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STABILIZATION OF BLEACH BATHS OF HIGH ALKALINITY

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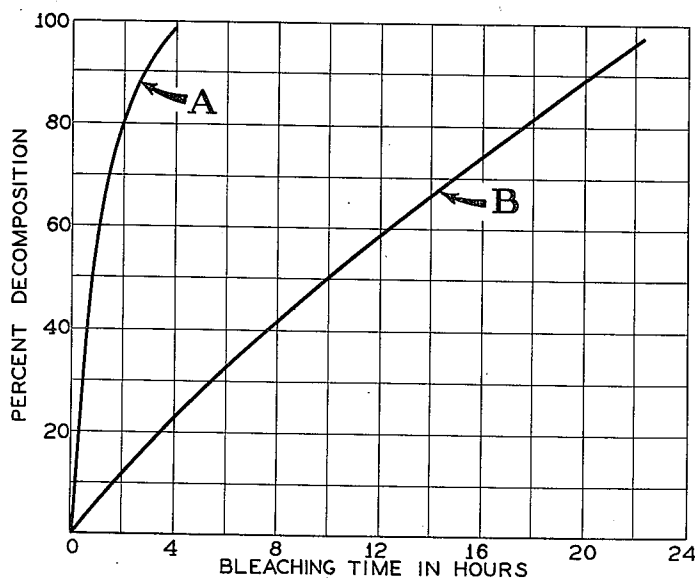


Fig. 1.

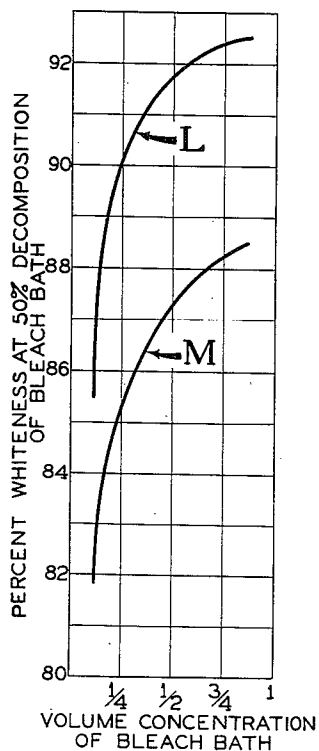


Fig. 2.

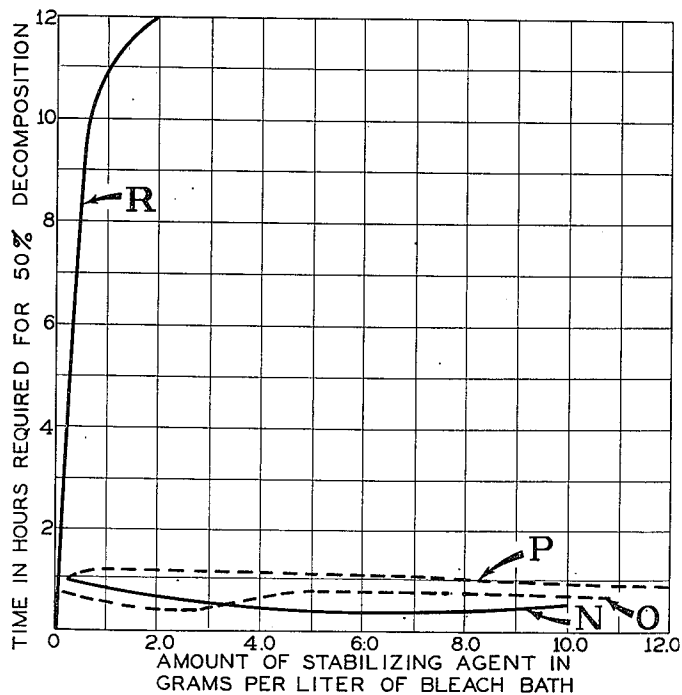


Fig. 3.

