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LIQUID SCOURING CLEANSER FOR REMOVING ORGANIC STAINS FROM HARD SURFACES

William Jerome Gangwisch, Jersey City, N.J., assignor to Colgate-Palmolive Company, New York, N.Y., a corporation of Delaware

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This invention relates to an acidic liquid scouring cleaner containing a particular chelating material which, in the present cleanser composition, acts to remove quickly organic stains which may be adhering to hard surfaces, e.g., porcelain sinks.

Scouring cleansers have been employed to remove rust stains and other discolorations from sinks. Bleaching agents also have found utility in converting colored stains to non-colored water soluble form. Liquid scouring cleansers, containing dispersed and suspended solid abrasive materials have been produced and by use of particular surface active agents and emulsifiers have been made of acceptable storage stability, so that they do not separate or settle to an objectionable extent. Despite these accomplishments, it has been difficult to produce a liquid scouring cleanser containing effective acidic and bleaching constituents. This has been attributed to the delicate balance of surface active agents, hydrotropes, emulsifiers, thickeners, salts, abrasive powder and aqueous medium, which had been found to be required to make a satisfactory stable cleanser of this type, which balance is readily disrupted by the addition of bleaching or highly acidic materials. The present invention provides a stable liquid bleaching composition in which a bleaching and chelating agent is present with suspended abrasive in an acidic aqueous medium.

In accordance with the present invention, such a stable and effective liquid scouring cleanser for removing stains from hard surfaces comprises about 0.2 to 5% of oxalic acid, 30 to 75% of very finely divided silex, 1 to 7% of an ionic synthetic organic detergent having a group which is a higher alkyl radical of 12 to 18 carbon atoms or a polymeric lower alkylene oxide chain containing 12 to 18 carbon atoms, 0.5 to 10% of a nonionic thickening agent having surface active and emulsifying properties and 15 to 60% water. It is preferred to have water soluble oxalate present and if present, the ratio of oxalic acid to oxalate should be within the range of 1:1 to 100:1. The pH of the resulting product should be from 1 to 3.8. Such a liquid scouring cleanser has the advantages of being non-settling, of regulatable viscosity, of stable and effective bleaching action, despite relatively long periods of storage and of being surprisingly rapid in its cleaning and bleaching action on persistent stains which are not readily removed by other scouring cleansers or conventional bleaches.

The oxalic acid employed is preferably chemically pure material but technical oxalic acid is also acceptable. It is preferably present with a water soluble oxalate, preferably an alkali metal oxalate, such as sodium or potassium oxalate, in such proportion as to form a buffered bleaching composition having a pH within the range of 1 to 3.8.

The very finely divided silicon dioxide, which is the principal active abrasive material in the present compositions should be of a particle size which will give effective cleaning action but which will not objectionably scratch the surfaces to be cleaned and bleached with the present products. It is preferred to employ silex of which at least 99.9% passes through a 60 mesh sieve (U.S. Standard Sieve Series) and in which less than 1% by weight of particles fail to pass through a 100 mesh sieve, with 83 to 93% through a 200 mesh sieve. Essentially,

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such silex is of particle diameter 99.9% less than 250 microns, 99.0% less than 150 microns and 83 to 93% less than 75 microns. For gentler cleaning, about 99% of the particles, by weight, may be smaller than 75 microns, with none greater than 150 microns in diameter. Of course, if the scouring cleanser is not intended for use on polished or delicate surfaces and scratching is not objectionable, other slightly larger particles sizes may be present, e.g., more particles up to about 250 microns, providing that the bulk of such particles will be small enough so that they can be effectively suspended in bleaching liquid abrasive cleansers.

