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LIQUID ABRASIVE CLEANSER

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This application is a continuation-in-part of my U.S. patent application Serial No. 38,754, filed June 27, 1960.

The present invention relates to abrasive cleansers. More particularly, it relates to abrasive cleaners in the form of pourable liquids.

In accordance with the present invention, a liquid abrasive cleanser consists essentially of a stable aqueous suspension of about 45 to 60% of a water-insoluble abrasive having a particle size such that about 99% thereof passes through a 200 mesh sieve, about 2 to 4% of water-soluble detergent selected from the group consisting of anionic and cationic detergent salts, about 3 to 7% of a condensate of a higher fatty acid monoethanolamide with from about 2 to 3 moles of ethylene oxide, said higher fatty acid containing from about 10 to 18 carbon atoms, and about 25 to 45% water, said liquid cleanser being pourable at room temperature and having an apparent viscosity between about 7,000 and 25,000 centipoises.

The physical character of the liquid abrasive cleanser of the present invention is that of a liquid in which the undissolved solids are stably suspended, the viscosity of the liquid being sufficiently low that the cleanser is readily pourable at room temperature, i.e., about 70° F., both at the time when the cleanser is made and after it has aged at room temperature for periods on the order of several, e.g. 3 months. As used herein, the term "stable suspension," refers to a dispension of undissolved solid particles in a liquid medium, the dispersion being of such nature that the solid particles do not settle to the bottom of the container in which the cleanser is packaged and form a hard, non-redispersible cake, but rather remain suspended throughout the entire liquid medium during quiescent aging for an extended period of time, e.g. at least 90 days at room temperature and 2 days at 140° F. Thus the present cleanser is free from visible caking and does not require shaking in order to achieve uniformity in the course of normal storage and/or use.

The compositions of the present invention are characterized by an apparent viscosity between about 7,000 and 25,000 centipoises. It has been found that liquid cleansers within this range of viscosity are sufficiently fluid that the bulk or body of the cleanser drains readily from the walls of suitable household-type dispensers during use and handling thereof and yet are sufficiently viscous that on application to a static vertical surface such as may be found in kitchen sinks, bathroom walls, and the like, droplets or a heavy film of the cleanser remains on such a surface at the point of application without substantial run-off until such time as it is convenient to scour the surface. Likewise, the instant cleanser will adhere without drippage to the underside of horizontal surfaces and to ceilings. Thus it may be seen that as compared to a conventional powdered abrasive cleanser or a less viscous liquid cleanser which do not remain on a vertical or the underside of horizontal surfaces, the present liquid abrasive cleansers are highly advantageous in that they remain at any desired work location. On the other hand, as contrasted with a thickened paste or other non-pourable form, the instant pourable liquid cleansers are of sufficiently low viscosity to permit ready handling and dispensing in liquid form, to disperse quickly in water when contacted therewith, and to be easily completely flushed and washed with water away from any surface on which they have been deposited.

The liquid abrasive cleansers of the present invention have also been found to be characterized by extremely effective grease soil removal, highly effective lathering in both soft and hard water, and rapid removal of all kinds of soils from glass, vitreous, woodwork, painted, enameled and metal surfaces such as aluminum ware, copper bottoms, and the like, with effective polishing action and virtually no scratching action. The cleanser is also effective for removing soil from the hands and from automobile tires, for removal of wax from waxed surfaces, and a variety of other applications. The instant compositions also possess the distinctive and highly desirable feature of readily achieving a stable, characteristic viscosity upon being subjected to suitable shearing action at the time of their manufacture, with the result that they are stable and that their viscosity does not change or drift during aging.

The particle size or fineness of the water-insoluble abrasive employed in the instant liquid cleansers influences the cleansing ability, scratchiness and the stability of the fluid suspension. For a proper balance of these characteristics, the abrasive is preferably of a particle size such that about 99% thereof passes through a 200 mesh sieve, although coarser material (i.e. 99% through 100 mesh) or finer material may be used. The abrasive may be selected from a large group of well known materials including inter alia synthetic alumina, corundum, volcanic ash, diatomaceous earth, bentonite, feldspar, pumice and mixtures thereof; however it is preferred to employ siliceous abrasives and more specifically silica as the abrasive in the present compositions.

The water-insoluble abrasive is employed in the compositions of the present invention in an amount of approximately 45 to 60% by weight.

