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DETERGENT COMPOSITIONS

Joseph S. Reichert, Samuel A. McNeight, and Arthur A. Elston, Niagara Falls, N. Y., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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This invention relates to certain new compositions of matter having bleaching and detergent properties. More particularly, it relates to dry stable mixtures containing an alkaline inorganic peroxygen compound, the anhydride of an organic acid, and a compound possessing detergent properties. This application is, in part, a continuation of our copending application Serial No. 332,728 filed May 1, 1940, now Patent 2,287,-064, issued June 23, 1942.

Our invention relates more especially to the new and improved compositions, suitable for use as detergents, prepared by compounding a solid peroxygen compound such as sodium perborate monohydrate, a solid organic acid anhydride such as succinic anhydride, phthalic anhydride, benzoic anhydride, maleic anhydride, or glutaric anhydride, and a dry, water-soluble detergent such as soap, trisodium phosphate, or various synthetic detergent agents. More generally, our invention relates to stable dry compositions obtained by compounding an alkaline detergent, a solid inorganic peroxygen compound, and an organic acid anhydride, which compositions, when added to water, will yield detergent preparations having bleaching and oxidizing properties. These solutions are characterized by the presence of either an organic monoperacid or its salt.

In the past, bleaching and oxidizing compositions of high activity comprising peracids or persalts, suitable for utilization under various conditions of alkalinity or acidity, could be produced only by chemical reaction directly at the point of use. Stable dry compositions suitable for addition of water or aqueous liquids to form bleaching and oxidizing compositions of activity greater than that of the inorganic peroxides, or suitable when containing an alkaline detergent for use as a combined bleaching and cleaning agent of high activity, were not available to the industry. Previous attempts to prepare for commercial use dry compositions which are stable on storage and which would possess useful detergent properties when dissolved in water have generally aimed at producing mixtures which, upon dissolution in water, yielded oxidizing solutions having the characteristics and bleaching activity of hydrogen peroxide. Our principal aim is the preparation of dry compositions, stable on storage, which compositions when added to water or aqueous liquids will form detergent compositions containing, not peroxides or their salts, but organic monoperacids or their salts. The organic peracids and persalts possess increased bleaching activity and exert their oxidizing effects at lower temperatures and with greater rapidity than the peroxides or inorganic percompounds.

The organic monoperacids are a class of organic acids which are produced when the hydroxyl group containing the ionizable hydrogen atom of an organic acid is replaced by the perhydroxyl group, —OOH. Thus, monopersuccinic acid having the formula

$$\begin{matrix} CH_2.COOOH \\ | \\ CH_2.COOH \end{matrix}$$

may be regarded as derived from succinic acid, having the formula

$$\begin{matrix} CH_2.COOH \\ | \\ CH_2.COOH \end{matrix}$$

by replacement of one of the hydroxyl groups containing an ionizable hydrogen atom by the perhydroxyl group —OOH.

Our previous work with the peracids, and especially with the monoperacids, has impressed us with the fact that these acids and their salts are definitely superior to inorganic peroxide compounds such as hydrogen peroxide when employed for oxidizing or bleaching purposes. Their bleaching and oxidizing activity is greater than that of inorganic peroxides such as hydrogen peroxide, and it is exerted with greater rapidity and at lower temperatures. The peracids and persalts, especially the monoperacids and monopersalts, also function over a wider range of acidity and alkalinity, and therefore may be regarded as more suited for universal application under the various conditions encountered in commercial bleaching operations.

Since solutions of the peracids and persalts are not stable when stored for any considerable period of time, it has been necessary in the past to prepare the solution by chemical reaction wherever needed. Methods available for their preparation have required careful control of reactants, careful maintenance of reaction conditions, the use of relatively high concentrations of the reacting chemical compounds, and of fairly long reaction periods. As a result the art has made little or no industrial use of these oxidizing compounds.

