

1

3,793,221

THICKENED ACID CLEANER

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9 Claims

ABSTRACT OF THE DISCLOSURE

A thickened acid cleaner concentrate composition comprising an aqueous hydrochloric acid, an organic acid, e.g. oxalic, a nonionic surfactant, an anionic surfactant and water is useful in cleaning vehicles such as railroad rolling stock equipment without subsequent neutralization.

BACKGROUND

(1) Field of the invention

This invention relates to thickened acid cleaner composition and method of applying the composition to obtain exterior cleaning of vehicles (such as railroad rolling stock) without subsequent neutralization.

(2) Description of the prior art

Use of acid in cleaning compositions is known, for instance, U.S. Pat. 2,257,467 discloses a solidified acid composition for cleaning toilet bowls and the like wherein the composition consists of sodium silicate, water and hydrochloric acid. Another acid cleaner is disclosed in U.S. Pat. 3,271,319 wherein it is taught that stains can be removed from glass surfaces by the use of an acid cleaner consisting of water, hydrofluoric acid, a carboxymethylcellulose thickener and a small amount, usually less than 1 percent, of an alkyl sulfate or alkyl aryl sulfonate wetting agent. A still more recent patent, U.S. Pat. 3,622,391, teaches removing aluminide coatings from cobalt base or nickel base superalloys by the use of a hydrofluoric acid and water composition which permissibly includes a low foaming or nonfoaming wetting agent. It is further disclosed that the composition can be thickened by adding a condensation product of ethylene oxide with a molecular weight of 4,000 and gum tragacanth. However, the use of this composition requires a follow-up neutralization with an alkali solution followed by water rinsing.

Mineral acids have also been used in cleaning compositions as a defoamer. This technique is illustrated in U.S. Pat. 3,650,965 wherein the foaming qualities of nonionic surfactants for food industry cleaning can be reduced by the use of an organic acid coupled with a mineral acid such as phosphoric acid, the acid component being more than the surfactant component.

It has also been known to clean transportation equipment such as trains, boxcars and the like by the use of an acid cleaner to remove siliceous soils followed by an alkaline cleaner to remove organic and oily soils then finally followed by water rinsing.

SUMMARY OF THE INVENTION

In accordance with this invention there is provided a thickened acid cleaner concentrate composition comprising:

- (1) An aqueous hydrochloric acid in an amount from about 15 to about 40 weight percent;
- (2) An organic acid selected from the group consisting of oxalic, tartaric, citric and mixtures thereof in an amount from about 1 to about 6 weight percent;
- (3) A nonionic surfactant in an amount from about 7 to about 23 weight percent;

2

(4) An anionic surfactant in an amount from about 1 to about 7 weight percent; and

(5) Water in an amount from about 76 to about 24 weight percent.

5 All weight percents being based on a total composition. Provided that said nonionic surfactant and said anionic surfactant when taken together constitute from about 10 to about 30 weight percent of said composition and said nonionic surfactant constitutes from about 75 to about 90 10 weight percent of the combined weight of the nonionic and anionic surfactants.

The concentrate when diluted with 1 to 5 parts of water per part of concentrate is effectively used to remove siliceous and/or oily soils from metal vehicles without 15 a subsequent alkaline rinsing by flowing on a continuous coat of the cleaner, allowing the cleaner to remain on the surface of the vehicle for a period of time followed by a simple rinsing with water under impingement force pressure.