Liquid abrasive cleansers in accordance with the present invention also preferably contain a water-soluble inorganic alkaline buffer salt in an amount from about 1 to 3%. These salts, which for the most part are salts of weak acids with alkali metal bases, are characterized by a pH in dilute aqueous solution (1%) of from about 5.0 to about 12.0. Examples of suitable such salts include trisodium phosphate, disodium phosphate, sodium carbonate, tetrasodium pyrophosphate, tetrapotassium pyrophosphate, pentasodium tripolyphosphate, borax, sodium silicate such as sodium silicate having an Na_2O to SiO_2 ratio of 1:2.35, and sodium sesqui carbonate. The presence of these inorganic salts facilitates the preparation of a liquid product of the desired stability and viscosity characteristics.

The liquid abrasive cleanser compositions of the present invention further contain from about 0.5 to 4.0% and preferably about 1.5 to 2% of a detergent selected from the group consisting of anionic and cationic detergent salts, a preferred detergent being a water-soluble higher alkyl benzene sulfonate detergent salt wherein the alkyl group contains from about 10 to 16 carbon atoms. Examples of this preferred detergent salt are alkali metal and triethanolamine salts of alkyl aryl sulfonic acids, the commercial sodium salt of tetrapropylene benzene sulfonic acid, the triethanolamine salt of dodecyl benzene sulfonic acid, and the sodium salt of pentapropylene benzene sulfonic acid. Other suitable detergent salts comprise water-soluble anionic sulfated and sulfonated detergent salts containing a hydrophobic alkyl moiety of from 10 to 18 carbon atoms such as higher alkyl sulfate, e.g. sodium lauryl sulfate, and higher fatty acid monoglyceride sulfates such as the sodium salt of the monosulfate of coconut oil fatty acid monoglyceride, soaps such as the potassium soap of mixed oleic and coconut oil fatty

acids, and cationic detergents such as dialkyl dimethyl ammonium chloride or bromide in which the alkyl groups are derived from to allow fatty acids by reduction thereof. If desired, other appropriate water-soluble detergents such as ampholytic or polyethoxylated non-ionic types may also be employed in whole or in part as the detergent constituent.

In addition to its customary foaming and detergent action during use of the final composition, the detergent component of the instant liquid abrasive cleanser serves as a viscosity adjusting agent and influences the solids-suspending characteristics of the product. Thus, as the proportion of detergent is increased throughout the specified range, both the viscosity and abrasive suspending powers of the present liquid cleansers increase.

Another essential constituent of the instant compositions is a condensate of a higher fatty acid monoethanolamide with from 2 to about 3 moles of ethylene oxide, the higher fatty acid containing from about 10 to 18 carbon atoms. These condensates are exemplified by the condensation product of the monoethanolamide of coconut oil fatty acids with two moles of ethylene oxide, and the condensation product of lauric monoethanolamide with two moles of ethylene oxide. If desired, analogous products in which there is present a substantial proportion C_{18} carbon-atom fatty acids or 3 to 4 carbon-atoms hydroxyalkyl amine radicals may be substituted in compatible amounts, although the most preferred polyethoxyethanol fatty amide condensates are those of two moles of ethylene oxide with the monoethanolamide of mixed saturated higher fatty acids containing 12 to 14 carbon atoms. The low melting point of these mixed condensates is particularly beneficial in that they are readily handled and incorporated in the instant liquid products even though insoluble in water per se. The condensate which is present in an amount from about 3 to 7% by weight of the composition, is a primary thickening and viscosity adjusting agent present in the system. In addition to viscosity control the instant condensate appears to contribute to the present liquid cleanser highly beneficial properties not conferred by a wide variety of other viscosity-adjusting agents. Thus, the instant condensates not only increase the viscosity of the system, but they render it extremely stable, i.e. once formulation and processing is completed, the viscosity of the instant liquid cleansers remain remarkably constant and free of "drift" on aging. In addition, the instant condensate-containing cleansers exhibit improved stability towards chemical decomposition on aging over a wide range of pH values, facilitating the preparation of liquid cleansers having a pH as high as 12.5. The condensates also serve to increase substantially the suspending power of the instant compositions for undissolved solids (e.g. abrasive particles) and to contribute improved grease soil removal and foaming and detergency to the finished product.

Yet another essential constituent of the present liquid abrasive cleansers is water, which comprises from about 25 to 45% by weight of the final product. In the presence of the preferred water-soluble inorganic alkaline buffer salt mentioned hereinabove, the present aqueous product will have a characteristic pH between about 5.0 and 12.0, although suitable products may be prepared at a pH as low as 1.5 when the product contains an acidic material such as tridecyl benzene sulfonic acid.

