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3,705,103

## STAIN-REMOVING SOLID CLEANSERS

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5 Claims

## ABSTRACT OF THE DISCLOSURE

Solid cleaners for nonmetallic surfaces such as ceramic and "Formica," which can be used to remove stains from such surfaces, are made with the oxidizing constituent thereof being a water-soluble peroxydiphosphate, the cleaner yielding a pH in water of not over 2.5.

## BACKGROUND OF THE INVENTION

Solid cleaning compositions are widely used to remove dirt and stains from a variety of nonmetallic surfaces such as ceramics, glass, and thermoset melamine-formaldehyde and are made in a variety of ways. In general, they contain either an oxidizing agent or a reducing agent, to handle different types of stains. Typical cleaners include:

- (a) Scouring powders, which are usually abrasive material, detergent and an oxidizer which yields chlorine or bromine to act on stains, and to act as a sanitizing agent. They are generally of high pH.
- (b) Toilet bowl cleaners, ordinarily comprising soda ash, sodium bisulfate and a chlorine-producing oxidizer. These are on the acid side.
- (c) Ceramic tile cleaners, generally composed of trisodium phosphate and sodium tripolyphosphate, with or without a chlorine oxidizer.
- (d) Rust removers, generally mixtures of oxalic acid and sodium bisulfate. They are not useful in removing stains other than rust.

These cleansing compositions are useful, but are either objectionable to many people because of the odor of halogen released in use or are specific to rust stains. Peroxygen chemicals such as sodium perborate have been suggested as alternates for the halogen-producing oxidizers to overcome the odor, but have not been as effective.

## STATEMENT OF THE INVENTION

I have discovered that excellent stain-removal properties can be imparted to solid cleaners used with water for nonmetallic surfaces by formulating them with about 1 to 10% of a water-soluble peroxydiphosphate as oxidizing agent, together with acid chemicals which will produce a pH in water of about 2.5 or less.

## DETAILED DESCRIPTION OF THE INVENTION AND SPECIFIC EXAMPLES

Until recently, the peroxydiphosphates have been laboratory chemicals. More recently, they have become commercial, particularly as the potassium salt  $\text{—K}_4\text{P}_2\text{O}_8\text{—}$  made by the method of the Mucenieks application Ser. No. 688,525, filed Dec. 6, 1967, now U.S. Pat. 3,616,325. This and other peroxydiphosphates are sources of active oxygen.

I have found that peroxydiphosphates give excellent and very rapid stain removal in various solid cleaning compositions useful on nonmetallic surfaces, if they are combined with chemicals which will produce a pH of about 2.5 or less when the composition is mixed with water in use.

In general, the compositions should contain about 1 to 10% of peroxydiphosphate as the potassium salt, or an

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equivalent amount of other water-soluble salt. In this range, good stain removal is obtained rapidly if the pH is 2.5 or less. At higher pH, stain removal is much slower, and uneconomic higher concentrations of peroxydiphosphates are necessary.

- Typical scouring powders will contain about 60 to 90% of very fine silica, 3 to 4% of a surfactant (which may be anionic, nonionic or cationic), and optionally 1 to 4% of a sodium acid phosphate (either mono- or disodium acid phosphate). To this is added as oxidizer 1 to 10% of a peroxydiphosphate, preferably the commercially available  $\text{K}_4\text{P}_2\text{O}_8$ , together with 60% or more, based on peroxydiphosphate, of  $\text{NaHSO}_4$ , to ensure the desired low pH of 2.5 or lower. Fillers such as sodium sulfate or sodium chloride, if necessary, make up the balance.

A typical scouring cleanser is the following:

## Example 1.—Scouring powder

|                                                                                                                    | Parts by weight |
|--------------------------------------------------------------------------------------------------------------------|-----------------|
| Silica (at least 85% by weight passing through a wire sieve in which the openings between the wires are 0.074 mm.) | 79.5            |
| Sodium dodecyl benzene sulfonate                                                                                   | 4.0             |
| Tetrapotassium peroxydiphosphate                                                                                   | 6.0             |
| Sodium bisulfate                                                                                                   | 10.0            |
| Perfume                                                                                                            | 0.5             |
|                                                                                                                    | 100.0           |

- In a static test, this cleanser removed iron tartrate stains from porcelain-coated metal and from a standard melamine-formaldehyde laminate ("Formica") in 5 to 15 seconds. Almost immediate removal is obtained on rubbing.

- The composition can be varied widely, particularly in that any commercial detergent can be used, whether anionic, nonionic or cationic. Note that in the specific example the peroxydiphosphate acts both to provide active oxygen and to sequester metal. However, phosphate can be added as in conventional scouring powder.