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DESCRIPTION OF THE PREFERRED EMBODIMENT

The hydrochloric acid employed in this invention is of course an aqueous solution inasmuch as hydrogen chloride is a gas that is not suitable for convenient handling in laboratory and factory. In dealing with the term hydrochloric acid or aqueous hydrochloric acid it is meant commercially available concentrated hydrochloric acid which typically has an acid value of 36 to 37 percent by weight. Furthermore, it is within the scope of this invention to use as a partial replacement, that is up to but no more than 50 percent by volume of hydrochloric acid, an equal volume amount of concentrated sulfuric acid or phosphoric acid. For the purpose of this invention sulfuric acid is considered to be the readily commercially available acid having a concentration of about 96% by weight. While phosphoric acid is readily available commercially in several acid strengths it is convenient to use and handle 75% phosphoric acid, and for the purpose of this invention phosphoric acid will be understood to have a concentration of 75% by weight. In view of the amounts of water which are also added to the cleaner concentrate of this invention, the hydrogen ion concentration variation between the foregoing mineral acids is not critical. However, it should be pointed out that the use of sulfuric acid and/or phosphoric acid as partial replacement for the hydrochloric acid of this invention is not favored for more than economic reasons.

50 For instance, sulfuric acid introduces the formation of siliceous sulfate salts which are more difficult to remove in the washing process. Large volume usage of the cleaner concentrate of this invention containing phosphoric acid will result in accumulation of phosphate salts which are undesirable from an ecological balance viewpoint. However, owing to the peculiarities of the soil to be removed and availability of acids at any given instance small amounts of either or both sulfuric acid and phosphoric acid can be used as part of the hydrochloric acid component of this invented composition. On a weight percent basis the acid cleaner of this invention will contain from about 15 to about 40 percent acid and more preferably the acid content will be from about 20 to about 30 weight percent.

65 The second component of the invented composition is an organic acid, preferably oxalic, tartaric, citric or mixtures thereof in an amount from about 1 to about 6 weight percent and more preferably in an amount from about 2 to about 4 weight percent. The organic acid suitable for use in this invention is characterized by an ability of chelating iron such that no more than about 3.5 parts of acid are required to chelate one part of iron.

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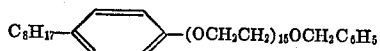
Furthermore, the organic acid or should we say chelating acid for iron must be soluble in the completed cleaner composition of this invention. It has been found that oxalic acid dihydrate, tartaric acid, and citric acid meet these requirements.

The particular surfactants employed in the invented composition in addition to having a cleaning effect also exhibit unusual thickening properties for this composition which were entirely unexpected. Therefore the surfactants of this invention are doubly critical. The nonionic surfactant is present in an amount from about 7 to about 23 weight percent of the final composition and more preferably in an amount from about 12 to 18 weight percent.

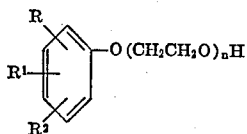
The nonionic surface active agents which are advantageously employed in the compositions of the invention are generally the polyoxyalkylene adducts of hydrophobic bases wherein the oxygen/carbon atom ratio in the oxyalkylene portion of the molecule is greater than 0.40. Those compositions which are condensed with hydrophobic bases to provide a polyoxyalkylene portion having an oxygen/carbon atom ratio greater than 0.40 include ethylene oxide, butadiene dioxide and glycidol, mixtures of these alkylene oxides with each other and with minor amounts of propylene oxide, butylene oxide, amylene oxide, styrene oxide, and other higher molecular weight alkylene oxides. Ethylene oxide, for example, is condensed with the hydrophobic base in an amount sufficient to impart water dispersibility or solubility and surface active properties to the molecule being prepared. The exact amount of ethylene oxide condensed with the hydrophobic base will depend upon the chemical characteristics of the base employed and is readily apparent to those of ordinary skill in the art relating to the synthesis of oxyalkylene surfactant condensates.

Typical hydrophobic bases which can be condensed with ethylene oxide in order to prepare nonionic surface active agents include mono- and polyalkyl phenols, polyoxypropylene condensed with a base having from about 1 to 6 carbon atoms and at least one reactive hydrogen atom, fatty acids, fatty amides and fatty alcohols. The hydrocarbon ethers such as the benzyl or lower alkyl ether of the polyoxyethylene surfactant condensates are also advantageously employed in the compositions of the invention.

