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- [54] **COMPLEXING ACID PRE-WASH
COMPOSITION AND METHOD**
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[57] **ABSTRACT**

A pre-wash composition adapted to be sprayed onto a soiled fabric before washing consisting essentially of from 1 to 20% by weight of an organic complexing acid, from 0 to 30% by weight of a surface active agent and from 99 to 50% by weight of water. The method for assisting the removal of soil from a fabric comprises spraying a soiled fabric with the above composition followed by laundering the same in a conventional manner.

18 Claims, No Drawings

COMPLEXING ACID PRE-WASH COMPOSITION AND METHOD

This invention relates to a pre-wash composition and a method for utilizing the same. More particularly, this invention relates to a pre-wash composition utilizing as its primary active ingredient an organic acid capable of complexing the stain-forming metallic ions in the soil.

Although organic acid solutions have a wide variety of uses including the removal of white casein type adhesives as disclosed in U.S. Pat. No. 3,551,230, the removal of fish odors and fish residue as in U.S. Pat. No. 3,650,968 and in the prevention of the yellowing of freshly spun synthetic and natural fibers as in U.S. Pat. Nos. 3,083; 3,383,350; 2,922,728 and 3,256,100 as well as the utilizations as a dishwashing rinsing aid, such as in U.S. Pat. No. 3,563,901 and also as salts of these acids as various builders for synthetic detergents, these materials have not been utilized as pre-washing agents which assist the subsequent cleaning properties of a detergent in removing stain forming materials.

The problem of metal ions which are present in various soils forming irremovable metal stains on clothing has plagued housewives and laundry operators for a long time. Prior attempts to remove these stains have centered on removal, rather than prevention, with the most common method being bleaching fabrics which are heavily soiled or stained.

Accordingly, it is within the above environment that the composition and process of the present invention was developed. Briefly, the composition of the present invention which allows for the effective sequestering of metal ions through a pre-wash composition, consists essentially of from 1 to 20% by weight of an organic complexing acid, from 0 to 30% by weight of a surface active agent and from 99 to 50% by weight of water, the process of the present invention comprising applying an effective amount of an organic complexing acid onto a fabric before washing.

It is, therefore, the primary object of the present invention to provide a novel method for pre-treating fabrics so as to assist the detergents in a subsequent washing cycle.

It is a further object of the present invention to provide a pre-wash composition which is especially well adapted for the removal of clays and other solids containing ferric and other ions which tend to stain the cloth.

It is a still further object of the present invention to provide a method which quickly and efficiently prevents any mineral staining and aids in the subsequent laundry removal of ground-in dirt.

Still further objects and advantages of the present invention will become more apparent from the following more detailed description thereof.

The process of the present invention comprises applying a solution comprising from 1 to 20% by weight of an organic complexing acid to a fabric and laundering the treated fabric.

The composition of the present invention consists essentially of from 1 to 20% by weight of an organic complexing acid, from 0 to 30% by weight of a surface active agent and from 99 to 50% by weight of water.

The composition of the present invention as utilized in the process of the present invention is an aqueous solution comprising from 1 to 20% and, preferably, from 5 to 15% and most preferable about 5% by weight of an

organic complexing acid selected from citric acid, succinic acid, tartaric acid, maleic acid, fumaric acid, adipic acid, and mixtures of these acids. Although any of the above acids may be utilized, in the process and composition of the present invention citric and tartaric acids are preferred, with citric acid being most preferred.

Although in conventional compositions and processes, the salts of these organic, complexing acids are often utilized with similar or equivalent results, the sodium salts of the above noted acids as well as the other alkaline and the alkaline earth salts of these acids are not effective in the composition and process of the present invention since these salts do not have the complexing properties necessary for the enhancement of the removal of the soil from the fabric. Accordingly, in the process and composition of the present invention, only the acids themselves and not their salts may be utilized.

Furthermore, only the organic complexing acids aid in the removal of these ions since the removal is not a function of pH as demonstrated by the inability of mineral acid solutions to effectively prevent staining from irremovable metal ions. Also, these latter acids are much too strong for continued use since they tend to degrade the fibers.

Although the solvent for the pre-wash composition utilized in the process of the present invention is normally water, the water may be mixed with up to 10% of various other materials, such as lower monohydric alcohols. However, these lower monohydric alcohols should be quite limited in their use and solutions of the complexing acids in water alone are preferred.

In addition to the water and the citric acid, the composition of the present invention may also include up to 30% of an optional non-ionic or anionic surface active agent. These surface active agents, if present, aid the complexing properties of the acids since the surfactants tend to disperse the acid through the soiled fabric. Of the various non-ionic and anionic surface active agents, those containing straight chains and those which are biodegradable are most preferred.