In our copending patent application Serial No. 317,318, filed February 5, 1940, now U. S. P. 2,284,-477, we have described a method for the preparation of the peracids and persalts which is more readily carried out with less control of the conditions involved than are the methods previously known to the art. However, the method of our copending application nevertheless requires control of the reaction to the extent of maintaining the proper and correct proportioning of the separate reagents employed in the preparation of the peracid or persalt. Moreover, it does not result in solutions which are stable during long periods of storage, and when employing the method of our copending application it is generally necessary to prepare the solution of the peracid or the persalt at the place where its use is intended.

By providing a dry, stable mixture containing,

in addition to one or more alkaline detergents, an inorganic peroxygen compound and an organic acid anhydride or its equivalent, we have provided a method permitting preparation of the peracids as needed without the necessity for exercising control of the proportions of the reagents, or careful control of the reaction at the time and place at which it is desired to utilize the compositions. Since our compositions are dry, stable, solid mixtures which when dissolved in water or aqueous liquids readily and simply provide solutions of peracids or persalts, it is evident that carefully weighing out amounts, controlling reaction conditions within narrow limits, and providing a fairly long period of reaction are no longer necessary at the place where the peracids or persalts are to be utilized for industrial purposes.

Our improved compositions, while capable of producing the peracid or persalt as needed by simply adding the mixture to water at the place of use, nevertheless possess satisfactory stability for commercial storage and shipment. It is evident that our improved stable, dry mixtures of detergent, peroxygen compound and acid anhydride may be viewed, for all purposes, as a stable peracid composition, thus rendering it possible to utilize the peracids and the persalts in commercial deterging operations conveniently and without the necessity for careful control or proportioning at the point of use.

Accordingly, one of the objects of this invention is the preparation of a stable dry composition which composition, when dissolved in water or in aqueous solutions, will yield an effective detergent solution exerting the superior oxidizing and bleaching properties characteristic of the organic peracids and their salts. Another object of this invention may be said to be the preparation of a dry stable detergent composition which may be stored for indefinite periods without danger of chemical instability but which will, nevertheless, when dissolved in water yield solutions of the monoperacids or their salts, chemical compounds which in aqueous solution exhibit marked and effective bleaching activity. In brief, the primary object of our invention is the preparation of a stable dry composition which can be stored indefinitely but which is instantly available, simply by dissolving the solid mixture in water or aqueous liquids, to yield solutions of superior detergent properties. The attainment of these objects involves developments of the utmost importance in the art of preparing detergent preparations exerting bleaching and oxidizing properties, for never before has it been possible to prepare a dry stable composition capable of yielding a peracid or persalt when dissolved in water which would be stable for an indefinite period. Nor has it been previously possible to prepare detergent preparations containing stable solutions of peracids or persalts, as needed, without the necessity for careful proportioning of the reagents and control of the reaction used to produce the peracids or persalts at the point where their use is intended.

In the past organic acids such as succinic acid have sometimes been incorporated in admixture with solid percompounds such as sodium perborate. The purpose of these acids, however, has been solely that of reducing the alkalinity of the solution resulting when the preparation is dissolved in water. The acid employed for this purpose is one which reacts with alkali to form a solution of reduced alkalinity. As contrasted with this, the compounds that we use, the organic acid anhydrides or their equivalents, e. g. succinic anhydride, phthalic anhydride, glutaric anhydride, etc., instead of reacting with the alkali to result in a solution of lowered alkalinity, react with the percompound when dissolved in water to form a peracid or persalt of the peracid. Acids corresponding to the anhydrides mentioned, for example succinic acid, phthalic acid, and glutaric acid, do not react in aqueous solution with percompounds such as sodium perborate to form the peracids. They merely react with any alkali present to reduce the alkalinity of the detergent preparation resulting. Accordingly, we utilize in admixture with the solid inorganic peroxygen compound such as sodium perborate, the organic acid anhydrides or their equivalents. Although the latter will ordinarily hydrolyze in aqueous solution, they react preferentially with the peroxygen compound under these conditions, to form the desired monoperacid or its salt. The ability to react in aqueous solution in this way is characteristic of the organic acid anhydrides and equivalent substances.

