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ABRASIVE CLEANING COMPOSITION

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The present invention relates to an abrasive cleaning composition exhibiting alkaline and acidic pH conditions in a predetermined order of succession in water, and to a process for preparing the same.

Scouring powders and similar abrasive compositions are well-known in the art. Such cleansers may contain alkaline inorganic salts for certain cleansing effects, particularly for grease removal. Cleaning compositions containing abrasive material and an acidic ingredient to obtain more effective removal of stains from metal surfaces have been proposed also. Heretofore, abrasive preparations containing both acidic and alkaline ingredients have not been made as articles of commerce. It would appear that the presence of both acidic and alkaline ingredients in one composition would result in a tendency of these materials to neutralize one another upon admixture with water such that separate and distinct alkaline and acidic cleansing properties would not be obtained thereby.

In accordance with the present invention, it has been discovered that there can be prepared an abrasive cleansing composition comprising essentially a mixture of a water-insoluble abrasive material, and an alkaline ingredient and an acidic ingredient, said composition exerting both alkaline and acidic cleansing properties in water in any desired order. More particularly, the present invention relates to an abrasive cleaning composition which upon admixture with water is adapted to yield an alkaline pH condition and an acidic pH condition to the resulting cleaning solution in a predetermined order of succession which comprises essentially a mixture of a water-insoluble abrasive material, a water-soluble alkaline ingredient which upon contact with water renders the solution alkaline, a water-soluble acidic ingredient which upon contact with water renders the solution acidic, one of the two latter ingredients dissolving sufficiently upon admixture of said composition with water so that the resulting cleansing solution initially has either an alkaline or acidic condition and the other ingredient being adapted to dissolve in an amount sufficient to subsequently convert said cleansing solution to the opposite pH condition. A preferred embodiment relates to a scouring cleanser containing a major proportion of a water-insoluble siliceous abrasive, and minor proportions of a water-soluble alkaline builder salt and a normally solid water-soluble acid, said acid having a coating of a water-dispersible material to retard the rate of solubility of said acid. Various other preferred embodiments will be apparent in the following description.

For convenience of illustration, the invention will be described particularly with respect to the composition yielding successive alkaline and acidic pH conditions though it is to be understood that compositions exhibiting the inverse order are within the scope of the invention. Where reference is made to either an alkaline or acidic pH condition in the specification and claims, it is intended that such condition be illustrated by a 20% slurry of the composition in water.

The ingredient which produces the abrasive characteristics primarily is a water-insoluble abrasive material in particulate form. These abrasive agents suitable for use in scouring powders and the like are well-known in the art and are generally siliceous materials. Suitable examples are silex, tripoli, pumice, volcanic ash, pumicite, bentonite, diatomaceous earth, feldspar, etc. and mixtures thereof. The abrasive may vary in hardness and particle size as desired with the mesh size of the particles varying from about 40 to about 400 generally, and preferably being not larger than 100 mesh, as determined on a U.S. standard sieve. The amount of the abrasive is variable but is usually a major proportion of the total solids (e.g. at least about 50%), and preferably about 60 to about 98% by weight.

Any water-soluble ingredient which yields an alkaline pH of above 7, preferably a pH of 8 to 12, to the aqueous solution or slurry may be employed in admixture with the abrasive. Such materials are known and abrasive compositions containing the same are disclosed in U.S. Patent No. 2,625,514, issued January 13, 1953. The alkaline materials are the water-soluble inorganic alkaline builder salts preferably, such as the alkali metal carbonates (e.g. sodium carbonate), the alkali metal phosphates (e.g. trisodium phosphate, tetrasodium pyrophosphate, sodium tripolyphosphate), the alkali metal silicates (e.g. sodium metasilicate) and the alkali metal borates (e.g. sodium borate). Any suitable base such as sodium and potassium hydroxide, and tetramethylammonium hydroxide may be employed also. It is preferred to use the normally solid alkaline salts and bases but, if desired, a normally liquid alkaline material may be employed by suitable combination with a solid carrier such as by adsorption upon diatomaceous earth, bentonite or the like. The alkaline ingredient may be used in any desired amount depending upon the specific ingredient, but there is used usually about ½ to about 25% and preferably about 1 to 15% by weight. These alkaline ingredients are used generally in the form of particles of any suitable size. The particle size of the alkaline ingredient is not critical and may correspond to the approximate particle size of the abrasive.