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STABILIZATION OF BLEACH BATHS OF
HIGH ALKALINITY

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This invention relates to the stabilization of bleach baths comprising aqueous solutions of peroxygen compounds. More particularly, it relates to the stabilization of bleach baths of relatively high alkalinity such as those resulting from the dissolution of alkali metal peroxides in water or from the preparation of solutions of inorganic peroxides such as hydrogen peroxide containing relatively large amounts of unneutralized alkali.

Unneutralized aqueous solutions of alkali metal peroxides, such as unneutralized aqueous solutions of sodium peroxide, have been used to a limited extent for the bleaching of cotton materials. These solutions are prepared by dissolving a commercial alkali metal peroxide, such as the sodium peroxide sold under the trade mark name "Solozone," in water or similar aqueous liquid without the introduction of acid or acidic substances for purposes of regulating the pH of the bleaching bath. While this is the most convenient way of preparing solutions of inorganic peroxides containing relatively large quantities of dissolved alkali, such solutions can of course also be prepared by introducing fairly large amounts of alkaline agents into an aqueous solution of hydrogen peroxide.

While solutions of inorganic peroxides containing fairly large amounts of dissolved alkali have been successfully employed in the bleaching of textile goods such as cotton, such baths, by reason of their relatively high content of dissolved alkali, have been relatively unstable, even when maintained at relatively low temperatures such as those corresponding to room temperature or below. This invention is particularly directed to new and improved stabilizers for stabilizing such solutions of inorganic peroxides of relatively high dissolved alkali content.

One object of this invention may be said to involve the stabilization of bleach baths comprising inorganic peroxygen compounds, which bleach baths are of relatively high pH and contain considerable quantities of unneutralized alkali. An ancillary object of our invention is the utilization of a mixed stabilizer comprising magnesium sulfate and sodium pyrophosphate in combination, for stabilizing solutions of inorganic peroxides containing fairly large amounts of alkali per liter, such as solutions resulting from the dissolution in water of alkali metal peroxides without the addition of sufficient acids or acid materials to neutralize the alkali metal hydroxide formed. These and further objects of our invention will be apparent from the ensuing disclosure of certain preferred embodiments thereof.

The solution of inorganic peroxides which it is a primary object of this invention to stabilize are those having pH values of 11.5 or above. Such solutions may be prepared by dissolving an alkali metal peroxide such as sodium peroxide in water, the quantity of sodium peroxide added being at least 0.75 pound per 100 gallons of bleach bath, and there being introduced into said solution no acid or acid substance for the purpose of neutralizing or partially neutralizing any of the sodium hydroxide formed as a result of the dissolution of the sodium peroxide in water. They may also be prepared from solutions of other inorganic peroxides such as hydrogen peroxide by introducing therein sufficient of an alkaline material such as caustic soda or soda ash to yield a solution having a pH of 11.5 or above. The amount of alkali thus introduced will be at least equivalent to that produced by dissolving 0.75 pound of sodium peroxide per 100 gallons of bleach liquor without any neutralization or partial neutralization by the addition of acids or acid substances.

We have found that when baths of the specified high alkalinity, having a pH of 11.5 or above, are stabilized by the addition thereto of a mixed stabilizer comprising magnesium sulfate and sodium pyrophosphate, the results are much more satisfactory than when either stabilizer is utilized alone. This mixed stabilizer is more satisfactory than any other stabilizer that we have investigated in the course of our study of the problem of stabilizing solutions of inorganic peroxides of high alkali content. We prefer to use the ordinary commercial magnesium sulfate, magnesium sulfate heptahydrate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Epsom salts), and tetrasodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$, although the crystalline salt, sodium pyrophosphate decahydrate, $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$, is equally suitable. Of course the use of the hydrated salts is not essential, and anhydrous magnesium sulfate may be utilized with equal success. In place of the sodium pyrophosphate, other alkali metal pyrophosphates may be used, although, by reason of its relative cheapness and ready availability, we prefer to utilize sodium pyrophosphate decahydrate. In place of the magnesium sulfate any soluble magnesium salt such as magnesium chloride may be used with equally satisfactory results. For purposes of convenience, however, our invention will be described with particular reference to our preferred compounds, sodium pyrophosphate and magnesium sulfate.