Among the suitable nonionic surface active agents are the polyoxyethylene condensates of alkyl phenols having from about 6 to 20 carbon atoms in the alkyl portion and from about 5 to 30 ethenoxy groups in the polyoxyethylene radical. The alkyl substituent on the aromatic nucleus may be octyl, diamyl, n-dodecyl, polymerized propylene such as propylene tetramer and trimer, isocetyl, nonyl, etc. The benzyl ethers of the polyoxyethylene condensates of monoalkyl phenols impart good properties to the compositions of the invention and a typical product corresponds to the formula:



Higher polyalkyl oxyethylated phenols corresponding to the formula:



wherein R is hydrogen or an alkyl radical having from about 1 to 12 carbon atoms, R¹ and R² are alkyl radicals having from about 6 to 16 carbon atoms and n has a value from about 5 to 30 are also suitable as nonionic surface active agents. A typical oxyethylated polyalkyl phenol is dinonyl phenol condensed with 14 moles of ethylene oxide.

Other suitable nonionic surface active agents are co-generic mixtures of conjugated polyoxyalkylene com-

pounds containing in their structure at least one hydrophobic oxyalkylene chain in which the oxygen/carbon atom ratio does not exceed 0.40 and at least one hydrophilic oxyalkylene chain in which the oxygen/carbon atom ratio is greater than 0.40.

Polymers of oxyalkylene groups obtained from propylene oxide, butylene oxide, amylene oxide, styrene oxide, mixtures of such oxyalkylene groups with each other and with minor amounts of polyoxyalkylene groups obtained from ethylene oxide, butadiene dioxide, and glycidol are illustrative of hydrophobic oxyalkylene chains having an oxygen/carbon atom ratio not exceeding 0.40. Polymers of oxyalkylene groups obtained from ethylene oxide, butadiene dioxide, glycidol, mixtures of such oxyalkylene groups with each other and with minor amounts of oxyalkylene groups obtained from propylene oxide, butylene oxide, amylene oxide and styrene oxide are illustrative of hydrophilic oxyalkylene chains having an oxygen/carbon atom ratio greater than 0.40.

Further suitable nonionic surface active agents are the polyoxyethylene esters of higher fatty acids having from about 8 to 22 carbon atoms in the acyl group and from about 5 to 30 ethenoxy units in the oxyethylene portion. Typical products are the polyoxyethylene adducts of tall oil, rosin acids, lauric, stearic and oleic acids and the like. Additional nonionic surface active agents are the polyoxyethylene condensates of higher fatty acid amines and amides having from about 8 to 22 carbon atoms in the fatty alkyl or acyl group and about 10 to 30 ethenoxy units in the oxyethylene portion. Illustrative products are coconut oil fatty acid amides condensed with about 5 to 30 moles of ethylene oxide.

Other suitable polyoxyalkylene nonionic surface active agents are the alkylene oxide adducts of higher aliphatic alcohols and thioalcohols having from about 8 to 22 carbon atoms in the aliphatic portion and about 5 to 30 oxyalkylene portion. Typical products are synthetic fatty alcohols, such as n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-hexadecyl, n-octadecyl and mixtures thereof condensed with 5 to 30 moles of ethylene oxide, a mixture of normal fatty alcohols condensed with 8 to 20 moles of ethylene oxide and capped with benzyl halide or an alkyl halide, a mixture of normal fatty alcohols condensed with 5 to 30 moles of a mixture of ethylene and propylene oxides, a mixture of several fatty alcohols condensed sequentially with 2 to 20 moles of ethylene oxide and 3 to 10 moles of propylene oxide, in either order; or a mixture of normal fatty alcohols condensed with a mixture of propylene and ethylene oxides, in which the oxygen/carbon atom ratio is less than 0.40 followed by a mixture of propylene and ethylene oxides in which the oxygen/carbon atom ratio is greater than 0.40 or a linear secondary alcohol condensed with 3 to 30 moles of ethylene oxide, or a linear secondary alcohol condensed with a mixture of propylene and ethylene oxides, or a linear secondary alcohol condensed with a mixture of ethylene, propylene, and higher alkylene oxides.

