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3,248,336 AQUEOUS BLEACHING SOLUTIONS OF PEROXYCARBOXYLIC ACIDS

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The present invention relates to a process for producing stable, aqueous solutions of peroxybenzoic acid and substituted peroxybenzoic acids for use as bleaching agents.

This is in a continuation-in-part of application Serial No. 119,325, now U.S. Patent 3,130,169, filed on June 26, 1961, in the name of John H. Blumbergs et al.

In the process of laundering textile garments in domestic washing machines, it is common to employ a bleaching agent in addition to a detergent to maintain the original whiteness of the garments after laundering. It is preferred to add the bleach in the form of a dilute, aqueous solution to avoid localized bleaching and for ease in measuring and adding the varied amounts of bleach required with different garments and different washing loads.

Bleaching agents presently in use have been found to have serious drawbacks. For example, sodium hypochlorite, a commonly used bleach, has the disadvantage of not being stable in aqueous solutions and losing its effective bleaching power on storage. In addition, it causes measurable degradation of the fabric during bleaching and is capable of causing localized over-bleaching by direct contact of the bleach with the fabric in the absence of water. Other active chlorine bleaching agents, such as the chlorinated isocyanuric acids, are more stable than sodium hypochlorite but these too can cause measurable degradation of the fabric and are subject to localized overbleaching.

Other types of bleaches have been suggested to overcome the problem of fabric degradation, e.g. sodium perborate and potassium persulfates (Caroates). In the case of sodium perborate, fabric degradation is reduced but the bleaching action is inferior to the prior sodium hypochlorite bleaches when conducted under conventional domestic washing conditions. Similarly, the potassium persulfate bleaches give improved bleaching action over sodium persulfate but are inferior to sodium hypochlorite. Further, potassium persulfates are not stable in aqueous solutions, and therefore, cannot be supplied in the form of dilute, aqueous bleaching solutions.

Peroxybenzoic acid and substituted peroxybenzoic acids give good bleaching action and do not degrade the bleached fabric but they have not been used as domestic laundry bleaching agents because of the poor stability of these compositions in solution and the inability to form stable, aqueous-based solutions thereof.

In U.S. Patent 3,075,921, issued on January 29, 1963, to Peter Brocklehurst et al., there is described a process for making a dry detergent composition containing as a bleaching agent, selected, substituted peroxybenzoic acids which are more stable than peroxybenzoic acid per se. The substituted peroxybenzoic acids are present as discrete, dry solids in the dry detergent composition; no provision is taught for preparing aqueous-based, clear bleaching solutions of these peroxy acids for easy addition in domestic washing machines. As a result, there has been a need for an effective bleaching agent which can be supplied as a stable, aqueous solution and which does not degrade the fabric during bleaching.

It is an object of the present invention to provide a stable, aqueous solution of a bleaching agent which is

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effective in giving a high degree of brightness without degrading the fabric during bleaching.

I have now found that peroxybenzoic acid and substituted peroxybenzoic acids which do not contain oxidizable groups can be made up into stable, aqueous-based bleaching solutions by dissolving these acids in a mixed solvent comprising water and tert-butyl alcohol, in which the tert-butyl alcohol is present in a weight ratio relative to the water of up to 1:1, but always in amounts sufficient to both dissolve and stabilize the peroxy acid and to form a homogeneous solution.

It is most unexpected to find that tert-butyl alcohol can be used to make up stable, homogeneous, aqueous solutions of these non-oxidizable peroxybenzoic acids, particularly since these peroxy acids alone are virtually insoluble in water. In my parent application U.S. Serial No. 119,325, filed on June 26, 1961, I have taught that certain tertiary alcohol solvents are capable of stabilizing peroxycarboxylic acids. In that application, the tertiary alcohol was used either alone as the entire solvent or mixed with small amounts (no more than 20% by weight) of another organic solvent for the peroxycarboxylic acid. In the present application, as little as 10% by weight of the tertiary alcohol in a water solution has been found effective in stabilizing the peroxycarboxylic acid.

The only tertiary alcohol useful in the present invention is tert-butyl alcohol. Other tertiary alcohols, which are sparingly soluble in water, have not been found effective in making up the present homogeneous, aqueous bleaching solutions. The tert-butyl alcohol can be used to make up the aqueous-based solutions of the peroxybenzoic acids up to about 12% by weight when the alcohol is present in a 1:1 weight ratio with water. Lower amounts of the tert-butyl alcohol can be used to make up more dilute peroxy acid solutions. A dilute solution of about 2% by weight peroxy acid requires about 10% by weight of the tertiary alcohols to impart stability and homogeneity to the aqueous solution.