Any water-soluble acidic ingredient which will dissolve in the cleansing solution to yield an acidic pH of below 7, preferably a pH from 2 to 7, to the slurry may be employed in the product. In general, it is preferred to employ a normally solid acid or acid salt in particulate form. If desired, a normally liquid material may be employed by suitable combination with a solid carrier in particulate form, such as diatomaceous earth or bentonite. The particle size of the acidic material is not critical and it may be employed in any suitable size as illustrated for the abrasive. Examples of suitable materials are the organic acids such as tartaric acid, maleic acid, boric acid, glutamic acid, citric acid, acetic acid, oxalic acid, gluconic acid and its lactone, and the like. Suitable inorganic acids and acid salts such as sulfamic and phosphoric acids and sodium bisulfate may be employed also. These materials enhance the removal of tarnish and oxidant stains, particularly from metallic surfaces such as copper, aluminum, steel and the like during use of the product.

The acidic ingredient should be used in any amount sufficient to convert the alkaline solution to an acidic solution, preferably to a solution having a pH from about 2 to 5, when the quantity of acid has been dissolved or otherwise released in the cleansing solution. In general, it is preferred that the amount of acid be from about ½ to 25% and preferably from about 1 to 15% by weight. If a mixture containing the alkaline and acidic ingredients in powdered form are added to water, the two materials tend to neutralize one another such that the cleansing solution will have either an alkaline or an acidic pH condition depending upon the proportion and strength of the different ingredients. In order to obtain successive action of a separate and distinct nature it has been found that it is necessary to defer or retard the rate of solubility of one of these essential ingredients, preferably of the solid acid constituent. For example, this deferred acidification permits the user to utilize initially the alkaline properties of the product followed by use of the acidic properties of the product. Accordingly, the rate of solution of the acidic constituent is to be sufficiently depressed

to permit the alkaline builder on use to dissolve first. The acidic constituent must then be present in stoichiometric excess over the alkaline ingredient so that when it is dissolved or released after a predetermined time the pH of the cleansing solution is reduced to the desired acidic level.

The rate of solubility of the acidic constituent may be reduced in any suitable manner. It is preferred to coat the normally solid acid particles with a solution inhibitor such as a water-dispersible coating agent. The presence of such a film or coating upon the particles of the acid will inhibit and retard the solubility of the acid when the composition is admixed with water. The amount of the coating is not critical and may vary from a monomolecular film to a coating of any particular size depending upon the specific coating agent, its water-dispersibility and the particular time interval which is desired before the change in the pH condition of the aqueous cleaning solution. Thus, the predetermined time interval may be controlled so as to be a few seconds up to any point desired in the use of the product such as up to about 30 minutes. It is preferred that the change in pH occur from about 15 seconds to 15 minutes after the product is slurried in water.

Any suitable material may be used as the coating agent such as the higher fatty alcohols, preferably having 12 to 18 carbon atoms (e.g. lauryl alcohol, coconut fatty alcohol, cetyl alcohol, stearyl alcohol), mineral oil, the higher fatty acid amide compounds, preferably having 12 to 18 carbon atoms in the acyl radical (lauric acid and coconut acid and myristic acid primary amides and the corresponding monoethanolamides, isopropanolamides and diethanolamides) and their ethylene oxide reaction products having up to about 5 moles of ethylene oxide; the higher fatty acids, preferably having 12 to 18 carbons also such as stearic acid, palmitic acid, tallow fatty acids and the like. Other coating materials are the wax-like polymers of ethylene glycol such as "Carbowax 1500," "2025" and "4000," the soluble starches and dextrins and the like. These materials may have highly limited solubility in water to extreme water solubility but are effective to delay the solubility or release of the acid in the cleansing solution. The term "water-dispersible coating agent" or equivalent as used herein refers to agents of varying water solubility or dispersibility but which have been found to be dispersed or dissolved under conditions of use of the product. For example, organic materials such as lauryl alcohol and lauric acid amides and alkylolamides have limited water solubility but in the presence of organic detergent material tend to dissolve in the cleansing solution.