Further in connection with the matter of pH, it has been found unexpectedly that the liquid suspensions of the present composition may be rendered more highly resistant to separation into a plurality of liquid layers by suitable adjusting of the pH of the system as desired such as by adjustment to a range of from about 5.0 to 10.5, and accordingly a superior liquid product of such pH adjusted for improved stability is considered a highly preferred embodiment of the invention. A further advantage of such compositions is a reduced tendency towards distortion of the walls of polyethylene dispensers in which the product is packaged.

An additional preferred constituent of the present liquid cleanser is copper phthalocyanine which is a water dispersible green pigment and which has been found to be highly effective in amounts as low as about 0.002% by weight. In addition to desired coloring effects it may desirably modify other properties such as by increasing the viscosity of the present liquid systems depending upon their particular composition. Suitably this pigment is used in amounts on the order of up to about 0.01% and higher, preferred proportions being about 0.004 to 0.008%.

The scouring cleanser compositions of the present invention may also contain as a balance of its constituents a wide variety of optional water-soluble and water-insoluble adjuvants including oxidative or reductive bleaching and/or stain removing agents, e.g., sodium perborate, sodium thioglycolate, oxalic acid, potassium monopersulfate, sodium hydrosulfite and sodium sulfite, sodium hypochlorite, dyes and pigments, crysteine, organic sequestering agents such as ethylene diamine tetraacetic acid and its salts, polyvinylpyrrolidone, organic solvents such as deodorized kerosene, essential oils, germicides and bactericides such as hexachlorophene, lanolin, clays such as bentonite and attapulgite, fluorescent dyes, silicones, organic phosphate esters such as sodium lauryl orthophosphate, melamine, N-chlorinated melamine, betaine, and the like. The resulting compositions may be packaged in a variety of containers or dispensers, such as glass bottles, metal cans, and the like, but it is particularly preferred to dispense these compositions from pressure propelled dispensers in which the propelling pressure is obtained by virtue of the presence of a propellant gas or by manual compression of flexible or resilient walls, e.g. a polyethylene or polypropylene squeeze bottle.

The following examples are given additionally to illustrate the nature of the invention and it will be understood that the invention is not limited thereto. In these examples, as in the remainder of the specification and claims, proportions indicated are by weight unless otherwise specified, viscosities are apparent viscosities determined using a Brookfield Viscometer Model No. LVF with a No. 4 spindle at 6 r.p.m., and the term "coloring" refers to a water dispersible commercial green pigment consisting of 33% copper phthalocyanine and 67% extender (dextrin).

Example I

A liquid abrasive cleanser having an apparent viscosity of about 17,000 centipoises has the following composition:

	Parts
Silica	55.865
Water	31.007
Trisodium phosphate, dodecahydrate, granular	3.851
Tridecylbenzene sulfonate, sodium salt (as aqueous slurry containing 54% solids, the solids consisting of 88% organic sulfonate and 12% sodium sulfate)	4.925
Condensation product of the monoethanolamide of coconut oil fatty acids with two moles of ethylene oxide	4.137
Perfume	0.200
Coloring	0.015
	100.000

The pH of this product is 11.2.

The silica used in this formulation is of such particle size that 100% passes a 60 mesh sieve, a maximum of 0.5% is retained on a 100 mesh sieve, at least 99.3% passes through a 200 mesh sieve, and maximum of 94% passes through a 325 mesh sieve.

8.5 fluid ounces of the composition of this example are packaged in a polyethylene "squeeze bottle" dispenser

in the form of a vertical cylinder having a base or diameter of about 2 inches and a height of about 6½ inches. The top of the container is provided with a spout carrying a snap-on cap which opens to expose an opening at the end of the spout which has a cross sectional area of about 4 square millimeters. On squeezing of the side walls of the container (which walls are flexible being approximately 1/16 of an inch thick), the cleanser is dispensed in the form of a stream or jet of fluid which readily adheres to bathtube sidewall surfaces and tiled bathroom walls and ceilings. On the other hand, the composition is sufficiently fluid that on inversion, it readily drains toward the spout of the dispenser thereby facilitating complete emptying of the container during use.

Example II

The composition of Example I is packaged in conventional aerosol dispensers with liquefied gaseous propellants as follows:

	Parts
Composition of Example I	94.2
Trichloromonofluoromethane	5.4
Dichlorodifluoromethane	0.4

The dispenser is sealed, being equipped with a valve of the type known as whipped cream valve, which requires inversion of the can and sidewise pressure on the valve for dispensing of product. The product of this example dispenses from such a container as a foamy stream which readily adheres to vertical ceramic surfaces without rapid drainage or run-off and which, when contacted with water or a wet cloth for purposes of scouring, readily disperses throughout the water employed.

