volume, as given in Examples I to IV; this concentration may be varied from 6.5 to 8.0%, weight to volume. The ratio of dipropylene glycol to aqueous alkaline detergent solution should be 10 to 15 parts dipropylene glycol to 100 parts alkaline detergent solution by volume.

The ingredients comprising the alkaline detergent solution may vary as follows in grams per 100 ml. of solution:

	Range-grams
60 Sodium metasilicate pentahydrate -----	2.24-2.76
Trisodium phosphate dodecahydrate -----	2.18-2.68
Primary sodium phosphate monohydrate ----	0.78-0.96
Sodium sulphate -----	up to 0.71
65 Tetrasodium salt of ethylenediaminetetraacetic acid -----	up to 0.71
Anionic surfactant (100% active) -----	0.38-0.47
Nonionic surfactant (100% active) -----	0.34-0.42

70 It will be evident to those skilled in the art that the compositions of this invention are not limited to the details of the foregoing illustrative examples, and that changes may be made in the types and amounts of alkaline salts, neutral builders, chelating agents, anionic-nonionic surfactant mixtures and glycols.

What is claimed is:

1. A cleaning composition consisting of the following ingredients:

	Grams	
(a) sodium metasilicate pentahydrate	2.24- 2.76	5
(b) trisodium phosphate dodecahydrate	2.18- 2.68	
(c) primary sodium phosphate monohydrate	.78-96	
(d) sodium sulphate	up to .71	
(e) tetrasodium salt of ethylenediamine-tetraacetic acid	up to .71	10
(f) sodium oleate, 100% active	.38- .47	
(g) nonylphenoxypolyethyleneoxy ethanol having 30 moles of ethylene oxide per mole of nonyl phenol	.34- .42	15
(h) water to make 100 ml.		
(i) hexylene glycol (per 100 ml.)	.ml.. 3.75-10.0	

2. A cleaning composition consisting of the following ingredients:

	Grams	
(a) sodium metasilicate pentahydrate	2.59	20
(b) trisodium phosphate dodecahydrate	2.51	
(c) primary sodium phosphate monohydrate	0.90	
(d) sodium sulphate	0.67	
(e) sodium oleate	0.44	25
(f) nonylphenoxypolyethyleneoxy ethanol having 30 moles of ethylene oxide per mole of nonyl phenol	0.39	
(g) water to make 100 ml.		
(h) hexylene glycol (per 100 ml.)	.ml.. 3.75	30

3. A cleaning composition consisting of the following ingredients:

	Grams	
(a) sodium metasilicate pentahydrate	2.76	35
(b) trisodium phosphate dodecahydrate	2.34	
(c) primary sodium phosphate monohydrate	0.90	
(d) sodium keryl benzene sulphonate being 40% active	1.11	
(e) polyoxyethylene octyl phenol having 9 to 10 moles of ethylene oxide per mole of octyl phenol	0.39	40
(f) water to make 100 ml.		
(g) hexylene glycol (per 100 ml.)	.ml.. 5	

4. A cleaning composition consisting of the following ingredients:

	Grams
(a) sodium metasilicate pentahydrate	2.24
(b) trisodium phosphate dodecahydrate	2.18
(c) primary sodium phosphate monohydrate	0.78
(d) sodium sulphate	0.58
(e) sodium dodecyl sulphate	0.38
(f) 30 mole ratio ethylene oxide adduct of decyne-4,7-diol	0.34
(g) water to make 100 ml.	
(h) hexylene glycol (per 100 ml.)	.ml.. 3.75

5. A cleaning composition consisting of the following ingredients:

	Grams
(a) sodium metasilicate pentahydrate	2.76
(b) trisodium phosphate dodecahydrate	2.68
(c) primary sodium phosphate monohydrate	0.96
(d) tetrasodium salt of ethylenediaminetetraacetic acid	0.71
(e) sodium dodecyl sulphate	0.47
(f) 30 mole ratio ethylene oxide adduct of decyne-4,7-diol	0.42
(g) water to make 100 ml.	
(h) hexylene glycol (per 100 ml.)	.ml.. 3.75

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