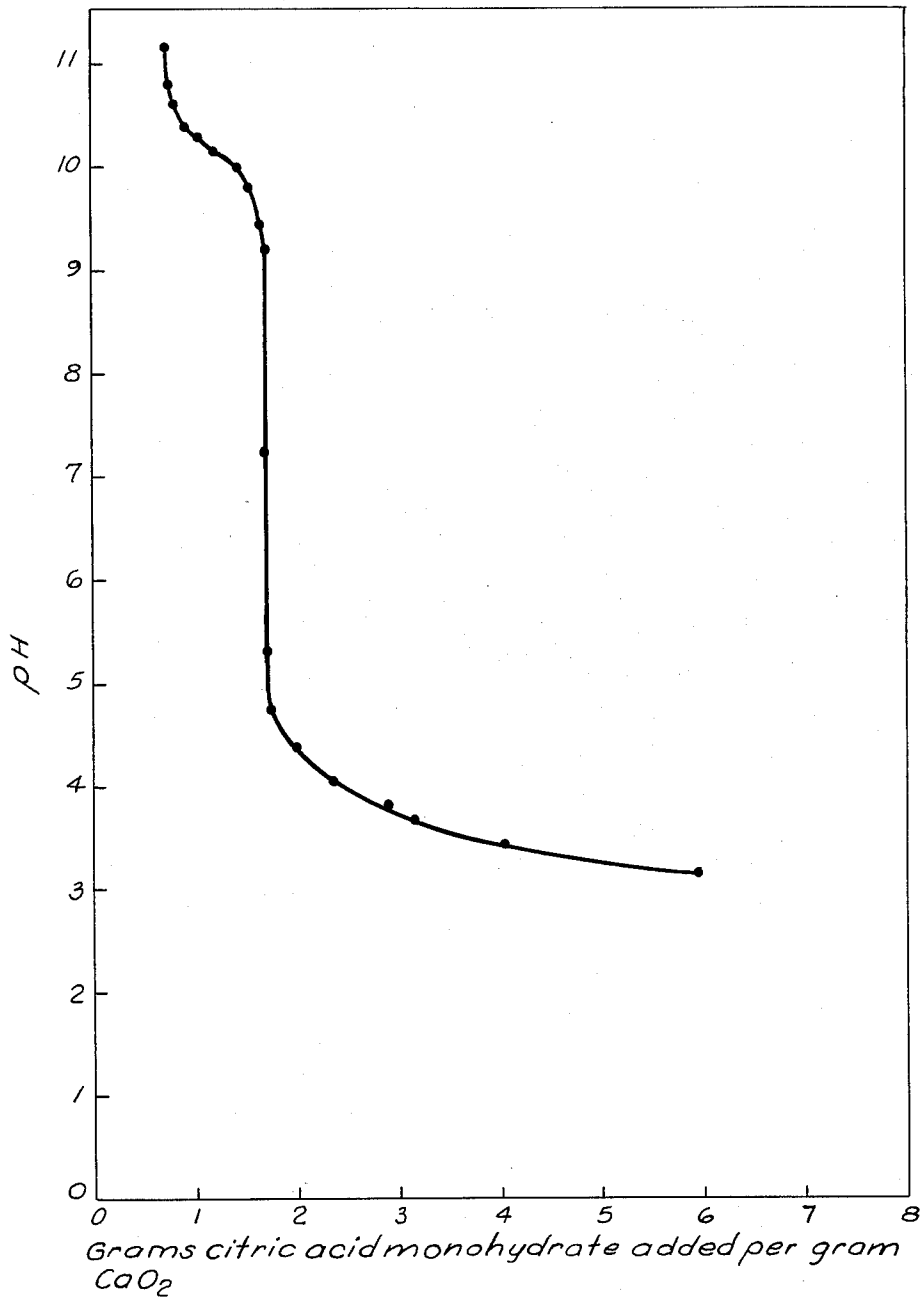
July 5, 1966 J. R. MOYER 3,259,584

BLEACHING COMPOSITION

Filed Sept. 23, 1963



INVENTOR.
John R. Moyer

BY

Griswold & Burdick
ATTORNEYS

United States Patent Office

3,259,584

Patented July 5, 1966

3,259,584

BLEACHING COMPOSITION

John R. Moyer, Midland, Mich., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Delaware

Filed Sept. 23, 1963, Ser. No. 310,670
5 Claims. (Cl. 252—186)

This invention relates to a bleaching composition and, more particularly, to such a composition comprised of calcium peroxide and citric acid or citric acid monohydrate and to a process for using the same.