Example III

The composition of Example I is placed in a conventional aerosol dispenser equipped with a top mounted valve and a siphon tube, and is pressurized with nitrogen to a pressure of 100 pounds per square inch. On operation of the valve, the liquid abrasive cleanser is ejected in the form of a stream which readily adheres to virtually any surface to which it is applied.

Examples IV–VII

	(In Parts by Weight)			
	Example IV	Example V	Example VI	Example VII
Silica of Example I	53.700	56.720	56.515	56.800
Water	29.900	31.425	31.400	30.775
Trisodium phosphate dodecahydrate	3.700	3.910	3.910	3.810
Condensation product of the monoethanolamide of coconut oil fatty acids with two moles of ethylene oxide	5.835	4.230	3.060	3.900
Tridecylbenzene sulfonate of Example I	6.650	3.600	5.000	5.400
Perfume	0.200	0.100	0.100	0.100
Coloring	0.015	0.015	0.015	0.015

Example VIII

A liquid abrasive cleanser containing the condensation product of lauric monoethanolamide with two moles of ethylene oxide has the following formula:

	Parts by weight
Silica of Example I	55.865
Water	31.007
Trisodium phosphate, dodecahydrate	3.851
Tridecyl benzene sulfonate of Example I	4.925
Condensation product of lauric monoethanolamide with two moles of ethylene oxide	4.137
Perfume	0.200
Coloring	0.015
	100.000

Examples IX–XI

The following formulations are also stable liquid abrasive cleansers:

	Examples in Parts by Weight		
	IX	X	XI
Silica [1]	55.0	55.0	55.0
Water	35.6	37.8	35.3
Potassium Oleate	3.9		
Cetyl Dimethyl Ethyl Ammonium Chloride		3.0	
Sodium lauryl sulfate			3.8
Condensation product of the monoethanolamide of coconut oil fatty acids with two moles of ethylene oxide	3.4	3.1	4.7
Trisodium phosphate	2.1	1.1	1.2
	100.0	100.0	100.0
Viscosity, centipoises	13,500	23,000	8,000

[1] Silica particle size is at least 99% thru 200 mesh sieve.

Examples XII–XIII

The following formulations are liquid cleanser compositions containing various abrasives and having desired stability:

	Examples in Parts by Weight	
	XII	XIII
Alumina (99% thru 200 mesh sieve)	55.0	
Pumice (99% thru 200 mesh sieve)		50.0
Water	37.8	40.0
Potassium oleate	3.9	3.9
Condensation product of the monoethanolamide of coconut oil fatty acids with two moles of ethylene oxide	3.3	3.3
Trisodium phosphate		2.8
	100.0	100.0
Viscosity, centipoises	12,000	20,000

Although the present invention has been described with reference to particular embodiments and examples, it will be apparent to those skilled in the art that variations and modifications of this invention can be made and that equivalents can be substituted therefor without departing from the principles and true spirit of the invention.

What is claimed is:

1. A liquid abrasive cleanser consisting essentially of a stable aqueous suspension of about 45 to 60% of a water-insoluble inorganic abrasive having a particle size such that about 99% thereof passes through a 200 mesh sieve, about 2.0 to 4% of a water-soluble detergent selected from the group consisting of organic anionic and cationic detergent salts, about 3 to 7% of a condensate of a higher fatty acid monoethanolamide with about 2 to 3 moles of ethylene oxide, said higher fatty acid containing from about 10 to 18 carbon atoms, and about 25 to 45% water, said liquid cleanser being pourable at room temperature and exhibits an apparent viscosity between about 7,000 and 25,000 centipoises, said percentages being by weight of the composition.

2. A liquid abrasive cleanser as set forth in claim 1 having an adjusted pH from 1.5 to 12.0.

3. A liquid abrasive cleanser as set forth in claim 1 having an adjusted pH from 5.0 to 10.5.

4. A liquid abrasive cleanser as set forth in claim 1 which contains at least about 0.002% of copper phthalocyanine.

5. A liquid abrasive cleanser consisting essentially of about 45 to 60% of a water-insoluble inorganic abrasive having a particle size such that about 99% thereof passes through a 200 mesh sieve, about 2.0 to 4% of water-soluble higher alkyl benzene sulfonate detergent salt wherein the alkyl group contains from about 10 to 16 car-

bon atoms, about 3 to 7% of a condensate of a higher fatty acid monoethanolamide with about 2 to 3 moles of ethylene oxide, said higher fatty acid containing from about 10 to 18 carbon atoms, and about 25 to 45% water, said liquid cleanser being a stable suspension of undissolved solids in a fluid liquid, which suspension is pourable at room temperature and having an apparent viscosity between about 7,000 and 25,000 centipoises, said percentages being by weight of the composition.