We have found that the ratio of the amount of sodium pyrophosphate to the amount of magne-

sium sulfate or other soluble magnesium salt in the stabilizer may vary within certain limits. Thus, the mixed stabilizer may consist of one part by weight of magnesium sulfate heptahydrate and as little as two or three parts by weight of sodium pyrophosphate decahydrate. Ratios of sodium pyrophosphate to magnesium sulfate in excess of three to one will, under some circumstances, be found to yield slightly better stabilizing action. When the ratio of the salts comprising the stabilizing agent is one part by weight of magnesium sulfate heptahydrate to four parts by weight of sodium pyrophosphate decahydrate, the stabilizer functions very satisfactorily, and very superior stabilization is secured up to a ratio of one part of the magnesium sulfate to seven parts by weight of the sodium pyrophosphate. With ratios ranging from one part by weight of magnesium sulfate to seven parts by weight of sodium pyrophosphate, to one part by weight of magnesium sulfate to thirteen parts by weight of sodium pyrophosphate, a high degree of stabilizing action is secured, although stability of the solutions for equal quantities of the stabilizer may be somewhat less than that of solutions wherein stabilizers higher in ratio of magnesium sulfate content to sodium pyrophosphate content are present.

We have found that the amount of stabilizer necessary to secure satisfactory stabilizing action is not unduly critical. Amounts of the stabilizer sufficient to introduce into the solution from 3 to 8 ounces of $MgSO_4 \cdot 7H_2O$ per 100 gallons of bleach bath are entirely sufficient to impart a high order of stability. However, somewhat larger quantities of the stabilizer will give bleach baths of somewhat improved stability.

While our mixed stabilizer is effective in stabilizing all bleach baths of high alkalinity having a pH of 11.5 or above, ordinarily we prefer not to utilize it in baths very much more concentrated than 1 volume, i. e., containing more than 6.0 pounds of sodium peroxide or any equivalent alkali content per 100 gallons of bleach bath. It may here be noted that the concentration of a peroxygen compound such as sodium peroxide or hydrogen peroxide in a bleach bath is frequently expressed in terms of volume concentration, one volume concentration being that concentration of peroxygen compound yielding a solution which will release one volume of oxygen gas, measured at 0° C. and 760 mm. of mercury pressure, from one volume of the solution measured at 20° C. When sodium peroxide is utilized as the peroxygen compound, a solution of 0.75 volume concentration corresponds substantially to one having dissolved therein 4.5 pounds of sodium peroxide per 100 gallons of bleach liquor. Similarly, a solution of 0.50 volume corresponds to a bath containing substantially 3.0 pounds of sodium peroxide per 100 gallons of bleach bath, while a bleach bath of 0.25 volume concentration will contain 1.50 pounds of sodium peroxide per 100 gallons of bleach bath. We have secured satisfactory stabilizing action with bleach baths as low as 0.125 volume (equivalent to 0.75 pound of sodium peroxide per 100 gallons of solution) or of even lower sodium peroxide concentration. Such baths will all have pH values of substantially 11.5 or above.

It may here be noted that commercial solutions of hydrogen peroxide, such as those sold under the trade-mark name "Albone," are all of 100 volume concentration, which is equivalent to 27.6% H_2O_2 by weight.

While our combined stabilizing agent, formed by utilizing magnesium sulfate and sodium pyrophosphate conjointly, is entirely effective for stabilizing bleach baths of much higher alkali content than that corresponding to unneutralized sodium peroxide of 1 volume concentration, with solutions of higher alkali content there is danger of precipitation of the magnesium. Thus, with bleach baths containing concentrations of alkali higher than that corresponding to a 1 volume solution of unneutralized sodium peroxide, there is a tendency for the bath to become somewhat turbid. With solutions containing an alkali content equivalent to that produced by preparing a bath of 2 volume concentration by the use of unneutralized sodium peroxide (12 pounds of sodium peroxide per 100 gallons of bleach liquor) there is observed a flocculent precipitate. While the presence of this flocculent precipitate is not necessarily objectionable and does not appear to interfere with the stabilizing action of our new and improved stabilizing agent, in bleach baths where clarity and the absence of turbidity or a precipitate is important we prefer to utilize solutions having an alkali content not over that corresponding to a bleach bath of 1 volume concentration, prepared by the dissolution of unneutralized sodium peroxide.