The bleaching industry makes much use of aqueous hydrogen peroxide as a bleaching agent. Hazardous shipping and storage problems associated with the handling of aqueous hydrogen peroxide have produced a need for a new solid composition of matter which can be handled conveniently and shipped and stored safely without the fear of decomposition, explosion and the like and which can easily be used in making aqueous hydrogen peroxide when desired.

Sodium peroxide is a dry solid which can be used in making aqueous hydrogen peroxide. However, sodium peroxide as a solid is thermally unstable, losing a significant portion of its peroxygen value on prolonged storage through decomposition. It is also corrosive to personnel and to many materials thus making ordinary handling quite hazardous.

Calcium peroxide, on the other hand, in the usual commercial grades (75 percent CaO_2) is a free flowing solid having a greater thermal stability than sodium peroxide in both short and prolonged storage and is non-corrosive to handling personnel and to the materials it is likely to contact. It would thus be desirable to include calcium peroxide as the peroxygen source in a bleaching composition. Ordinarily, calcium peroxide is insoluble in water. However, this invention makes the peroxygen content of insoluble calcium peroxide soluble.

The object of the present invention is to provide a free flowing solid composition of matter to be used for bleaching purposes employing calcium peroxide as the peroxygen source, which is stable upon prolonged storage, nontoxic in ordinary usage and non-corrosive.

A further object of the invention is to provide a solid bleaching composition employing calcium peroxide so that when employed in an aqueous mixture, a substantially complete release of its peroxygen value is obtained.

Another object is to provide a process for bleaching using a bleaching composition employing calcium peroxide as the peroxygen source.

Other objects and advantages will become apparent from reading the detailed description disclosed hereinafter.

In a copending application, Serial No. 262,511, I have disclosed a bleaching composition prepared by admixing potassium pyrosulfate with calcium peroxide in a weight ratio of pyrosulfate to peroxide within the range of from 3.4 to about 7.5 and with sufficient water to make either a pasty aqueous composition, a slurry, or solution having a pH of from about 9.5 to about 1. A particular advantage of that bleaching composition is that the aqueous bleaching mixture so prepared may have a pH of not greater than 3, if desired.

The bleaching composition of this invention may be added to water to produce an aqueous bleaching mixture which may have a pH ranging from about 5 to about 3, if desired. In the bleaching of textiles, this is a desirable pH range as will be later illustrated.

In accordance with the invention, calcium peroxide is

admixed with citric acid or with citric acid monohydrate in particular proportions to one another to form a bleaching composition such that when the composition is mixed with water, a complete release of the peroxygen value is obtained. In the case where the instant bleaching composition contains citric acid monohydrate said composition should contain a weight ratio of citric acid monohydrate to calcium peroxide of from about 1.6 to about 7 such that when mixed together in water, an aqueous bleaching mixture is produced having a pH within the range of from about 9.5 to about 3. When using citric acid in the instant invention, the above pH range is obtained when a weight ratio of citric acid to calcium peroxide in the range of from about 1.46 to about 6.4 is mixed together in water.

In one embodiment of this invention, a bleaching composition is prepared by admixing citric acid monohydrate with calcium peroxide in a weight ratio which ranges from about 1.7 to 7 parts by weight citric acid monohydrate to each part calcium peroxide. The mixture so obtained, when mixed with water, provides a pH of from about 5 to 3. The amount of water used is not critical but is generally dependent upon the nature of the material to be bleached. For example, for use on wooden floors, the bleaching composition could be made into a paste by the addition of water thereto. However, for use as a textile bleachant, a sufficient quantity of water is added to the bleaching composition so as to insure complete dissolution of said composition.