The tertiary alcohols used in making up the aqueous bleach solution should be free of impurities that can cause rapid decomposition of the peroxybenzoic acids or which can be oxidized by these acids, thus wastefully consuming them. The most common offending impurities are heavy metals. Heavy metals initiate catalytic decomposition of the peroxybenzoic acids, and therefore, are highly undesirable, even in small amounts.

Two methods can be employed to eliminate decomposition by heavy metals. The first of these is to remove the heavy metals by distilling the tertiary alcohols in glass or glass-lined equipment. Another is to render the heavy metals inactive by adding a small amount, on the order of about 100 p.p.m., of a metal chelating agent. A compound such as dipicolinic acid is an ideal chelating agent and effectively ties up the heavy metal in a complex organic structure, thereby making it unavailable for initiating decomposition of the peroxybenzoic acids.

The peroxy acid which has been found most suitable in the present bleaching solution is peroxybenzoic acid because of its high solubility in the tert-butyl alcohol and because it has proportionately more active oxygen per molecular weight than do the substituted peroxybenzoic acids. Aqueous solutions having up to about 12% by weight of peroxybenzoic acid can be made up readily when tert-butyl alcohol is employed as the tertiary alcohol. In making up such solutions, they should contain about 44% by weight water, about 12% by weight peroxybenzoic acid, and from about 44% by weight tert-butyl alcohol. A preferred bleaching mixture contains from about 52% by weight water, about 9% peroxybenzoic acid, and 39% by weight of tert-butyl alcohol.

In addition to peroxybenzoic acid, substituted peroxybenzoic acids can be employed which do not contain groups that can be oxidized by the peroxybenzoic acids.

p. 1061. The concentration of the ingredients in the solution and the results of the analysis are listed in Table I below:

Table I

Sample No.	Sample Composition	Peracid and Hydrogen Peroxide Content			
		At Start	After 1 Month Storage	After 3 Months Storage	After 6 Months Storage
1	Peroxybenzoic Acid, percent	11.40	11.27	11.16	11.04
	Hydrogen Peroxide, percent	0.00	Trace	Trace	Trace
	Tert-butanol, percent	44.3			
	Distilled Water, percent	44.3			
	Dipicolinic Acid, p.p.m.	100			
2	Peroxybenzoic Acid, percent	7.22	7.10	7.05	6.92
	Hydrogen Peroxide, percent	0.00	0.03	0.03	0.02
	Tert-butanol, percent	32.7			
	Distilled Water, percent	60.0			
	Dipicolinic Acid, p.p.m.	100			
3	Peroxybenzoic Acid, percent	5.00	4.92	4.90	4.77
	Hydrogen Peroxide, percent	0.00	Trace	0.02	0.03
	Tert-butanol, percent	30.3			
	Distilled Water, percent	64.7			
	Dipicolinic Acid, p.p.m.	100			
4	Peroxybenzoic Acid, percent	1.40	1.39	1.31	1.22
	Hydrogen Peroxide, percent	0.00	Trace	Trace	0.02
	Tert-butanol, percent	9.5			
	Distilled Water, percent	89.1			
	Dipicolinic Acid, p.p.m.	100			

These substituted peroxybenzoic acids further must be sufficiently soluble in the tertiary alcohol-water mixture to reach the peroxy acid content desired. For example, nitro groups are non-oxidizable, but they are unsuitable in the present application because the nitro group so lowers the solubility of the resultant peroxybenzoic acid that it cannot be used in making up the present bleach solutions. Substituted peroxybenzoic acids which contain chloro, lower saturated aliphatic, methoxy, and other such groups have been found suitable. Compounds such as ortho-chloroperoxybenzoic acid, para-chloroperoxybenzoic acid, meta-chloroperoxybenzoic acid, para-tertiary butyl peroxybenzoic acid, and para-methoxy peroxybenzoic acid, have been found suitable. Examples of substituents on the peroxybenzoic acid which are oxidizable, and therefore unsuitable, include primary and secondary alcoholic groups, hydroxyl, ketonic and aldehydic groups.

In contrast to the present peroxybenzoic acids, the aliphatic peroxycarboxylic acids have not been found suitable in this application because they undesirably hydrolyze in aqueous solutions to the corresponding acid and hydrogen peroxide. Peroxybenzoic acid and substituted peroxybenzoic acids, in contrast, have negligible rates of hydrolysis in water solutions and therefore, are effective in retaining their active oxygen contents for a sustained period in aqueous solutions.