Of the foregoing described nonionic surface active agents or surfactants, a particularly preferred group is the polyethylene oxide condensates of alkyl phenols, particularly those having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branch chain configuration with ethylene oxide, the ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. This group of surfactants is exemplified by octylphenoxy polyethoxyethanol.

The second component of the surfactant system of this invented composition is an anionic surfactant which is present in an amount from about 1 to about 7 weight percent and more preferably in an amount from about 2 to about 3 percent.

Anionic synthetic non-soap detergents can be broadly described as organic sulfuric and sulfonic acid reaction

products having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. (Included in the term alkyl is the alkyl portion of higher acyl radicals.) Important examples of the synthetic detergents which form a part of the preferred compositions of the present invention are those obtained by sulfating the higher alcohols (C_8 - C_{13} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, including those of the types described in United States Letters Patent Nos. 2,220,099 and 2,477,383 (the alkyl radical can be a straight or branched aliphatic chain), alkyl glyceryl ether sulfonates, especially those ethers of the higher alcohols derived from tallow and coconut oil; coconut oil fatty acid monoglyceride sulfates and sulfonates; sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g. tallow or coconut oil alcohols) and about 1 to 6 moles of ethylene oxide; sulfuric acid and sulfonic acid esters of the reaction product of one mole of a higher fatty oil (e.g. coconut or castor oil) and about 1 to 6 moles of ethylene oxide; alkyl phenolethylene oxide ether sulfate with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain from 8 to about 12 carbon atoms; the reaction product of fatty acids esterified with isethionic acid where, for example, the fatty acids are derived from coconut oil; fatty acid amide of a methyl tauride in which the fatty acids, for example, are derived from coconut oil; and others known in the art, a number being specifically set forth in United States Letters Patent Nos. 2,486,921, 2,486,922 and 2,396,278. While less preferred the sodium and potassium salts of the foregoing sulfonic and sulfuric acid and/or ester anionic surfactants can also be used. The foregoing anionic surfactants are further exemplified in McCutcheon's Detergents & Emulsifiers, 1972 Annual, Allured Publishing Corporation, Ridgewood, N.J.

Particularly suited for the process and composition of this invention are the alkyl or aryl sulfonic acid anionic surfactants exemplified by a linear alkyl benzene sulfonic acid.

When taken together in considering the foregoing nonionic and anionic surfactants, it is critical to the success of this invention that the total amount of surfactant present constitute from about 10 to about 30 weight percent of the total cleaner composition and that the nonionic portion of the total surfactant portion be from about 75 to about 95 weight percent.

The final component of the invented cleaning composition is water which is present in an amount from about 76 to about 24 percent by weight and preferably in an amount from about 74 to about 45 weight percent.

In addition to the foregoing ingredients, as is well known in the detergent arts, to the cleaning composition can be added such things as dyes, perfumes, corrosion inhibitors and the like which do not detract from the present invention.

The foregoing acid thickened cleaner concentrate composition is diluted with water at the point of use to obtain the final cleaning composition. This dilution is preferably about 3 parts of water for each part of cleaner; however, dilution ratios of from about 1 part to about 9 parts of water per part of cleaner concentrate are satisfactory.

The compositions of this invention are prepared by standard well-known open kettle mixing techniques known in the industry. A convenient charge schedule for preparation of the composition at room temperature would be to charge the water to the vessel, dissolve in the organic acid, followed by the nonionic surfactant, then the anionic surfactant and finally the hydrochloric acid. Should it be desired to add other optional modifiers to the composition such as dyes, perfumes and inhibitors they can be added as convenient during the preparation of the composition.