The ionic synthetic organic detergent is preferably an anionic detergent, although in some cases cationic detergents, too, may be employed. Cationic detergents should not usually be present together with anionic materials, with which they often tend to react. Among the anionic detergents it is preferred to employ the water soluble higher alkyl aryl sulfonates in which the alkyl group contains from 12 to 18 carbon atoms, most preferably sodium tridecyl benzene sulfonate, in which the alkyl group is preferably a mixture of propylene tetramer and pentamer. Such detergent makes a product of exceptional stability. Other suitable synthetic anionic detergents include the water soluble sulfated and sulfonated detergent salts which contain a hydrophobic alkyl group of from 12 to 18 carbon atoms such as higher alkyl sulfate, e.g., sodium lauryl sulfate; higher fatty acid monoglyceride sulfates, e.g., sodium coconut oil fatty acids monoglyceride sulfate; higher fatty acid amide of amino lower alkylene sulfonic acids, e.g., potassium salt of oleic acid amide of N-methyl taurine; higher alkyl sulfonates; mono- and di-salts of alpha sulfo fatty acids; sulfated ethoxylated alcohols and sulfated ethoxylated esters of higher fatty acids; and other detergent materials of equivalent actions. Instead of sulfuric reaction product detergents, those derived from phosphoric acid are also useful, among which are water soluble orthophosphoric acid esters of higher polyoxyalkylated alkyl phenols, e.g., disodium salt of mono phosphoric acid ester of nonyl phenol polyoxyethylene ethanol and the monosodium salt of the diester of phosphoric acid and nonyl phenol polyoxyethylene ethanol, the alkylene oxide chain being of about 6 ethylene oxides in length. Although not preferred constituents of the present cleansers, cationic detergents, such as di-alkyl di-methyl ammonium chloride or bromide in which the alkyl groups are derived from hydrogenated tallow fatty acids, may also be used. Other equivalent cationic detergents are also useful but, as was previously mentioned, it is highly preferable to employ the anionic detergents instead.

The nonionic thickening agent having emulsifying properties is preferably an ethoxylated alkylolamide. Such a compound is the condensation product of a higher monoethanolamide with ethylene oxide. Among the preferred materials of this type are those in which the higher fatty acid is of 12 to 18 carbon atoms, preferably derived from coconut oil, and the lower alkylene oxide is ethylene oxide and from about 2 to 6 ethylene oxide groups are present in a chain condensed with the alkylolamide. Also useful are the higher fatty acid alkylolamides in which the alkylol group is ethanol, the higher fatty acid is of 12 to 18 carbon atoms, preferably coconut oil fatty acids and other useful compounds are monoethanolamides. Of these two types of surface active and emulsifying thickeners, the ethoxylated compounds possess a greater stability, on storage in acidic media, and therefore are much preferred over the ordinary alkylolamides. Other nonionic thickening agents may also be found useful in the present products.

Although it is preferred to use deionized or distilled water so as better to control the identity of the composi-

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tions made and to improve their stability, due to the discovered compatible combination of the other constituents of the invented compositions it has been found possible to make stable liquid scouring cleansers having bleaching properties from tap waters of the usual hardnesses and impurity contents.

In addition to oxalic acid and water soluble oxalate, other compatible bleaching compounds and chelating agents may be used, e.g., ethylenediamine tetraacetic acid, as its tetrasodium salt and other organic acids, e.g., tartaric acids and tartrates. Other bleaching agents, such as the chlorinated materials, tend to be of poor stability in acidic media and usually should not be included in the invented compositions. It is preferred to employ silica as the sole abrasive material but other abrasives such as feldspar, talc, etc., may also be included with it. Mixtures of the synthetic detergents mentioned may be used and in some circumstances it will be found preferable to mix together different nonionic emulsifying thickeners.

The proportions of the disclosed constituents should be carefully regulated so as to obtain a product of most desirable stability and effectiveness. It has been found that in these compositions less than 0.2% of oxalic acid is not sufficiently effective as a chelating agent for bleaching and more than 5% thereof makes the product too strong for general use. Within the range mentioned, it is preferred to regulate the oxalic acid content so as to be from about 0.6 to 2%. The water soluble oxalate, present with the oxalic acid to maintain it at a useful operative pH, is most desirably present at a proportion between 0.2 and 1% and the ratio of water soluble oxalic acid to oxalate is preferably between 1:1.5 and 10:1, resulting in a pH from 1 to 3.8, most preferably about 1.35.

The proportion of synthetic organic detergent present is 1 to 7% by weight of the finished product and is preferably from 2 to 5% thereof. From 0.5 to 10% of non-ionic thickening emulsifier is useful and 1 to 3% is most satisfactory. Moisture content of the finished product is within the range of 15 to 60%, preferably 20 to 45%, and silex content is preferably 40 to 65%.

Compositions made according to this invention with the constituents described in the proportions given, have unusually stable storage characteristics and exhibit excellent chelating and bleaching potential. They are especially useful for cleaning porcelain or ceramic sinks and for removing organic stains which tend to adhere thereto, held to the porcelain by means of a metallic linking agent such as iron or copper. The abrasive constituent removes from the stained surface any coatings which may inhibit intimate contact of the chelating bleach with the stain. At the low pH range, the oxalic acid in water soluble oxalate system acts to attack both the organic and the linking metallic portion of the stain, the chelating function causing the metallic link to be broken and the reducing action of the oxalic acid effectively destroying the colorant in the stain. Such effective double acting stain removal activity has been observed even in the use of compositions which have been stored for periods greater than a year. This is considered unusual, since most bleaching agents do lose some of their activity in highly acidic media during storage. Physical stability of the liquid cleanser made is also obtained, in that the silex remains substantially suspended or can be effectively re-dispersed by simple shaking, if that is necessary at all. The use of other detergents, nonionic emulsifiers and bleaching agents, in place of those of this invention, has led to the production of unsatisfactory cleansers in which the components thereof tend to deteriorate on storage.