It should be understood that in specifying the alkali content of the active oxygen bleach baths the stabilization of which forms the object of this invention, such baths may also be prepared in other ways than by dissolving an alkali metal peroxide such as sodium peroxide in water without the addition of any acid or acid substance to effect neutralization. Thus, they may be prepared from solutions of hydrogen peroxide by dissolving alkaline agents such as caustic soda or soda ash therein until the pH of the solution is 11.5 or above. Alternatively, they may be prepared by dissolving an alkali metal peroxide such as sodium peroxide in amounts larger than those herein specified and introducing greater or less amounts of acid to effect partial neutralization of the peroxide. The solutions whose stabilization forms the object of this invention have pH values of 11.5 or higher and contain a content of dissolved alkali at least equivalent to that present in a bleach bath of unneutralized sodium peroxide of 0.125 volume concentration, such a bath containing substantially 0.75 pound of sodium peroxide per 100 gallons of bleach liquor.

In the annexed drawing various experimental results are plotted as graphs to illustrate the remarkable effectiveness of sodium pyrophosphate and magnesium sulfate when used conjointly for the stabilization of bleach baths of high alkali content. In the drawing Fig. 1 is a graph wherein the bleaching time in hours is plotted against the percent of decomposition of the bleach bath. Fig. 2 shows the superior whiteness obtained at 50% decomposition of the bleach bath when the bleach bath is stabilized with our new and improved stabilizing agent, as compared with unstabilized bleach baths of equal concentration. Fig. 3 is a graph showing the great superiority of sodium pyrophosphate and magnesium sulfate when used conjointly for stabilizing bleach baths of high alkali content over either stabilizer when utilized alone. This figure also illustrates the superiority of the new and improved stabilizer over sodium silicate, an agent frequently utilized as a stabilizer in commercial bleach baths.

Referring first to Fig. 1, the bleaching time in hours is plotted against the percent decomposition of the bleach bath. The bleach bath was one of 0.5 volume concentration, produced by dissolving sodium peroxide in an unneutralized bath in amount corresponding to 3 pounds of the peroxide per 100 gallons of bleach liquor. The bath was then used for bleaching cotton goods in accordance with the usual commercial procedure at a temperature of 180° F., the amount of cotton goods being equivalent substantially to 50 grams per liter of bleach liquor.

Curve A represents the graph of results obtained utilizing no stabilizer in the unneutralized sodium peroxide bleach bath. Curve B is the curve resulting when our improved stabilizer was utilized comprising substantially one gram of magnesium sulfate heptahydrate and three grams of sodium pyrophosphate decahydrate per liter of bleaching solution.

The remarkable stability of the bleach bath stabilized with our stabilizer mixture is illustrated by the fact that over twenty-two hours were required for 100% decomposition of the bleach bath at the highly elevated temperature employed during the bleaching, contrasted with four hours for the unstabilized bath.

We have also observed that for equal amounts of active oxygen the whiteness of the resulting bleached cotton is greater when that cotton is bleached in baths stabilized with our stabilizer than it is when the cotton is bleached in unstabilized baths prepared by dissolving unneutralized sodium peroxide in water. This fact is illustrated by the graph comprising Fig. 2, wherein percentage of whiteness for 50% decomposition of the bleach bath is plotted against the volume concentration of various bleach baths formed of unneutralized sodium peroxide and having volume concentrations up to 1 volume. In each case the bath was used to bleach cotton which had been previously boiled out in accordance with the usual practice, the amount of cotton corresponding approximately to 50 grams of cotton per liter of bleach liquor. On this graph, curve L is the curve resulting when the unneutralized sodium peroxide bleach bath is one that has been stabilized by the use of our improved stabilizing agent, while curve M represents the results secured with unstabilized bleach baths. It will be apparent, for example, that when a bleach bath of $\frac{3}{4}$ volume concentration is utilized, bleached cotton of over 92% whiteness is secured by use of the stabilized bleach bath, as contrasted with cotton of only about 88% whiteness secured by the use of the unstabilized bath. The percentage whiteness values given on this graph are the whiteness values secured after 50% of the available peroxide present in the bleach bath has been consumed.