- Toilet bowl cleaners, which are generally soda ash combined with enough sodium bisulfate to get the pH on the acid side, and some surfactant (combined with magnesium carbonate to coat the surfactant if an anionic surfactant is used), include, in accordance with this invention, 1 to 10% of peroxydiphosphate as stain remover. The ratio of materials is adjusted so that enough bisulfate is present to get a pH of 2.5 or lower. The peroxydiphosphate does an excellent job of stain removal. The following specific example is typical:

## Example 2.—Toilet bowl cleaner

|                                                                                                              | Parts by weight |
|--------------------------------------------------------------------------------------------------------------|-----------------|
| Sodium bisulfate                                                                                             | 70              |
| Soda ash                                                                                                     | 15              |
| Anionic surfactant—sodium dodecyl benzene sulfonate (trade names "Ultrawet" by ARCO or "Sulframin" by Witco) | 3               |
| Magnesium carbonate                                                                                          | 5               |
| Tetrapotassium peroxydiphosphate                                                                             | 7               |
|                                                                                                              | 100             |

- This composition was tested extensively on toilet bowls in applicant's laboratories against a similar composition containing an active chlorine source, and was as effective in cleaning without the development of an undesirable odor.

- Ceramic tile cleaners made in accordance with this invention differ from conventional ceramic tile cleaners in the presence of peroxydiphosphate plus enough sodium bisulfate or other source of acid to get the desired pH of 2.5 or lower. Such ceramic cleaners will contain 1 to

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10% of  $K_4P_2O_8$ , 1.2 to 12% of  $NaHSO_4$  (in a weight ratio of 1.2 to 1 of  $K_4P_2O_8$ ), 1 to 3% of a surfactant, preferably nonionic, and the balance  $NaH_2PO_4$  alone or with filler. One to ten percent of  $Na_2H_2P_2O_7$  or other condensed phosphate may be used to replace  $NaH_2PO_4$ . The ratio of  $NaHSO_4$  to  $K_4P_2O_8$  must be high to get the desired low pH in the presence of the phosphate. A typical composition is as follows:

Example 3.—Ceramic tile cleaner

|                                                                                                  | Parts by weight |
|--------------------------------------------------------------------------------------------------|-----------------|
| Sodium dihydrogen orthophosphate ( $NaH_2PO_4$ )                                                 | 88.2            |
| Tetrapotassium peroxydiphosphate                                                                 | 4.0             |
| Sodium bisulfate                                                                                 | 4.8             |
| Nonionic surfactant — alkylphenoxypolyethoxyethane (trade name "Triton X100" by Rohm & Haas Co.) | 3.0             |
|                                                                                                  | 100.0           |

This composition was used on ceramic tile stained with iron tartrate, and removed such stains within a period of less than 15 seconds.

Rust removers made in accordance with this invention contain 1 to 10% of peroxydiphosphate in addition to the oxalic acid and sodium bisulfate of conventional rust removers. Such compositions will remove rust equally well as prior-art compositions, but will also remove other stains. Typically, they contain 1 to 10% of peroxydiphosphate, 50 to 70% of oxalic acid, and 20 to 40% of  $NaHSO_4$ . A typical composition is:

Example 4.—Destainer

|                                  | Parts by weight |
|----------------------------------|-----------------|
| Oxalic acid                      | 65              |
| Sodium bisulfate                 | 25              |
| Tetrapotassium peroxydiphosphate | 10              |
|                                  | 100             |

Obviously, the examples can be multiplied indefinitely

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without departing from the scope of the invention as defined in the claims.

I claim:

1. A solid stain-removing cleansing composition for removing stains from hard non-metallic surfaces consisting essentially of 1 to 10% of a water-soluble peroxydiphosphate, solid cleansing constituents selected from the group consisting of inorganic abrasive and polishing materials, water-dispersible anionic, nonionic and cationic surfactants, sodium carbonate, oxalic acid and inorganic phosphates, and sufficient inorganic acid-producing chemical to produce a pH of 2.5 or lower when the composition is mixed with water.

2. The composition of claim 1, in which the solid cleansing constituents are fine silica and a surfactant selected from the group consisting of water-dispersible anionic, cationic and nonionic surfactants.

3. The composition of claim 1, in which the solid cleansing constituents are soda ash and a surfactant selected from the group consisting of water-dispersible anionic, cationic and nonionic surfactants.

4. The composition of claim 1, in which the solid cleansing constituents are a phosphate and a surfactant selected from the group consisting of water-dispersible anionic, cationic and nonionic surfactants.

5. The composition of claim 1, in which the solid cleansing constituent is oxalic acid.

References Cited

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252—186; 8—111; 134—2, 3