In preparing our stable dry compositions of matter containing a compound possessing detergent properties, an alkaline inorganic peroxygen compound, and an organic acid anhydride or its equivalent, which compositions do not contain sufficient water or moisture to permit chemical reaction between the components of the mixture before the solid product is dissolved in an aqueous liquid, we may utilize a variety of individual compounds. We prefer, however, to utilize as the inorganic alkaline peroxygen compound sodium perborate monohydrate, $NaBO_3.H_2O$. As organic acid anhydride we may utilize a large variety of such anhydrides, but generally, because of their ready availability and somewhat lower cost, we prefer to use such organic acid anhydrides as succinic anhydride, phthalic anhydride, adipic anhydride, benzoic anhydride, and glutaric anhydride. Generally the non-toxic organic acid anhydrides are desirable for use in our compositions, but in some cases, of course, anhydrides of toxicity of a greater or less degree, e. g. maleic anhydride may be utilized. While sodium perborate monohydrate is a preferred solid inorganic peroxygen compound, by reason of its availability and low cost, we may utilize other solid peroxygen compounds such as other perborates; alkali, alkaline earth and other peroxides; percarbonates, persulfates, perphosphates, particularly the sodium and other alkali metal salts, etc. These peroxygen compounds may be either anhydrous or in the hydrated state as long as they do not contain sufficient free or uncombined water to interfere with the obtainment of a dry mixture. Among suitable peroxygen compounds are urea peroxide, zinc peroxide, magnesium peroxide, calcium peroxide and perphosphates such as those having the compositions $Na_4P_2O_7.2H_2O_2$ and $Na_2HPO_4.H_2O_2$.

The ratio of the amount of inorganic peroxygen compound to the amount of organic acid anhydride or equivalent in the composition will be controlled by the extent to which it is desired to have either one or both of these substances converted to the organic peracid or persalt. We generally prefer to use compositions containing equimolar amounts of the peroxygen compounds such as sodium perborate monohydrate and the acid anhydride. This means that the ratio of the amount of peroxygen compound to the amount of anhydride is the same as

the ratio of the molecular weights of these two compounds. When admixed with a water-soluble detergent, these compositions, when dissolved in water or aqueous liquids, will react to give greater yields of the peracid or its salt per unit weight of dry solid composition.

However, it is possible to control the acidity and alkalinity of the aqueous solution of the peracid to persalt by controlling the ratio of the amount of inorganic peroxygen compound present in the mixture to the amount of acid anhydride. In many cases, of course, it may be more desirable to obtain this control of the pH of the aqueous solution by other means, in which case ordinarily equimolar amounts of the peroxygen compound and acid anhydride would be utilized. Compositions containing other than equimolar proportions of the two components are nevertheless also useful. A composition containing a stoichiometric excess of one component over the other may be particularly suitable for some industrial or commercial purposes. For example, we have prepared mixtures containing from 40 mole percent to 83 mole percent of sodium perborate monohydrate and have utilized these compositions containing, in addition, an alkaline detergent, to prepare the peracid or its salt in aqueous solution, which solution is particularly useful by reason of its oxidizing and detergent properties.

In addition to the inorganic peroxygen compound and organic acid anhydride, there is present in the dry composition a compound possessing detergent properties. Ordinarily we prefer to utilize dry, water-soluble detergents such as MP–189 and MP–200, water soluble detergents of the so-called "Reed Process" type, which form the subject matter of U. S. P. 2,197,800. However, it is not essential to use synthetic detergents, as we have found that any detergent may be utilized, provided it does not adversely affect the stability of the compound, and is either substantially free from water, or contains moisture in such condition that the water is not available for reacting with the organic acid anhydride in the mixture. Among such suitable water-soluble detergents we may specify dehydrated solid soaps; anhydrous salts possessing detergent properties; alkyl and aryl sulfonates and their derivatives, as well as mixtures or combinations thereof; fatty alcohol sulfates and phosphates; organic phosphonic acid derivatives; naphthenic acid derivatives; and similar substances possessing detergent properties. We have, for example, secured very satisfactory detergent preparations when such substances as anhydrous sodium carbonate, tetrasodium pyrophosphate, trisodium phosphate, anhydrous soaps, or similar water-soluble agents have been included.