Representative non-ionic detergents include alkaryl polyglycol detergents such alkyl-phenol-ethylene oxide condensates (2-100 moles ethylene oxide), e.g., p-isooctyl phenol-polyethylene oxide (10 ethylene oxide units), long chain alcohol ethylene oxide condensation product (2-200 moles ethylene oxide), e.g., dodecyl alcohol-polyethylene oxides having 4 to 16 ethylene oxide units per molecule, polyglycerol monolaurate, glycol dioleate, sorbitan monolaurate, sorbitan monostearate, sorbitan monopalmitate, sorbitan monooleate, sorbitan sesquioleate, the condensation products of ethylene oxide with sorbitan esters of long chain fatty acids (Tweens), alkylolamides, amino oxide phosphine oxides, etc.

In addition to the above noted non-ionic detergents, anionic detergents may also be utilized in the composition and process of the present invention. Suitable anionic detergents include alkylbenzene-sulfonic acid and salts, having the formula alkyl-phenyl-SO₃-M, wherein alkyl is an alkyl radical of a fatty acid and M is hydrogen or an alkali metal, which compounds comprise a well known class of anionic detergents. Other suitable anionic detergents are the alkali metal salts of the higher alkyl and linear paraffin sulfonic acids and the alkali metal dialkylsulfosuccinates, e.g., sodium dioctylsulfosuccinate, and sodium dihexylsulfosuccinate.

sodium sulfoethylphthalate, sodium allyl-p-anisidine-sulfonate; sodium sodium tetradecanesulfonate; sodium diisopropylnaphthalenesulfonate; sodium octylphenoxymethoxyethylsulfonate, etc.; and the alkali metal alkyl sulfates.

Among the above noted alkylbenzene-sulfonic acid and salts thereof, there are included those which are biodegradable and which particularly characterized by a linear alkyl substituent of from C_{10} to C_{22} and preferably from C_{12} to C_{15} . It is, of course, understood that the carbon chain length represents, in general, an average chain length since the method for producing such products usually employs alkylating reagents of mixed chain length. It is clear, however, that substantially pure olefins as well as alkylating compounds used in other techniques can and do give alkylated benzene sulfonates wherein the alkyl moiety is substantially (i.e., at least 99%) of one chain length, i.e., C_{12} , C_{13} , C_{14} or C_{15} . The linear alkyl benzene sulfonates are further characterized by the position of the benzene ring in the linear alkyl chain, with any of the position isomers (i.e., alpha to omega) being operable and contemplated.

The linear alkyl benzene sulfonates are generally and conveniently prepared by sulfonating the corresponding alkyl benzene hydrocarbons which in turn may be prepared by alkylating benzene with a linear alkyl halide, a 1-alkene or a linear primary or secondary alcohol. Pure isomers (of the 1-phenyl isomer) are prepared by reduction of the acylated Wolff-Kishner reaction. The 2-phenyl isomer is obtained from n-undecyl phenyl ketone and methyl magnesium bromide to form the tertiary alcohol which is dehydrated to the alkene and then hydrogenated. The 5-phenyl isomer is obtained similarly from n-heptyl phenyl ketone and n-butyl magnesium bromide. The other isomers are obtained in a similar manner from the appropriate n-alkyl phenyl ketone and n-alkyl magnesium bromide.

In addition to the benzene sulfonates one may also employ the lower alkyl (C_1 to C_4) analogs of benzene such as toluene, xylene, the trimethyl benzenes, ethylbenzene, isopropyl benzene and the like. The sulfonates are generally employed in the water soluble salt form which includes as the cation, the alkali metals, ammonium and lower amine and alkanolamine.

Examples of suitable linear alkyl benzene sulfonates include:

- sodium n-decyl benzene sulfonate
- sodium n-dodecyl benzene sulfonate
- sodium n-tridecyl benzene sulfonate
- sodium n-tetradecyl benzene sulfonate
- sodium n-pentadecyl benzene sulfonate
- sodium n-hexadecyl benzene sulfonate

and the corresponding lower alkyl substituted homologues of benzene as well as the salts of the cations previously referred to. Mixtures of these sulfonates may, of course, also be used with mixtures which may include compounds wherein the linear alkyl chain is smaller or larger than indicated herein provided that the average chain length in the mixture conforms to the specific requirements of C_{10} to C_{22} .

The linear paraffin sulfonates are also a well known group of compounds and include water soluble salts (alkali metal, amine, alkanolamine, and ammonium) of:

- 1-decane sulfonic acid
- 1-dodecane sulfonic acid
- 1-tridecane sulfonic acid
- 1-tetradecane sulfonic acid

1-pentadecane sulfonic acid

1-hexadecane sulfonic acid

as well as the other position isomers of the sulfonic acid groups.

In addition to the paraffin sulfonates illustrated above, others with the general range of C_{10} to C_{22} alkyls may be used, with the most preferable range being from C_{12} to C_{20} .