The superiority of our conjoint stabilizer comprising an alkali metal pyrophosphate and a soluble magnesium salt, sodium pyrophosphate and magnesium sulfate being the preferred agents, for stabilizing bleach baths of high alkali content is strikingly illustrated in the graph of Fig. 3. This graph resulted from tests with a bleach bath of 0.5 volume concentration prepared by dissolving unneutralized sodium peroxide in water, the bath containing substantially 3 pounds of sodium peroxide per 100 gallons of bleach liquor. The tests were carried out at 180° F. in the presence of 50 grams per liter of cotton goods, these conditions approximating those encountered in commercial bleaching processes.

This curve shows the time required for 50% decomposition of the bleach bath plotted against various amounts of stabilizing agent. These stabilizing agents were as follows:

1. Sodium pyrophosphate alone (results shown on curve N).
2. Commercial sodium silicate of 42° Bé. concentration (results shown on curve O).
3. Magnesium sulfate and sodium silicate (results shown on curve P).
4. Our new and improved stabilizer comprising sodium pyrophosphate and magnesium sulfate (results shown on curve R).

In all cases except with our improved stabilizing agent, amounts up to 10 grams of the stabilizer per liter of bleach liquor or more were utilized. In the case of our improved stabilizer, by reason of the remarkable stability imparted to the solution by its use, it was unnecessary to use amounts over 2 grams per liter.

It will be noted that there is very little to choose between stabilizers 1, 2, and 3 above, plotted on curves N, O, and P. In all cases, even with amounts of stabilizer up to 10 grams per liter, 50% decomposition occurred within about one hour or less. With our improved stabilizer it required twelve hours for 50% decomposition of the bleach bath to occur when only two grams per liter of the stabilizing agent was employed. The superiority of our new agent, illustrated by curve R, is indeed remarkable when one considers the exceedingly elevated temperature at which the comparative bleaching trials were carried out.

We are of course aware that magnesium sulfate has previously been utilized both alone and in combination with sodium silicate for stabilizing bleach baths comprising peroxygen compounds. Similarly, sodium pyrophosphate has been used alone for stabilizing such bleach baths. It is indeed remarkable, however, that when utilizing conjointly magnesium sulfate and sodium pyrophosphate in bleach baths of the high alkali content with which this invention is concerned, having pH values of 11.5 or above, there is obtained that very surprising increase in stabilizing action resulting from the conjoint use of the two salts. As illustrated by Fig. 3, the increased stabilizing action is very much more than the sum of the stabilizing actions of the two individual components.

As an example of a bleaching process employing our new and improved stabilized bleach baths the following may be given:

Example

A bleach bath was prepared by dissolving 15 pounds of sodium peroxide, 10 pounds of sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$) and 5 pounds of magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) in 700 gallons of bleach liquor. This bleach bath was then used to bleach 700 pounds of raw cotton stock in a commercial vacuum type iron bleaching machine.

The cotton bleached was given a preliminary boil-off in a solution containing 20 pounds of soda ash per 700 gallons of solution. The boil-off was continued for twenty minutes in accordance with the usual pre-treatment procedure, whereupon the cotton was thoroughly rinsed in water for five minutes.

The boiled-out cotton was now introduced into the bleach bath maintained at an elevated temperature by the application of steam, and bleaching continued for about two hours. At the end of this period the cotton was bleached to a very

high degree of whiteness and was in every respect satisfactory. Fluidity determinations were made upon samples of the cotton to determine degradation, and the percentage degradation was found to be well within allowable limits. Although an iron machine was employed during the bleaching, no sign of attack or corrosion on the metal of the machine was observable.