The coating agent may be applied to the particles of the acid in any suitable manner. It is preferred that the coating agent be dissolved, suspended or dispersed in an appropriate solvent or heated to molten form and then sprayed or atomized on the individual acid particles to form the desired coating. Any suitable solvent may be employed, such as a normally gaseous propellant in a pressure container. Examples are the normally gaseous low-molecular weight hydrocarbon and halogenated hydrocarbon propellants, such as propane, butane, halogenated ethanes and methanes. The propellants known as the "Freons" and "Genetrons" are suitable, examples being dichlorodifluoromethane and monochlorodifluoroethane. Other solvents or dispersing mediums such as ethanol, isopropanol and aqueous alcoholic mixtures may be suitably employed also. In this manner there may be obtained complete or incomplete coating or film on the surface of the acid particles as desired. Where the coating agent is normally solid, it will dry to a film, and where it is normally liquid it will be adsorbed or absorbed upon the surfaces of the particles. The coating material may be applied also in solid form to the surfaces of the acid particles by mixing the coating agent in powdered form with the acid particles by suitable means for mechanical admixture including tumbling in a rotary drum. When the final composition is slurried in water to form an aqueous slurry or solution, the water-soluble alkaline ingredient dissolves to form an alkaline solution. Since the acid particles are coated with lauryl alcohol or any other suitable coating as indicated, its rate of solution is sufficiently depressed to permit the alkaline builder to dissolve first. After a predetermined time, which may be controlled as desired by selection of the particular coating agent, the coating material disperses in the aqueous medium whereupon the acid is released and dissolves so that the pH is reduced to the desired acidic condition.

As indicated, the alkaline ingredient may be coated in the manner described above so that uncoated acid particles are permitted to ionize or dissolve initially forming an acidic condition followed by release of the alkaline ingredient after the coating has been removed sufficiently.

A more specific feature of this invention is that an organic surface-active detersive agent be present in the composition. Such organic detersive agents may be either anionic, cationic or non-ionic agents as described in U.S. Patent No. 2,625,514. Examples of suitable anionic detergents are the water-soluble soaps and sulfated and sulfonated synthetic detergents. More particularly, it is preferred to employ an alkyl benzene sulfonate detergent wherein the alkyl group has about 8 to 16 carbon atoms. Suitable examples are sodium decyl benzene sulfonate, sodium dodecyl and pentadecyl sulfonates wherein the dodecyl and pentadecyl groups are derived from a propylene polymer, and sodium keryl benzene sulfonate. Other suitable agents are the surface-active sulfated or sulfonated aliphatic compounds, preferably having 8 to 22 carbon atoms. Examples thereof are sulfuric acid esters of polyhydric alcohols incompletely esterified with higher fatty acids (e.g. coconut oil monoglyceride monosulfate), the long-chain pure or mixed higher alkyl sulfates (e.g. lauryl sulfate, coconut fatty alcohol sulfate), the higher fatty acid ethanolamide sulfates; the higher fatty acid amides of amino alkyl sulfonic acids (e.g. lauric acid amide of taurine), the higher fatty acid esters of isethionic acid and the like.

Suitable cationic detergents which may be employed are the long-chain alkyl quaternary ammonium compounds (e.g. cetyl quaternary ammonium salts). Suitable examples are cetyl trimethyl ammonium chloride, cetyl pyridinium chloride, and the like.

Various non-ionic agents may be employed also, such as the non-ionic polyalkylene oxide condensates with an aliphatic or aromatic hydrophobic group. Such agents have about 5 to 50 alkylene oxide groups usually. Examples are the polyethylene oxide condensate with alkyl phenols having 8 to 20 carbons in the alkyl group such as Igepal CA and CO, the polyethylene oxide esters with higher fatty acids such as tall oil or lauric acid condensed with about 16 or 20 ethylene oxide groups, the polyethylene oxide condensates with higher aliphatic alcohols such as lauryl, myristyl, oleyl or stearyl alcohol with 6 to 30 moles ethylene oxide, and the like.