pH's ranging from about 9.5 to 5 may be obtained using a weight ratio of citric acid monohydrate to calcium peroxide ranging from about 1.6 to 1.7 parts citric acid monohydrate to each part calcium peroxide with various amounts of water, for example, from 1 to 250 parts of water per part of the dry mixture. Where citric acid is substituted for the monohydrate, weight ratios of the citric acid to the peroxide ranging from about 1.46 to about 1.55 may be used to obtain pH's of from 9.5 to 5. The desired pH value in this range is more easily attained by the addition of small amounts of either a standard base, e.g., sodium hydroxide, or an acid, e.g., hydrochloric acid.

At a pH of 9.5 and below, a substantially complete release of the peroxygen value of the calcium peroxide is obtained. Above a pH of 9.5, however, there is a significant reduction in the peroxygen release. The weight ratios required to obtain the desired pH within the above range are determined by reference to the graph in the appended drawing.

In another embodiment of this invention, a bleaching composition may be prepared by admixing citric acid with calcium peroxide in a weight ratio which ranges from about 1.55 to 6.4 parts citric acid for each part calcium peroxide. The mixture so obtained, when mixed with water, provides a pH range of from about 5 to 3.

The graph in the annexed drawing is a plot of the pH values obtained in the aqueous mixture of citric acid monohydrate and calcium peroxide in the weight ratios shown.

In obtaining the pH values plotted on the graph, aqueous slurries were prepared by adding 1 gram of 75 percent pure calcium peroxide and an amount of citric acid monohydrate to calcium peroxide represented by the heavy points on the graph to 100 milliliters of water. The pH of each of the so-prepared aqueous mixtures was determined by a Leeds and Northrup pH Indicator in combination with a Beckman glass electrode and a calomel reference electrode. The peroxygen value of each mixture was determined iodometrically using starch as an indicator. In the mixtures which registered a pH below 9.5, a com-

plete release of the peroxygen value of the calcium peroxide was noted. However, in the mixtures having a pH above 9.5, the release of the peroxygen value was reduced as the pH increased.

A particular advantage of the present bleaching composition is that the aqueous bleaching mixture prepared may have a pH of not greater than 5, if desired. Thus, materials such as wool fiber, naphthol-dyed goods and acetate rayon can be effectively bleached with such a weak acidic composition without the need for any stronger acidic compositions. An alkaline composition has a detrimental effect on these materials.

In carrying out the method of this invention, an aqueous mixture of citric acid monohydrate and calcium peroxide in a weight ratio within the range stated above is prepared. The mixture is dissolved in that quantity of water needed to provide the desired pH applicable to the material being bleached. The material to be bleached is then contacted with said aqueous mixture for a time sufficient to obtain the desired degree of bleaching, followed by removal of the so-bleached material from the aqueous mixture and rinsing with water.

The citric acid monohydrate may be substituted with citric acid in the aforesaid method.

The citric acid or citric acid monohydrate ingredient of the bleaching composition of this invention provides the acid needed to form hydrogen peroxide, the actual bleaching agent, from the calcium peroxide according to the following reactions: (1) wherein citric acid is used:

$$3CaO_2 + 2C_6H_8O_7 \xrightarrow{H_2O} 3H_2O_2 + Ca_3(C_6H_5O_7)_2$$

and (2) wherein citric acid monohydrate is used

$$3CaO_2 + 2C_6H_8O_7 \cdot H_2O \xrightarrow{H_2O} 3H_2O_2 + Ca_3(C_6H_5O_7)_2 + 2H_2O$$

If other grades of calcium peroxide are employed in the bleaching composition of the present invention, the weight ratios of citric acid monohydrate to calcium peroxide as used in obtaining the points on the aforementioned graph will be substantially the same as those using commercially pure materials and will require only slight modification, as determined by testing, to produce the pH in solution as indicated in the graph.

To further illustrate the utility of the present invention as applied to bleaching wool cloth, two aqueous bleaching mixtures were prepared in accordance herewith, each having the composition as indicated in Table 1 and a pH within the range of from about 7 to about 3.