The preparation of detergent solutions having increased oxidizing and bleaching activity is readily carried out simply by adding the dry stable composition to the desired quantity of water. The solution is agitated for a suitable time, usually only a few minutes are necessary, in order to insure complete solution of the material.

The loss of oxidizing and bleaching properties during storage of the composition is negligible, since our dry stable detergent preparations, as long as they remain out of contact with water, are stable for indefinite periods. Such compositions can be commercially stored or shipped, without danger of decomposition, in ordinary packages, as they do not require special containers or shipping means. The proper proportioning of the material in preparing solutions of peracids and persalts is automatically maintained when the initial dry composition is prepared, thus rendering unnecessary any special proportioning or careful control at the point of use when preparing the detergent solutions.

It is apparent that we have provided means for utilizing the rapid and powerful bleaching and oxidizing properties of the organic peracids and their salts in detergent preparations for industrial purposes without the necessity for special control or careful reaction at the point where the products are to be employed for commercial purposes. No special adjustments are necessary when the stable dry composition is dissolved in water, and the resulting detergent preparation is capable of immediate utilization.

As examples of our dry stable detergent preparations containing a compound possessing detergent properties, an inorganic peroxygen compound, and an organic acid anhydride, the following may be given. These examples demonstrate the stable character of our improved compositions during storage, as well as their effective detergent action. The concentration of an aqueous oxygen-yielding composition or solution is frequently given in terms of its "volume concentration." The volume concentration of such a solution is the number of cubic centimeters of oxygen gas, measured at 0° C. and 760 mm. of mercury pressure, which is released upon complete decomposition by one cubic centimeter of the solution at 20° C. Commercial solutions of hydrogen peroxide, such as those sold under the trade-mark name "Albone," are generally of 100 volume concentration, or yield, upon complete decomposition, 100 cc. of oxygen gas per cc. of solution. This corresponds to an H_2O_2 content of 27.6% by weight.

Example 1

In order to demonstrate the superior stability during storage of our dry stable compositions, mixtures of sodium perborate monohydrate and succinic anhydride were stored for various periods at 32° C.

The loss in active oxygen was determined for each preparation at various intervals during storage. The table below gives the composition of the mixture and the average loss of active oxygen per month over a seven-months storage period.

Mixture No.	Per cent sodium perborate monohydrate	Per cent succinic anhydride	Average loss per month in active oxygen (7 months storage)
I	10	10	2.7
II	40	40	1.4
III	10	10	2.6
IV	40	40	1.8

Example 2

A dry stable detergent preparation was prepared by mixing 25% of sodium perborate monohydrate, 25% of succinic anhydride, and 50% of the hereinabove identified synthetic detergent MP–189. All percentages are by weight based on the total weight of the solid detergent preparation.

Cotton fabric was washed in a solution containing approximately one pound of the dry stable detergent per 100 pounds of fabric treated. For purposes of comparison, other trials were made using various other detergents in connection with

the same cotton fabric, the amounts of these detergents being substantially one pound per 100 pounds of fabric treated. At the end of each treatment the average percent increase in whiteness per washing was obtained, the fabric being washed in each case twenty times in the alkaline detergent solution. The results are given in the following table.

Detergent composition	Average per cent increase in whiteness per washing obtained in 20 washings
Sodium perborate+succinic anhydride+MP-189	0.55
Soap	0.17
MP-189	0.15
Soap+sodium perborate	0.50
MP-189+sodium perborate	0.27
Sodium perborate+succinic anhydride+soap	0.48

Example 3

Samples of cotton muslin were stained with strawberry, raspberry, peach, tomato juice, black tea, green tea, cocoa containing milk, coffee containing cream, beer, and wine stains. The cotton muslin was then washed with the various detergent preparations given in Example 2. The various washing agents, as well as the percent stain removal, (average for all stains), are given in the following table. This table shows the percent stain removal after the first washing, after five washes, and after ten washes.