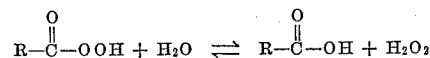
In addition to being excellent bleaching agents, the present aqueous-based peroxybenzoic acid solutions have been found to have high germicidal action. This is advantageous because the bleaching agent effectively sterilizes the soiled garments it contacts during conventional domestic laundering. In addition, if desired, the present aqueous solutions can be used as germicidal and disinfecting solutions because of their high germicidal action. The makeup of these germicides in an aqueous base facilitates their use and permits sterilization of equipment without residual organic solvents being retained thereon.

The following examples are given to illustrate the invention and are not deemed to be limiting thereof.

EXAMPLE 1

Peroxybenzoic acid was dissolved in tert-butyl alcohol and this solution was mixed with various proportions of distilled water. To these solutions were added small amounts of dipicolinic acid to act as sequestering agents for the removal of heavy metal ion impurities. The samples were stored at room temperature (about 25° C.) for up to 6 months and were analyzed periodically for their peroxy acid and hydrogen peroxide content by the method described in Analytical Chemistry, 20 (1948),

In this example, the amount of hydrogen peroxide in the sample indicates the degree of hydrolysis of the peroxybenzoic acid in accordance with the formula set forth below:



The greater the amount of hydrogen peroxide in the solutions, the greater the hydrolysis and the less effective is the bleaching and germicidal activity of the peroxybenzoic acid solution.

EXAMPLE 2

The peroxybenzoic acid solution identified as Sample 1 in Example 1, after storage for 6 months at room temperature, and which contained 11.04% by weight of peroxybenzoic acid, was tested for germicidal activity against *Staphylococcus aureus* by the standard procedure for phenol coefficient determination as described in Official Methods of Analyses of the A.O.A.C., published by A.O.A.C. (1960), pp. 63-65. The phenol coefficient was found to be 400, calculated on the basis of the active ingredient. An acceptable, active germicide should have a phenol coefficient of about 200.

EXAMPLE 3

The peroxybenzoic acid solution identified as Sample 1 in Example 1, after storage for 6 months at room temperature, and which contained 11.04% by weight of peroxybenzoic acid, was tested for bleaching effectiveness. The procedure used was as follows: Thirty-two cotton swatches (5" x 5" desized cotton Indianhead fabric, uniform in weave and thread count) were stained with tea, coffee and wine in the following manner: Five tea bags were placed in a liter of water and boiled for 5 minutes. Thereafter, the swatches were immersed in tea and the boiling continued for 5 minutes. Thirty-two additional swatches of the same cloth were coffee-stained by boiling 50 g. of coffee in a liter of water, immersing the swatches in the coffee solution and boiling for an additional 5 minutes. The wine stains were created by soaking swatches of the same cloth in a red wine at room temperature. The stained swatches were then squeezed to remove excess fluid, dried, rinsed in cold water and dried. Three of the stained cotton swatches were then added to each of a series of stainless steel Terg-O-Tometer vessels (produced by the U.S. Testing Company) containing 1,000 ml. of a 0.2% standard detergent solution at a temperature of 120° F. Measured amounts of the bleach solution were then added to each vessel sufficient to correspond to an active

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oxygen content of 20, 40, 60 and 80 p.p.m. respectively. The pH of the solutions were adjusted to 9.5, using soda ash. Cut-up pieces of white terry cloth toweling were then added to provide a typical household wash water/cloth ratio of 20:1. The Terg-O-Tometer was then operated at 72 cycles per minute for 15 minutes at a temperature of 120° F. At the end of the wash cycle, the swatches were removed, rinsed under cold tap water and dried in a Proctor-Schwartz skein dryer. The tests were run in triplicate and included detergent blanks. Reflectance readings of the swatches were then taken before and after the wash cycle with a Reflectometer and the readings were averaged. The percent stain removal was obtained in accordance with the following formula:

Total percent stain removal=

$$\frac{\text{Reflectance after bleaching} - \text{Reflectance before bleaching}}{\text{Reflectance before staining} - \text{Reflectance stained}} \times 100$$

The results are reported in Table II below:

Table II

Sample Tested (Sample 1 from Table I)	Contents, percent	Active Oxygen Content, p.p.m.	Percent Stain Removal		
			Tea	Coffee	Wine
Peroxybenzoic Acid.....	11.04	20	74.2	92.7	92.6
Hydrogen peroxide.....	Trace	40	79.3	97.0	96.2
Tert-butanol.....	44.3	60	80.0	96.4	96.8
Water.....	44.3	80	82.2	95.7	94.5
Dipicolinic Acid.....	1 100				
Detergent Blank.....			26.9	45.0	61.0

¹ Parts per million.