In addition to the described materials which are in the present liquid scouring cleansers, there may be added other adjuvants which are innocuous to the compounds in the invented composition and which contribute desirable properties to the product. Thus, perfumes, dyes,

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fluorescent materials, solvents, propellants (for making pressurized compositions) and compatible auxiliary materials for reinforcing the action of any of the required constituents may be added, providing they exhibit a satisfactory stability in the relatively minor proportions in which they would be employed.

The following examples illustrate compositions made according to this invention. They are illustrative and are not to be considered as limiting the scope of the claims.

Example I

Material:	Parts by weight
Oxalic acid -----	1.63
Sodium oxalate -----	0.34
Silix ¹ -----	57.63
Sodium tridecyl benzene sulfonate slurry ² --	7.11
Diethoxy coconut oil fatty acids monoethanolamide -----	1.63
Water -----	31.44
Pigment and perfume -----	0.22
	100.00

¹ 99.9% + through 60 mesh sieve, 99.0% + through 100 mesh sieve, 90% + through 200 mesh sieve.

² 47% sodium tridecyl benzene sulfonate, 7% sodium sulfate, 46% water.

An excellent liquid scouring cleanser of the above composition was made by adding the oxalic acid, sodium oxalate, perfume and colorant to the water at room temperature, and then serially adding, with agitation, the silix, detergent slurry and diethoxy coconut oil fatty acids monoethanolamide. Shearing agitation was maintained until a viscosity of 15,000 centipoises, as measured by a Brookfield Viscosimeter resulted. This viscosity is within the desirable range of about 7,000 to 25,000 centipoises, possible with the present compositions. The product obtained was a stable pourable suspension which maintains its stability and bleaching and sequestering powers for over a year of storage at normal ambient temperatures. At 140° F. it is stable for 50 days, remaining in homogeneous dispersion without decomposition or phase separation for that length of time.

The product was employed successfully in various household bleaching and scouring operations and removed inorganic (iron, copper) stains and organic (tea, grape juice) stains easily. In a tea stain removal test (on porcelain) adopted as a standard test for organic stain removal powers of scouring composition, the present composition removed 95% of the standard stain, compared to a lesser proportion removed by a well known chlorine releasing commercial scouring powder and none removed by a liquid cleanser which did not include the present buffered oxalate system.

Example II

Material:	Parts by weight
Oxalic acid -----	1.22
Sodium oxalate -----	0.76
Silix ¹ -----	57.47
Sodium tridecyl benzene sulfonate slurry ² --	7.10
Polyethoxy lauric monoethanolamide -----	1.83
Water -----	31.40
Dye and perfume -----	0.22
	100.00

See footnotes, Example I.

This product was made according to the method of Example I. It was an excellent stain removing liquid cleanser of 11,000 centipoises viscosity and pH of 2.0 stable for over 50 days at 140° F. and indefinitely at room temperature. In the standard tea stain removal test mentioned in Example I, 100% of the stain was removed in 30 seconds. After use this cleanser could be removed easily from the cleansed surface by light rinsing with water.

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Example III

Material:	Parts by weight
Sodium oxalate -----	0.54
Silex ¹ -----	60.57
Sodium tridecyl benzene sulfonate slurry ² --	2.14
Diethoxy cocomoethanolamide -----	2.35
Alkyl benzene sulfonate acid (detergent acid to form oxalic acid with the oxalate) -----	1.07
Water -----	33.11
Dye and perfume -----	0.22
	100.00

See footnotes, Example I.

This product, made as in Example I, was of viscosity of 19,000 centipoises and pH of 2.8. It was good for removing tea stains from a hard surface. It was stable indefinitely at room temperature and for more than 90 days at 140° F.

Example IV

Material:	Parts by weight
Sodium oxalate -----	2.09
Silex ¹ -----	59.07
Sodium higher alkyl benzene sulfonate ² ----	3.13
Diethoxy cocomoethanolamide -----	1.67
Tridecyl benzene sulfonic acid -----	1.56
Water -----	32.26
Dye, perfume -----	0.22
	100.00

See footnotes, Example I.