The linear alkyl sulfates which are contemplated in the process and composition of the present invention have alkyl groups in the range of from C_{10} to C_{22} . Specific examples include, sodium n-decyl sulfate; sodium n-dodecyl sulfate; sodium n-hexadecyl sulfate; sodium n-heptadecyl sulfate; sodium n-octadecyl sulfate; and ethoxylated (1 to 100 moles ethylene oxide) derivatives thereof. Of course, other water-soluble salt-forming cations mentioned above may also be used.

The above composition may be applied to the fabric according to the process of the present application by any of a number of methods. The solution may be sprayed onto the fabric utilizing either a mechanical spraying apparatus including a pump valve or an aerosol spray wherein the composition includes a small portion of an aerosol propellant, such as isobutane, and polar hydrocarbon and chlorinated propellants. Also the composition may be sprinkled on the fabrics although an even, finely dispersed spray is preferred since the complexing acid is more evenly dispersed.

Basically, the composition is sprayed onto the fabric either covering the entire fabric if the same is heavily soiled or only upon those areas which require special pre-treatment. Subsequent to the spraying of the fabrics in accordance with the process of the present invention, the fabrics may then be washed in any conventional manner utilizing either non-ionic, anionic or cationic detergents or soaps. Furthermore, since citric acid and the other acids also have some building properties, these materials, when added to the subsequent detergent in water composition, will also enhance the same be performing a supplemental building function, in addition to the original pre-wash complexing function.

Although not wishing to be bound by any specific theory with regard to the method by which the process of the present invention enhances the removal of soils, it appears that the various metal ions present in clay or other type soils complex with the various organic acids in preference to complexing with phenolic materials present in the fabrics which form highly colored stains and prevent these highly colored stains or phenolic complexes from becoming attached firmly to the fibers as phenolic-metal complexes during the wash cycle and thereby forming irremovable metal type stains.

The process and composition of the present invention will now be illustrated by way of the following illustrative examples which are for the purpose of illustration only and are to be taken as no way limiting.

EXAMPLE 1

A series of swatches of a 50% polyester, 50% cotton fabric having a permanent press finish is soiled with a dry clay soil. A second series of similar fabrics is soiled with a Spangler sebum containing particulate soil. The above series of swatches are then sprayed with the treating solutions as shown in Table I. Subsequent to spraying the the swatches are then washed with a detergent containing 12% by weight of a non-ionic detergent, 66% by weight of sodium carbonate, 2.4% by weight of carboxymethylcellulose, 9% by weight of so-

dium silicate, 2.1% by weight of sodium sulfate, with the balance to 100% being water. Subsequent to washing the average reflectance values of the swatches were then determined with the higher values indicating increased whiteness.

Table I

Example No.	Spray	Clay Soil(Rd)	Spangler Soil(Rd)
1	5% citric acid	80.9	74.1
2	5% tartaric acid	78.6	73.5
3	5% citric acid + 5% Neodol 45-11 ¹	82.6	74.3
4	5% tartaric acid + 5% Neodol 45-11	81.8	75.5
5	20% citric acid	83.1	—
Comp.1	HCl Solution of pH 2	75.4	72.0
Comp.2	5% Neodol 45-11	75.9	74.9
Comp.3	20% sodium citrate	72.3	—
Comp.4	NONE (control)	70.0	69.3

¹A mixed C₁₄₋₁₅ alcohol + 11EO.

Although all the pretreatments i.e., Examples 1-5 and Comparative Examples 1 and 2 show improved whiteness, both with respect to the clay soil and the Spangler soil, over Comparative Example 3 which is the control utilizing no pre-treatment, improved results are obtained when the complexing acids i.e., citric and tartaric acids are utilized, either alone or in combination with a non-ionic surfactant. Comparative Example 1 indicates that it is not the pH alone which affects the whiteness, while Comparative Example 2 shows that a pretreatment with a non-ionic detergent, although improving the whiteness does not improve the same to the degree possible utilizing the complexing acids. Furthermore, Comparative Example 3 shows that although a high amount of a citrate or complexing acid salt does slightly improve the whiteness, the performance of these salts is far below the performance of the complexing acids themselves.

Example 6

The procedure of Example 1, is repeated except that the 5% citric acid spray is replaced with the following spray compositions:

- A. 1% citric acid
- B. 1% tartaric acid
- C. 5% maleic acid
- D. 7% fumaric acid
- E. 10% adipic acid
- F. 4% succinic acid
- G. 20% tartaric acid
- H. 3% tartaric acid, 4% citric acid
- I. 20% maleic acid
- J. 1% adipic acid
- K. 4% citric acid, 2% maleic acid

Each of the above noted pretreatment sprays usually increases the whiteness with respect to an un-pretreated swatch of similar fabric laundered in the same manner.