The thickened acid cleaner concentrate after dilution is flowed unto the vehicle to be cleaned in an amount to obtain physical coverage of the vehicle so that a thin but continuous film is obtained. No brushing, scrubbing or other similar effort is required. The cleaner is allowed to remain at least one minute and preferably five minutes, however, up to 30 minutes is satisfactory when the vehicle is cleaned during cold weather. It is an advantage of the present composition that even if the water component of the composition evaporates during the period of application the cleaner can still be successfully rinsed afterwards. Rinsing is achieved by the use of water being sprayed on the vehicle with impingement force and is most conveniently achieved by simply passing the vehicle through the spray rinse. For locomotives a water delivery rate of 150 to 200 gallons per minute and at a pressure of 100 to 200 pounds per square inch is satisfactory. Preferably, the rinse will be applied at an angle starting at one end of the locomotive and sweeping forward to the other end and then reversing the angle and sweeping backward to the point of beginning. While the type of vehicle being washed will dictate the type of equipment being used, the acid cleaner composition of this invention is suitable for trucks and trailers, busses, airplanes, railroad engines, box-cars, passenger cars, cabooses, off-road equipment and similar equipment.

The acid cleaner composition of this invention avoids many of the problems associated with prior art cleaning compositions. For instance, the previously used inert thickeners presented problems in removing the thickener residue after the washing, contributed to dry down problems and the simple disposal problem of the thickener residue after it was removed from the cleaned vehicle. Dry down of course refers to the drying of the cleaner film prior to its removal. It is recognized of course that the acid cleaner can be used with water of any hardness in contrast to alkaline cleaners which are dependent upon a certain degree of water softness in order to obtain desirable effects. In contrast, the present composition with its novel arrangement of surfactants has increased cleaning efficiency, requires no alkaline afterwards, avoids the physical handling problem of the inert thickener residues and additionally facilitates the removal of the organic and oily road soils from the water while the water is in the holding tanks and ponds prior to being discharged into the natural waterways.

The practice of this invention is illustrated by, but not limited by the examples given below. Unless otherwise noted all parts or percents are parts or percents respectively by weight.

EXAMPLE I

To an open kettle mixing vessel was charged 54 parts of water and then 3 parts of oxalic acid dihydrate was dissolved therein. Then 14 parts of octylphenoxy polyethoxyethanol (Triton X-100 trademark), a nonionic surfactant of the ethoxylated monohydric alcohol type was added. With continuing mixing 2.5 parts of linear alkyl benzene sulfonic acid anionic surfactant of the alkane sulfonate type (Calsoft LAS-99 trademark) was blended in. Finally 26.5 parts of 37% hydrochloric acid was added. The completed thickened acid cleaner was then discharged from the mixing vessel.

The foregoing concentrate was diluted with 3 volumes of water and stirred to obtain a uniform mixture. The acid cleaner composition was then applied to a dirty locomotive by flowing on in contrast to the prior art teaching of misting on acid cleaners so that the locomotive had a very thin continuous coating of acid cleaner. Approximately 3 gallons were applied to the locomotive. The cleaner was allowed to remain on the locomotive for approximately 5 minutes. The locomotive was then rinsed by driving the locomotive forward through a fixed spray at a speed of 5 to 8 miles an hour and then reversing the locomotive and bringing it back through the fixed sprays once more so that the water was applied at two different

angles. The water pressure and delivery rate was 200 gallons of water per minute at 200 pounds per square inch. When dry the locomotive was uniformly clean, free of residual siliceous road soils and oily road soils, had no streaks or spots left from the washing and the painted surface was unaffected by the wash treatment.

EXAMPLE II

In this example the effectiveness of various mineral acids are compared. In each case the cleaning concentrate was prepared by the method of Example I. The cleaning ability was determined by laboratory cleaning of metal coupons under controlled replica conditions.

Ingredient	Composition (expressed in percent by weight) of—			
	A	B	C	D ¹
Hydrochloric acid, 20° Be.....	30.0	15.0	15.0	
Sulfuric acid, 50%.....		15.0		30.00
Phosphoric acid, 50%.....			15.0	
Oxalic acid.....	3.0	3.0	3.0	3.0
Nonionic surfactant of Example I.....	14.0	14.0	14.0	14.0
Anionic surfactant of Example I.....	2.5	2.5	2.5	2.5
Water.....	50.5	50.5	50.5	50.5
Totals.....	100.0	100.0	100.0	100.0

¹ Comparative.