The anionic and cationic surface-active agents are used commonly in the form of water-soluble salts. For the anionic compounds the alkali metal and ammonium salts are preferred whereas for the cationic agents the chloride, sulfate and acetate and the like acid salts are employed commonly.

Any amount of the detersive compound may be employed which does not substantially adversely affect the desired characteristics of the product. In general, it is preferred that the detergent be present in amounts from about ½ to about 15% by weight and preferably from 1 to 10% by weight. It is preferred to employ the anionic and non-ionic surface-active agents in a form where these materials have been premixed with the alkaline builder salts. The mixture containing the detergent and alkaline salts in the form of an aqueous slurry may be subjected to the usual drying procedures in order to obtain a rela-

tively dry homogeneous product such as by drum drying or spray drying of the mixture in known manner.

The abrasive material, alkaline and acidic ingredients containing a coating upon one of the latter two materials are mixed in particulate form to produce a dry, cleansing powder. The ingredients are admixed mechanically by tumbling, fluidizing or the like in conventional soap powder mixers known in the art or by any other suitable means for mechanical admixture.

It is a further feature of the present invention that the product may contain a bleaching agent which results in effective bleaching action during use of the product. The bleaching agent may be incorporated into the product in any suitable manner, such as during or after the mixing of the essential ingredients. In general, bleaching agents are more effective in one pH condition than another. Since the product during use will form both acid and alkaline solutions, there will be obtained at some stage optimum conditions for a particular bleaching agent. If desired, the bleaching agent may be coated with any suitable material such as the coating agents previously described so that the bleaching agent is released in the same manner. Examples of suitable bleaching agents are the known oxygen and chlorine-releasing substances, such as sodium perborate, sodium, calcium and lithium hypochlorites, dichlorocyanuric acid, trichlorocyanuric acid, Chloramine T, dichlorodimethyl hydantoin and the like. The amount of bleaching agent is not critical but will be usually from about 0.01 to 25% of the product.

There may be incorporated in the product a suitable color indicator which would demonstrate to the consumer when the change from one pH condition to the other pH condition occurs or when a particular pH level is obtained during use. The quantity of indicator is not critical except that it should be capable of producing a detectable coloration to the cleansing solution. In general, the amount of color indicator will vary with the type of indicator but is usually from about 5 parts per million to 3% of the product. If methyl orange is employed, the color of the slurry initially is yellow when the acid is coated, but when the acid dissolves subsequently the cleansing solution turns red. Another suitable color indicator is bromo thymol blue which changes color from blue to yellow on conversion of the cleansing solution from an alkaline to an acid nature. The color indicator may be incorporated in any suitable manner such as by spraying it directly upon the particles at any suitable stage in the mixing operation. If the indicator is solid it may be dissolved or dispersed in a suitable aqueous or alcoholic solution in order to form a liquid solution for ease of application to the particles. When the indicator solution dries upon the particles the particles will then have a coating of dye which dissolves or disperses upon the initial admixture of the product with water. Other suitable dyes are phenol red, thymol blue, metacresol purple, etc.

Various known materials may be incorporated in the product also as desired. Suitable examples are minor amounts of anti-caking agents such as hydrated magnesium trisilicate, sodium carboxymethyl-cellulose, perfume, antiseptics, germicides, skin emollient materials and the like.

The following examples are illustrative of the present invention and it will be understood that the invention is not limited thereto. All proportions indicated are by weight unless otherwise specified.

Example I

A powdered sulfamic acid is pretreated to apply a coating to the particles as follows: 200 parts of the powdered sulfamic acid are tumbled in a Mason jar. Through an opening in the cover of the jar, a spray of a lauryl alcohol solution is introduced until 1 part of the lauryl alcohol has been deposited on the surface of the sulfamic acid powder. The spraying composition contains 30% lauryl alcohol dissolved in 70% of a 1:1 mixture of Freon-11 and 12 in a pressure resistant container.