Those skilled in the art will appreciate that numerous changes, modifications and adaptations of our invention may be made without departing from its novel teachings. Thus, while our invention has been particularly described with reference to our preferred agents, sodium pyrophosphate and magnesium sulfate, it should be understood that the use of other alkali metal pyrophosphates and of other soluble magnesium salts is comprehended within its scope. All changes and modifications as come within the scope of the appended claims are intended to be embraced therein.

We claim:

1. A stabilized bleach bath comprising an aqueous solution of a peroxygen compound having a pH of at least 11.5 and containing an alkali metal pyrophosphate and a soluble magnesium salt as the stabilizing agent.
2. A stabilized bleach bath comprising an aqueous solution of a peroxygen compound having a pH of at least 11.5 and containing sodium pyrophosphate and magnesium sulfate as the stabilizing agent.
3. A stabilized bleach bath comprising an aqueous solution of an inorganic peroxide having a pH of at least 11.5 and containing, as the stabilizing agent, sodium pyrophosphate and magnesium sulfate.
4. A stabilized bleach bath comprising an aqueous solution of an alkali metal peroxide having a pH of at least 11.5 and containing sodium pyrophosphate and magnesium sulfate as stabilizer.
5. A stabilized bleach bath comprising an aqueous solution of sodium peroxide having a pH of at least 11.5 and containing sodium pyrophosphate and magnesium sulfate as stabilizer.
6. A stabilized bleach bath comprising an aqueous solution of hydrogen peroxide having a pH of at least 11.5 and containing sodium pyrophosphate and magnesium sulfate as stabilizer.
7. A stabilized bleach bath having a pH of at least 11.5 and containing from 0.75 pound of sodium peroxide per 100 gallons of bleach bath to 6.0 pounds of sodium peroxide per 100 gallons of bleach bath, said solution containing no acidic constituents introduced for the purpose of regulating the alkali content thereof, and containing as stabilizer therefor, sodium pyrophosphate and magnesium sulfate.
8. A stabilized bleach bath having a pH of at least 11.5 and containing from 0.75 pound of sodium peroxide per 100 gallons of bleach bath to 6.0 pounds of sodium peroxide per 100 gallons of bleach bath, said solution containing no acidic constituents introduced for the purpose of regulating the alkali content thereof, and containing as stabilizer therefor, an alkali metal pyrophosphate and a soluble magnesium salt.
9. The process of stabilizing a bleach bath comprising an aqueous solution of an inorganic peroxide having a pH of at least 11.5 which comprises adding thereto sodium pyrophosphate and magnesium sulfate.
10. The process of stabilizing a bleach bath comprising an unneutralized solution of an alkali metal peroxide having a pH of at least 11.5 which comprises adding thereto sodium pyrophosphate and magnesium sulfate.
11. The process of stabilizing a bleach bath comprising an unneutralized solution of an alkali metal peroxide which comprises adding thereto an alkali metal pyrophosphate and a soluble magnesium salt, the pH of said solution of alkali metal peroxide being at least 11.5.
12. The process of stabilizing a bleach bath comprising an alkaline solution of hydrogen peroxide having a pH of at least 11.5 which comprises introducing therein, as stabilizing agent, sodium pyrophosphate and magnesium sulfate.
13. The process of stabilizing a bleach bath comprising an unneutralized solution of sodium peroxide having a pH of at least 11.5 which comprises adding thereto sodium pyrophosphate and magnesium sulfate.
14. The process of stabilizing a bleach bath comprising an unneutralized solution of an alkali metal peroxide containing at least 0.75 pound of sodium peroxide per 100 gallons of bleach liquor which comprises adding thereto sodium pyrophosphate and magnesium sulfate.
15. A stabilized bleach bath comprising unneutralized sodium peroxide, said bleach bath containing at least 0.75 pound of sodium peroxide per 100 gallons of bleach liquor and also containing, as stabilizer for said bath, sodium pyrophosphate and magnesium sulfate.

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