Detergent composition	Per cent stain removal after—		
	1 wash	5 washes	10 washes
Sodium perborate + succinic anhydride+MP-189	78.6	(1)	(1)
Soap	54.3	57.8	58.5
MP-189	48.3	58.6	58.5
Soap+sodium perborate	59.6	65.9	74.6
MP-189+sodium perborate	45.1	80.3	81.9
Sodium perborate + succinic anhydride+soap	51.0	73.5	73.1

[1] Complete.

The results plainly show the superiority of our new detergent, comprising a dry stable mixture of sodium perborate monohydrate, succinic anhydride, and synthetic detergent MP-189 (so-called Reed process type product).

In preparing our improved compositions we prefer to use succinic anhydride, as well as other solid non-hygroscopic anhydrides, such as phthalic anhydride, maleic anhydride, and glutaric anhydride. However, condensation products of anhydrides with certain other organic compounds, such as the product formed by reaction between maleic anhydride and cyclopentadiene, may be used in place of the organic acid anhydride in preparing our improved detergent compositions.

Ordinarily we prefer to use an equal weight of sodium perborate and of the dry solid detergent utilized in preparing our improved composition. However, the amount of detergent may be varied widely to meet special needs. Similarly, while we prefer to utilize molar equivalent weights of sodium perborate monohydrate, or other solid peroxygen compound, and the organic acid anhydride in order to secure substantially complete conversion into the peracid of both the perborate and the anhydride, these proportions may, however, be varied widely to meet special needs.

There may be present in our composition, in addition to the organic acid anhydride, peroxygen compound, and solid detergent, an agent for controlling the pH of the solution resulting when the composition is dissolved in water or other aqueous liquid. Among such agents are alkali salts such as anhydrous soda ash, trisodium phosphate, and tetrasodium pyrophosphate. Dry solid materials which are acidic in reaction, such as citric acid, preferably dehydrated citric acid, as well as tartaric acid, may also be included in our composition for controlling the alkalinity or acidity of the resulting solution.

Our improved detergent compositions are valuable in commercial laundry and bleaching operations. They are also valuable as household laundering compounds, scouring mixtures for various purposes, combined bleaches and shampoos, deodorizing agents, for cleaning and bleaching leather, as a flux for cleaning metals, and as preparations to be utilized in place of soap.

It should be understood that various changes may be made in the proportions, ingredients, and amounts which have been given as illustrative of preferred embodiments of our invention without departing from the scope thereof. Thus, various additional ingredients may be incorporated in the dry stable composition, or the proportions of the ingredients may be varied from those hereinbefore given as illustrative. The scope of the invention is therefore not to be restricted merely to preferred embodiments thereof, but is to be interpreted in accordance with the prior art and appended claims.

We claim:

1. A dry stable detergent composition which yields in aqueous solution an oxidizing agent of high activity, said composition comprising a solid inorganic peroxygen compound, an organic acid anhydride, and a solid detergent.

2. A dry stable detergent composition, suitable for yielding a solution exhibiting oxidizing properties when dissolved in water, which composition comprises a solid inorganic peroxygen compound, an organic acid anhydride, and a solid detergent, said composition containing less than sufficient available moisture to permit chemical reaction between the constituents threof upon standing during storage.

3. A dry stable detergent composition which when dissolved in water yields an oxidizing solution of high activity, said composition comprising sodium perborate monohydrate, an organic acid anhydride, and a solid detergent.

4. A dry stable detergent composition comprising sodium perborate monohydrate, succinic anhydride, and a solid water-soluble detergent.

5. A dry stable detergent composition comprising sodium perborate monohydrate, phthalic anhydride, and a solid water-soluble detergent.

6. A dry stable detergent composition comprising sodium perborate monohydrate, glutaric anhydride, and a solid water-soluble detergent.

7. A dry stable detergent composition comprising a solid inorganic peroxygen compound, an organic acid anhydride, a solid water-soluble detergent, and a buffer.

JOSEPH S. REICHERT.
SAMUEL A. McNEIGHT.
ARTHUR A. ELSTON.