The coupons were cleaned of siliceous and oily soils at room temperature by flowing on a thin film of each cleaner after dilution as indicated below. After 10 minutes the coupons were inspected for dry down, i.e. loss of wet look, rinsed twice and evaluated for cleaning. The cleaning or soil removal was rated on a scale of 0 to 10 with 10 being completely clean in all respects. A rating less than 7 is considered to be unsatisfactory. The results are tabulated below:

	Composition of—			
	A	B	C	D ¹
Concentrated cleaner:				
Dry down.....	No....	No....	No....	No....
Cleaning rate.....	10....	7....	10....	5....
Diluted 1:4 with water:				
Dry down.....	No....	No....	No....	No....
Cleaning rate.....	9....	5....	8....	4....
Diluted 1:9 with water:				
Dry down.....	Yes....	Yes....	Yes....	Yes....
Cleaning rate.....	7....	4....	6....	0....

¹ Comparative.

Ingredient:	Composition of—			
	A	B	C	D
Hydrochloric acid, 20° Be.....	30.0	30.0	30.0	30.0
Oxalic acid.....	3.0			
Citric acid.....		3.0	5.0	
Tartaric acid.....				5.0
Nonionic surfactant of Example I.....	14.0	14.0	14.0	14.0
Anionic surfactant of Example I.....	2.5	2.5	2.5	2.5
Water.....	50.5	50.5	50.5	50.5
Total.....	100.0	100.0	100.0	100.0
Cleaning rating:				
Concentrated.....	10	9	10	10
Diluted 1:4 with water.....	9	8	9	9
Diluted 1:9 with water.....	7	6	7	7

In the foregoing cleaning test each coupon after 10 minutes application was free of dry down.

EXAMPLE IV

Following the procedures of Example II additional compositions containing various surfactants and amounts were prepared to further illustrate the advantages of the present invention. The formulations and evaluations are tabulated below.

	Compositions of—						
	Of the invention				Comparative		
	A	B	C	D	E	F	G
Hydrochloric acid, 20° Be.....	30.0	30.0	30.0	30.0	30.0	30.0	30.0
Oxalic acid.....	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Nonionic:							
A.....	14.0			14.0	8.5	14.0	5.0
B.....		14.0					
C.....			14.0				
Anionic:							
D.....	2.5	2.5	2.5		8.0		2.5
E.....				4			
Water.....	50.5	50.5	50.5	49.0	50.5	53.0	59.5
Total.....	100.0	100.0	100.0	100.0	100.0	100.0	100.0

NOTE:
Nonionic A=The nonionic of Example I.
Nonionic B=Ethoxylated fatty alcohol having an ethylene oxide content of about 60% (Plurafac A-26 trademark).
Nonionic C=Coconut oil ethoxylated with 5 moles ethylene oxide (Amldox C5 trademark).
Anionic D=The anionic of Example I.
Anionic E=Sulfonated castor oil (80% active) (Monopole Oil trademark).

	Composition of—						
	Of the invention				Comparative		
	A	B	C	D	E	F	G
Concentrated cleaner:							
Dry down.....	No....	No....	No....	No....	No....	No....	No....
Cleaning rating.....	10....	10....	10....	10....	8....	9....	7....
Diluted 1:4 with water:							
Dry down.....	No....	No....	No....	No....	Yes....	Yes....	Yes....
Cleaning rating.....	9....	9....	9....	9....	6....	7....	5....
Diluted 1:9 with water:							
Dry down.....	(1)....	(1)....	(1)....	(1)....	(2)....	(2)....	(2)....
Cleaning rating.....	Yes....	Yes....	Yes....	Yes....	Yes....	Yes....	Yes....
Cleaning rating.....	7....	7....	7....	7....	0....	0....	0....