This product was made by the method described previously. It had a pH of 3.7, viscosity of 8,500 centipoises, was stable indefinitely at room temperature and for more than 80 days at 140° F. It was an effective cleanser with useful bleaching and chelating stain removal properties.

The above examples illustrate the invention but are not to be considered as limiting it. The scope of the invention is measured by the claims and equivalents to the claimed compositions.

What is claimed is:

1. A stable liquid scouring cleanser effective to remove organic stains from porcelain which comprises 0.2 to 5% of oxalic acid, 0.2 to 1% of a water soluble alkali metal oxalate selected from the group consisting of sodium and potassium oxalate, 30 to 75% of silex of particle size less than 250 microns, 1 to 7% of a higher alkyl benzene sulfonate in which the alkyl radical is of 12 to 18 carbon atoms, 0.5 to 10% of a polyethoxylated monoethanolamide of a fatty acid of 12 to 18 carbon atoms, in which 2 to 6 ethylene oxide groups are in the polyethoxy portion, and 15 to 60% water, of viscosity between about 7,000 and 25,000 centipoises and pH of 1 to 3.8, said percentages being by weight of the composition.

2. A stable liquid scouring cleanser effective quickly to remove organic stains from porcelain and other hard surfaces, which comprises 0.6 to 2% of oxalic acid, 0.2 to 1% of sodium oxalate, 40 to 65% of silex, having a particle size such that at least 99% thereof passes through a 100 mesh sieve, U.S. Standard Series, 2 to 5% of sodium tridecyl benzene sulfonate, 1 to 3% of polyethoxyetha-

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nolamide of coconut oil fatty acids, in which the polyethoxy chain is of 2 to 6 ethylene oxide groups and 20 to 45% of water, with a product viscosity between about 7,000 and 25,000 centipoises and a pH of 1 to 3.8, said percentages being by weight of the composition.

3. A stable and effective liquid scouring cleanser for removing stains from hard surfaces which comprises about 0.2 to 5% of oxalic acid, 30 to 75% of silex of particle size less than 250 microns, 1 to 7% of a water-soluble organic non-soap detergent selected from the group consisting of organic, synthetic anionic and cationic detergents, 0.5 to 10% of a nonionic amide thickening agent having surface active and emulsifying properties therefor selected from the group consisting of higher fatty acid ethanolamides and higher fatty acid polyethoxylated ethanolamides containing up to 6 ethylene oxide groups in the polyethoxy portion, the higher fatty acid radical of said amides having 12 to 18 carbon atoms, and 15 to 60% of water, said percentages being by weight of the composition.

4. A stable liquid scouring cleanser effective to remove organic stains from porcelain which comprises 0.2 to 5% of oxalic acid, 30 to 75% of silex of particle size less than 250 microns, 1 to 7% of a water-soluble organic non-soap detergent selected from the group consisting of organic, synthetic anionic and cationic detergents, 0.5 to 10% of a nonionic higher fatty acid ethanolamide having 12 to 18 carbon atoms in the higher fatty acid radical and 15 to 60% of water, said percentages being by weight of the composition.

5. A stable liquid scouring cleanser effective to remove organic stains from porcelain which comprises 0.2 to 5% of oxalic acid, 30 to 75% of silex of particle size less than 250 microns, 1 to 7% of a water soluble higher alkyl benzene sulfonate in which the higher alkyl radical is of 12 to 18 carbon atoms, 0.5 to 10% of a polyethoxylated ethanolamide, in which 2 to 6 ethylene oxide groups are in the polyethoxy portion and the ethanolamide is of a higher fatty acid containing 12 to 18 carbon atoms, and 15 to 60% water, said percentages being by weight of the composition.

References Cited by the Examiner

UNITED STATES PATENTS

2,629,696	2/53	Dodd et al.	252—136
2,672,449	3/54	Snell et al.	252—100
2,892,795	6/59	Dalton	252—128 XR
2,920,045	1/60	Hearn et al.	252—89

FOREIGN PATENTS

635,321	1/62	Canada.
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OTHER REFERENCES

"Alrosol," Technical Bulletin, Alrose Chemical Co. (1946), Providence, R.I. (page 3).

Zussman: "Metal Complexing Agents in Soap and Detergent Products," Soap and Sanitary Chemicals, November 1952, pages 79, 80, 81.

"Synthetic Detergents" by John W. McCutcheon, (1950), MacNair-Dorland Co. (page 381).

JULIUS GREENWALD, *Primary Examiner*.