An abrasive alkaline scouring cleanser is prepared by tumbling about 89 parts of silex particles, about 0.5 parts of sodium perborate powder and about 10.5 parts of an alkaline detergent material. This alkaline detergent material is a spray-dried product containing about 30% sodium dodecyl benzene sulfonate detergent, about 40% sodium tripolyphosphate, with the balance being primarily sodium sulfate. During this mixing operation, about 5 drops of methyl orange indicator are added slowly to obtain good distribution. About 6 parts of the coated sulfamic acid particles are added and the agitation is continued until the product is a uniform, homogeneous mixture.

When one volume of this composition is added to two volumes of water with mild agitation the resulting slurry turns a yellow color indicating that the product gives an alkaline reaction initially. After 2 minutes and 25 seconds the cleansing solution and the slurried produce change to a red color indicating an acidic reaction. The composition shows effective cleansing and bleaching properties during use.

In comparison a product prepared in similar manner except that uncoated powdered sulfamate acid particles are admixed with the alkaline scouring cleanser does not yield equivalent results. When the product is added to water with mild agitation, the color turns red immediately indicating that the product did not give an alkaline reaction at any time.

Example II

The procedure of Example I is repeated except that the lauric acid amide is applied similarly to the alkaline detergent particles and not to the sulfamic acid. The ingredients are mixed thereafter in the same manner and the resulting product exhibits initially an acidic reaction in water followed by an alkaline reaction.

Example III

The procedure of Example I is repeated using 240 parts of powdered sodium bisulfate in place of the 200 parts of sulfamic acid with similar results.

Example IV

Following the procedure of all of the above examples, the following coating materials are employed in place of the lauryl alcohol in Example I and the lauric acid amide in Example II with equivalent results: coconut fatty acid diethanolamide, lauric and stearic monoethanolamide, cetyl alcohol, stearyl alcohol, "Carbowax 1500" and "4000" and commercial stearic acid.

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. An abrasive cleaning composition which upon admixture with water is adapted to yield an alkaline pH condition and an acidic pH condition to the resulting cleaning solution in a predetermined order of succession which comprises a mixture of a major proportion of a water-insoluble siliceous abrasive material, about ½ to 25% by weight of a water-soluble alkaline inorganic builder salt which upon contact with water renders the solution alkaline, about ½ to 25% by weight of a water-soluble normally solid acid which upon contact with water renders the solution acidic, one of the two latter ingredients dissolving sufficiently upon admixture of said composition with water so that the resulting cleansing solution initially has one of said pH conditions and the other ingredient having a coating of water-dispersible

material resulting in a retarded rate of solubility so that it is not sufficiently soluble in said solution initially but subsequently dissolves in said solution to convert it to the other of said pH conditions.

2. An abrasive cleaning composition which upon admixture with water is adapted to yield an alkaline pH condition and an acidic pH condition to the resulting cleaning solution in a predetermined order of succession which comprises a mixture a major proportion of a water-insoluble siliceous abrasive material, a minor proportion from about ½ to 25% by weight of a water-soluble alkaline ingredient which upon contact with water renders the solution alkaline, and a minor proportion from about ½ to 25% by weight of a water-soluble acidic ingredient which upon contact with water renders the solution acidic, one of the two latter ingredients dissolving sufficiently upon admixture of said composition with water so that the resulting cleaning solution initially has one of said pH conditions and the other ingredient having a coating of a water-dispersible material to retard its initial solubility but being present in a stoichiometric excess so that it subsequently converts said cleaning solution to the other of said pH conditions.

3. An abrasive cleaning composition in accordance with claim 2 wherein said acid is sulfamic acid.

4. An abrasive cleaning composition in accordance with claim 2 wherein said coating is a higher fatty alcohol.

5. An abrasive cleaning composition in accordance with claim 2 which contains about ½ to 15% by weight of a water-soluble organic detergent.

6. An abrasive cleaning composition in accordance with claim 2 which contains about ½ to 25% by weight of a bleaching agent.

7. An abrasive cleaning composition in accordance with claim 2 which contains a color indicator whereby said composition upon admixture with water results in differently colored solutions in said alkaline and acidic pH conditions.