EXAMPLE 7

The procedure of Example 1 is repeated with the exception that the citric acid spray is replaced by the following spray solutions in water:

- A. 5% citric acid + 5% mixed C₁₂₋₁₅ alkyl alcohol polyoxyethylene having 7 ethylene oxide units per molecule
- B. 3% tartaric acid + 7% polyglycerol monolaurate
- C. 15% maleic acid + 30% sorbitan monostearate

- D. 8% succinic acid + 4% dodecyl benzene sulfonate
- E. 8% tartaric acid + 2% sodium n-dodecyl benzene sulfonate
- F. 4% citric acid + 9% sodium 1-dodecane sulfonate

Each of the above mixtures when utilized as a pre-wash spray generally increases the soil removal capacity of the detergent as reflected by higher average reflectance value of the swatches when compared with similarly soiled swatches washed in the same detergent and not having the above noted pre-wash treatments.

EXAMPLES 8-10 AND COMPARATIVE EXAMPLES 5-9

A 50-50 blend of a polyester cotton fabric is soiled with a dry clay soil and sprayed with the pre-wash compositions as shown in Table II.

Table II

Example No.	Spray	Clay Soil(Rd)
8	1.0% citric acid	80.3
9	5.0% citric acid	81.5
10	20.0% citric acid	81.4
Comp. 5	No spray	79.4
Comp. 6	Water spray	79.6
Comp. 7	0.01% citric acid	78.4
Comp. 8	0.1% citric acid	79.7
Comp. 9	0.5% citric acid	79.7

Subsequent to pretreatment these fabrics are washed in a detergent comprising 23% by weight of a linear dodecyl benzene sulfonate, 25% by weight of a sodium silicate, 4.5% of a non-ionic detergent, 2% by weight of carboxymethylcellulose, 2% by weight soap with the remainder being filler and water at a detergent concentration of 1 gram per liter. As shown by Comparative Examples 6-9 which utilize either a water spray or a citric acid spray having a concentration below the concentration of complexing acid in the composition of the present invention. The reflectance values are roughly unchanged from Comparative Example 5, wherein no spray whatsoever is utilized. However, in Examples

8-10 which are in accordance with the composition of the present invention the average final reflectance values are higher than Comparative Example 5 wherein no spray at all is utilized.

While the composition and process of the present invention has been illustrated by way of the foregoing specific Examples the same are for the purposes of illustration only and are in no way considered as limitative of the present invention which is properly defined by way of the following appended claims.

What is claimed is:

1. An aqueous pre-wash aerosol spray soil release composition, for use in conjunction with a detergent or soap in a laundering procedure, consisting essentially of from 1-20% by weight of an organic complexing acid capable of complexing the stain-forming metallic ions in the soil, from about 2 to 30% by weight of a surface active agent and 99-50% by weight of water and an effective amount of an aerosol propellant.

2. The composition of claim 1, wherein said composition consists essentially of from 5 to 15% by weight of said organic complexing acid and from 95 to 85% by weight water.

3. The composition of claim 2, wherein said organic complexing acid is selected from the group consisting of citric acid, tartaric acid, maleic acid, fumaric acid, adipic acid, succinic acid and mixtures thereof.

4. The composition of claim 3, wherein said organic complexing acid is citric acid.

5. The composition of claim 4, wherein said citric acid is present in a concentration of 5% by weight.

6. The composition of claim 1, wherein said surface active agent is a non-ionic surface active agent.

7. A process for assisting in the removal of soil complexes from a fabric comprising applying to a soiled

fabric a pre-wash composition consisting essentially of from 20% by weight of an organic complexing acid capable of complexing the stain-forming metallic ions in the soil, from 2 to 30% by weight of a non-ionic or anionic surface active agent and from 99-50% by weight of water and laundering said soiled fabric using a washing agent selected from non-ionic detergents, cationic detergents, anionic detergents and soap.

8. The process of claim 7, wherein the composition consists essentially of from 5 to 15% by weight of said organic complexing acid and from 95 to 85% by weight water.

9. The process of claim 7, wherein said organic complexing acid is selected from the group consisting of citric acid, tartaric acid, maleic acid, fumaric acid, adipic acid, succinic acid and mixtures thereof.

10. The process of claim 9, wherein said organic complexing acid is citric acid.

11. The process of claim 10, wherein said citric acid is present in a concentration of 5% by weight.

12. The process of claim 7, wherein said surface active agent is a non-ionic surface active agent.

13. The process of claim 7, wherein said composition is sprayed onto said fabrics.

14. The process of claim 7, wherein said composition is applied to said fabric in the form of an aerosol spray.

15. The process of claim 7, wherein said composition is applied to said fabric as a spray discharged from a pump valve.

16. A fabric treated in accordance with the process of claim 7.

17. A fabric treated with the composition of claim 1.

18. A fabric as defined in claim 16 comprised of polyester and cotton.

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