¹ Dry but with no residue.

² Dry with objectionable residue.

EXAMPLE III

Following the procedure of Example II, additional compositions of this invention were prepared and evaluated. In this example the various organic acids were compared. The formulations and evaluations are tabulated below.

From the foregoing Examples II, III and IV it will be seen that the cleaner concentrate of this invention is suitable for dilution with up to nine volumes of water. However, this dilution is more desirable when dealing with lightly soiled vehicles rather than the more heavily soiled

vehicles. For the more heavily soiled vehicles a dilution with up to five volumes of water is preferred. While dilutions as low as one volume of water are satisfactory, the most preferred general purpose dilution is about three volumes of water.

EXAMPLE V

An invented U shaped drive through cleaner for trucks and trailers was charged with 10 gallons of the cleaner concentrate of Example I and 30 gallons of tap water. A dirty road soiled tractor with an aluminum tank trailer attached to it were driven through the unit as the diluted cleaner composition was applied. At the end of about five minutes the tractor-trailer unit was given a pressure water rinse. The blue paint and windows of the tractor cab were clean and bright. The aluminum surface on the trailer was bright but not etched. No gas was generated on the surface or etching and whitening of the surface observed in contrast to what happens when typical aluminum brighteners are used. The results were considered excellent by the commercial terminal operator.

Similar results are obtained on other vehicles such as off the road equipment when cleaned in the manner disclosed in the foregoing example.

The foregoing examples and methods have been described in the foregoing specification for the purpose of illustration and not limitation. Many other modifications and ramifications will naturally suggest themselves to those skilled in the art based on this disclosure. These are intended to be comprehended as within the scope of this invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A thickened acid cleaner concentrate composition consisting essentially of:

- (1) an aqueous hydrochloric acid in an amount from about 15 to about 40 weight percent,
 - (2) an organic acid selected from the group consisting of oxalic, tartaric, citric acid and mixtures thereof in an amount from about 1 to about 6 weight percent,
 - (3) a nonionic surfactant in an amount from about 7 to about 23 weight percent,
 - (4) an anionic surfactant in an amount from about 1 to about 7 weight percent, and
 - (5) water in an amount from about 76 to about 24 weight percent;
- all weight percents being based on the total composition,
- provided that the said nonionic surfactant and the said anionic surfactant when taken together constitute from about 10 to about 30 weight percent of said composition and

said nonionic surfactant constitutes from about 75 to about 90 weight percent of the combined weight percent of nonionic and anionic surfactants.

2. The composition according to claim 1 wherein the aqueous hydrochloric acid contains at least 50 weight percent aqueous hydrochloric acid and the remaining acid is selected from the group consisting of hydrochloric acid, sulfuric acid and phosphoric acid.

3. The composition according to claim 2 wherein all the acid is aqueous hydrochloric acid.

4. The composition according to claim 1 wherein the organic acid is oxalic acid.

5. The composition according to claim 1 wherein the nonionic surfactant is an alkyl or alkylaryl polyether alcohol.

6. The composition according to claim 1 wherein the anionic surfactant is an alkyl or alkylaryl sulfonic acid.

7. The composition according to claim 1 wherein said aqueous hydrochloric acid is in an amount from about 20 to about 30 weight percent, said organic acid is in an amount from about 2 to about 4 weight percent, said nonionic surfactant is in an amount from about 12 to 18 weight percent, said anionic is in an amount from about 2 to about 3% and said water is present in an amount from about 74 to about 45 weight percent.

8. The composition according to claim 7 wherein said aqueous acid is all aqueous hydrochloric acid, said organic acid is oxalic acid, said nonionic surfactant is an alkylaryl polyether alcohol and said anionic surfactant is an alkyl sulfonic acid containing from 8 to 20 carbon atoms.

9. A thickened acid cleaner composition comprising about one to nine parts of water per part of thickened acid cleaner concentrate composition according to claim 1.

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