8. An abrasive cleaning composition which upon admixture with water is adapted to yield an alkaline pH condition and an acidic pH condition successively to the resulting cleaning solution which comprises a mixture of a major proportion of a water-insoluble siliceous abrasive material, about ½ to 25% by weight of a water-soluble inorganic phosphate salt which upon contact with water renders it alkaline, about ½ to 25% by weight of a water-soluble normally solid acid which upon contact with water renders it acidic, said acid having a coating of a water-dispersible material and said composition upon admixture with water yielding an alkaline pH condition in water which is subsequently converted to an acidic pH condition.

9. An abrasive cleaning composition in accordance with claim 8 which contains particles of sulfamic acid coated with said material.

10. An abrasive cleaning composition in accordance with claim 8 which contains about ½ to 25% by weight of sodium perborate.

11. An abrasive cleaning composition in accordance with claim 8 which contains a color indicator to indicate by color change when the cleaning solution is converted from said alkaline to said acidic pH condition.

12. An abrasive cleaning composition which upon admixture with water is adapted to yield an alkaline pH condition and an acidic pH condition successively to the resulting cleaning solution which comprises a mixture of a major proportion of a water-insoluble siliceous abrasive material, about ½ to 25% of a water-soluble inorganic alkaline builder salt which upon contact with the water renders the solution alkaline, about ½ to 25% by weight of water-soluble normally solid acid which upon contact with the water renders it acidic, said acid having a coating of a water-dispersible material to retard its rate of solubility, but being present in stoichiometric excess so that said composition upon admixture with water yields an alkaline pH condition initially which is subsequently converted to an acidic pH condition.

13. A method of preparing an abrasive cleaning composition characterized by a mixture of a major proportion of a water-insoluble siliceous abrasive material, a minor proportion from about ½ to 25% by weight of a water-soluble alkaline compound and a minor proportion from about ½ to 25% by weight of a water-soluble acidic compound which upon admixture with water is adapted to yield an alkaline pH condition and an acidic pH condition to the resulting cleaning solution in a predetermined order of succession which comprises coating with a water-dispersible compound one of the latter two ingredients to retard its rate of solubility in water, and admixing the resulting coated compound in an amount in stoichiometric excess with the other ingredient and with said abrasive to form a uniform mixture.

14. A method of preparing an abrasive cleaning composition characterized by a mixture of a major proportion of water-insoluble siliceous abrasive material, and minor proportions of about ½ to 25% by weight each of a water-soluble alkaline ingredient and a water-soluble acidic ingredient adapted to yield an alkaline pH condition and an acidic pH condition successively upon admixture with water which comprises treating said acidic ingredient to apply a coating of a water-dispersible material, and admixing the coated acidic material with said abrasive and alkaline material to form a homogeneous mixture.

15. A method in accordance with claim 14 wherein said acidic ingredient is a normally solid water-soluble acid.

16. A method in accordance with claim 14 which comprises admixing a color indicator with said mixture to indicate by color change when the resulting cleaning solution is converted from said alkaline to said acidic pH condition.

References Cited in the file of this patent

UNITED STATES PATENTS

284,494	Michaelis	Sept. 4, 1883
856,672	Best et al.	June 11, 1907
871,612	Nesfield	Nov. 19, 1907
980,936	Federer	Jan. 10, 1911
1,075,663	Meerbott	Oct. 14, 1913
1,854,235	Stoddard	Apr. 19, 1932
1,966,203	Gravell	July 10, 1934
1,989,765	Moss et al.	Feb. 5, 1935
2,034,361	Sutton	Mar. 17, 1936
2,196,901	Ham et al.	Apr. 9, 1940
2,228,483	Raeke	Jan. 14, 1941
2,308,992	Mertens	Jan. 19, 1943
2,430,233	Magill	Nov. 4, 1947
2,497,057	Pape et al.	Feb. 7, 1950
2,498,344	Rider et al.	Feb. 21, 1950
2,540,253	Gakenheimer	Feb. 6, 1951
2,578,270	Strain	Dec. 11, 1951
2,589,108	Mark	Mar. 11, 1952
2,625,514	Kirschenbauer	Jan. 13, 1953
2,763,618	Hendrix	Sept. 18, 1956

FOREIGN PATENTS

749,857	Great Britain	June 6, 1956