EXAMPLE 4

Meta-chloroperoxybenzoic acid was dissolved in tert-butyl alcohol and this solution was mixed with various proportions of distilled water. To these solutions were added small amounts of dipicolinic acid to act as sequestering agents for the removal of heavy metal ion impurities. The samples were stored at room temperature (about 25° C.) for up to 6 months and were analyzed periodically for their peroxy acid and hydrogen peroxide content by the method described in Analytical Chemistry, 20 (1948), p. 1061. The concentration of the ingredients in the solution and the results of the analysis are listed in Table III below:

Table III

Sample No.	Sample Composition	Peracid and Hydrogen Peroxide Content			
		At Start	After 1 Month Storage	After 3 Months Storage	After 6 Months Storage
1.....	Meta-chloroperoxybenzoic Acid, percent.....	10.89	10.89	10.77	9.80
	Hydrogen Peroxide, percent.....	0.00	Trace	Trace	Trace
	Tert-butanol, percent.....	44.5			
	Distilled Water, percent.....	44.5			
	Dipicolinic Acid, p.p.m. 100.....				
2.....	Meta-chloroperoxybenzoic Acid, percent.....	10.84	10.60	10.16	9.95
	Hydrogen Peroxide percent.....	0.00	Trace	Trace	Trace
	Tert-butanol, percent.....	44.5			
	Distilled Water, percent.....	44.5			
	Dipicolinic Acid, p.p.m. 100.....				

In this example, the amount of hydrogen peroxide in the sample indicates the degree of hydrolysis of the meta-chloroperoxybenzoic acid. The greater the amount of hydrogen peroxide in the solutions, the greater the hydrolysis and the less effective is the bleaching and germicidal activity of the meta-chloroperoxybenzoic acid solution.

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EXAMPLE 5

The solution identified as Samples 1 and 2 used in Example 4, after storage for 6 months and having meta-chloroperoxybenzoic acid contents of 9.80% and 9.95% respectively, were each tested for germicidal activity in the same way as described in Example 2. The phenol coefficients of these samples are given in Table IV and are calculated on the basis of the active ingredient.

Table IV

Sample Tested	Microorganisms	Phenol Coefficient
1.....	Staphylococcus aureus.....	383
2.....	do.....	400

EXAMPLE 6

The solution identified as Sample 1 in Example 4, after storage for 6 months at room temperature and having a meta-chloroperoxybenzoic acid content of 9.80%, was tested for its bleaching activity as set forth in Example 3. The results of these bleaching tests are given in Table V below:

Table V

Sample Tested (Sample 1 from Table 3)	Contents, Percent	Active Oxygen Content, p.p.m.	Percent Stain Removal		
			Tea	Coffee	Wine
Meta-chloroperoxybenzoic acid.....	9.80	20	61.5	89.3	85.4
Hydrogen Peroxide.....	0.00	40	70.5	93.3	92.0
Tert-butanol.....	44.5	60	73.6	95.3	95.3
Distilled Water.....	44.5	80	75.8	96.2	94.5
Dipicolinic Acid.....	1 100				
Detergent Blank.....			26.9	45.0	61.0

¹ Parts per million.

Pursuant to the requirements of the patent statutes, the principle of this invention has been explained and exemplified in a manner so that it can be readily practiced by those skilled in the art, such exemplification including what is considered to represent the best embodiment of the invention. However, it should be clearly understood that, within the scope of the appended claims, the invention may be practiced by those skilled in the art, and having the benefit of this disclosure otherwise than as specifically described and exemplified herein.

What is claimed is:

1. A stable, aqueous based composition which consists

essentially of a peroxybenzoic acid, said acid being free of groups which can be oxidized by peroxycarboxylic acids, dissolved in a mixed solvent consisting essentially of water and tert-butyl alcohol, in which the tert-butyl alcohol is present in weight ratios relative to the water of up to 1:1, and in amounts sufficient to form a homogeneous solution.

2. The composition of claim 1 in which the peroxy-

benzoic acid is present in amounts of from about 2% to about 12% by weight of the solution.

3. A stable, aqueous-based composition consisting essentially of peroxybenzoic acid dissolved in a mixed solvent consisting essentially of water and tert-butyl alcohol, in which the tert-butyl alcohol is present in weight ratios relative to water of up to 1:1, and in amounts sufficient to form a homogeneous solution.

4. The composition of claim 3 in which the peroxybenzoic acid is present in amounts of from about 2% to about 12% by weight.

5. A stable, aqueous-based composition consisting essentially of meta-chloroperoxybenzoic acid dissolved in

a mixed solvent consisting essentially of water and tert-butyl alcohol, in which the tert-butyl alcohol is present in weight ratios relative to water of up to 1:1, and in amounts sufficient to form a homogeneous solution.

References Cited by the Examiner

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JULIUS GREENWALD, *Primary Examiner*.