6. A liquid abrasive cleaner consisting essentially of a stable aqueous suspension of about 45 to 60% of a water-insoluble inorganic abrasive having a particle size such that about 99% thereof passes through a 200 mesh sieve, about 2.0 to 4% of water-soluble higher alkyl benzene sulfonate detergent salt wherein the alkyl group contains from about 10 to 16 carbon atoms, about 3 to 7% of a condensate of a higher fatty acid monoethanolamide with about 2 to 3 moles of ethylene oxide, said higher fatty acid containing from about 10 to 18 carbon atoms, and about 25 to 45% water, said liquid cleanser being pourable at room temperature and having an apparent viscosity between about 7,000 and 25,000 centipoises, said percentages being by weight of the composition.

7. A liquid abrasive cleanser consisting essentially of a stable aqueous suspension of about 45 to 60% of a water-insoluble inorganic abrasive having a particle size such that about 99% thereof passes through a 200 mesh sieve, about 1 to 3% of a water-soluble inorganic alkaline buffer salt, about 2.0 to 4% of a water-soluble organic, synthetic detergent selected from the group consisting of anionic and cationic detergent salts, about 3 to 7% of a condensate of a higher fatty acid monoethanolamide with about 2 to 3 moles of ethylene oxide, said higher fatty acid containing from about 10 to 18 carbon atoms, and about 25 to 45% water, said liquid cleanser being pourable at room temperature and having an apparent viscosity between about 7,000 and 25,000 centipoises, said percentages being by weight of the composition.

8. A liquid abrasive cleanser consisting essentially of a stable aqueous suspension of about 45 to 60% of silica having a particle size such that at least 99% thereof passes through a 200 mesh sieve, about 1 to 3% of a water-soluble inorganic alkaline buffer salt, about 2.0 to 4% sodium salt of tridecyl benzene sulfonate, about 3 to 7% of the condensate of two moles of ethylene oxide with one mole of the monoethanolamide of coconut oil fatty acids, abut 0.002 to 0.01% of copper phthalocyanine, and about 25 to 45% water, said liquid cleanser being pourable at room temperature and having an apparent viscosity between about 7,000 and 25,000 centipoises, said percentages being by weight of the composition.

9. A liquid abrasive cleanser as set forth in claim 8 wherein said buffer salt is trisodium phosphate.

10. A liquid cleanser adapted to be dispensed as a pressure-propelled stream of fluid, on to static vertical surfaces, which contains a liquid abrasive cleanser consisting essentially of a stable aqueous suspension of about 45 to 60% of silica having a particle size such that at least 99% thereof passes through a 200 mesh sieve, about 1 to 3% of a water-soluble inorganic alkaline buffer salt, about 2.0 to 4% sodium salt of tridecyl benzene sulfonate, about 3 to 7% of the condensate of two moles of ethylene oxide with one mole of the monoethanolamide of coconut oil fatty acids, and about 25 to 45% water, said liquid cleanser being pourable at room temperature and having an apparent viscosity of about 17,000 centipoises, whereby on application to a static vertical surface, a heavy film of said cleanser remains thereon without substantial run-off, said percentages being by weight of the composition.

11. A liquid cleanser adapted to be dispensed as a pressure-propelled stream of fluid, on to static vertical surfaces, which contains a liquid abrasive cleanser consisting essentially of a stable aqueous suspension of about 45 to 60% of a water-insoluble abrasive having a particle size such that about 99% thereof passes through a 200 mesh sieve, about 2.0 to 4% of a water-soluble detergent selected from the group consisting of synthetic organic anionic and cationic detergent salts, about 3 to 7% of the condensate of two moles of ethylene oxide with one mole of the monoethanolamide of coconut oil fatty acids and about 25 to 45% water, said liquid cleanser being pourable at room temperature and having an apparent viscosity between about 7,000 and 25,000 centipoises, whereby on application to a static vertical surface, a heavy film of said cleanser remains thereon without substantial run-off, said percentages being by weight of the composition.

References Cited by the Examiner

UNITED STATES PATENTS

2,002,613	5/35	Orthner et al.	
2,275,049	3/42	Keller	252—89 XR
2,655,480	10/53	Spitzer et al.	252—305 XR
2,892,795	6/59	Dalton	252—128 XR
2,920,045	1/60	Hearn et al.	252—137
2,945,815	7/60	Diaz	252—131
2,991,296	7/61	Scherr	252—152 XR

FOREIGN PATENTS

547,503	10/57	Canada.

OTHER REFERENCES

Venkataraman: Synthetic Dyes (Academic Press Inc.), publishers, N.Y. (1952), vol. II (pages 1118–1125).

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