Adjustments to obtain the desired pH values within this range were made, for convenience, by the addition to said aqueous mixtures of small amounts of either 0.1 N NaOH or 0.1 N HCl. A piece of unbleached wool cloth was immersed in each of the so-prepared aqueous mixtures, maintained at a temperature of about 40° C. for 5 minutes, wrung dry without rinsing and then dried for about 45 minutes at 100° C. The brightness of each of the so-bleached pieces was next determined by using a Photovolt Reflectometer with a Hunter green tri stimulus filter, with MgO as a standard having a percent brightness of 100. The results of these tests are recorded in Table 1.

In addition, as blanks for comparison purposes, two aqueous hydrogen peroxide solutions were prepared yielding the same quantity of oxygen as that of the above two aqueous mixtures prepared in accordance with the invention. In the blanks, pieces of wool of the same grade and type as those used with the invention were bleached using the same procedure and under the same conditions and tested for brightness, with the results recorded in Table 1.

As a further comparison, a piece of the unbleached wool cloth was tested for brightness and the results recorded in Table 1 below.

Table 1

Example	Composition				Ratio of $C_6H_8O_7 \cdot H_2O$ to CaO_2	pH [3]	Brightness (Percent) [4]
	H_2O (Grams)	H_2O_2 (ml.) [1]	CaO_2 (Grams) [2]	Citric Acid Monohydrate			
Blank	500					7	70.5
Blank	492	7.5				7	73.5
1	500		7.25	12.5	3.54:1	7	75.3
Blank	492	7.5				3	75.1
2	500		7.25	12.5	3.53:1	3	74.4

[1] Ml. of 30 percent H_2O_2
[2] Using 73 percent pure CaO_2
[3] Before immersing piece of wool cloth.
[4] Of dry piece of wool cloth after bleaching.

The results shown in Table 1 demonstrating the improvement in brightness obtained in the bleached cloth clearly illustrate the utility and effectiveness of the composition of the present invention as a bleachant.

Various modifications can be made in the present invention without departing from the spirit or scope thereof, for it is to be understood that I limit myself only as defined in the appended claims.

What is claimed is:

1. A dry solid stable bleaching composition consisting essentially of citric acid monohydrate and calcium peroxide wherein the ratio of the weight of said citric acid monohydrate to calcium peroxide is from about 1.7 to about 7 such that when mixed together in water, an aqueous bleaching mixture is produced having a pH of within the range of from about 5 to about 3.

2. A dry solid stable bleaching composition consisting essentially of citric acid monohydrate and calcium peroxide wherein the ratio of the weight of said citric acid monohydrate to that of said calcium peroxide is within the range of from about 1.6 to about 1.7 such that when mixed together in water an aqueous bleaching mixture is produced having a pH value within the range of from about 9.5 to about 5.

3. A dry solid stable bleaching composition consisting essentially of citric acid and calcium peroxide wherein the ratio of the weight of said citric acid to calcium peroxide is from about 1.46 to about 6.4 such that when mixed together in water, an aqueous bleaching mixture having a pH within the range of from about 9.5 to about 3 is produced.

4. A dry solid stable bleaching composition consisting essentially of citric acid and calcium peroxide wherein the ratio of the weight of said citric acid to calcium peroxide is from about 1.55 to about 6.4 such that when mixed together in water, an aqueous bleaching mixture is produced having a pH within the range of from about 5 to about 3.

5. A dry solid stable bleaching composition consisting essentially of citric acid and calcium peroxide wherein the ratio of the weight of said citric acid to that of said calcium peroxide is within the range of from about 1.46 to

about 1.55 such that when mixed together in water, an aqueous bleaching mixture is produced having a pH value within the range of from about 9.5 to about 5.

References Cited by the Examiner

UNITED STATES PATENTS

850,606 4/1907 Schroeder ..... 252—186

OTHER REFERENCES

Becco: Bulletin No. 7, Alkaline Earth Metal Peroxides, Food Machinery and Chemical Corp., Buffalo 7, New York, page 3.

ALBERT T. MEYERS, *Primary Examiner.*

JULIUS GREENWALD, *Examiner.*

M. WEINBLATT, *Assistant Examiner.*