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BLEACHING PROCESS AND COMPOSITION

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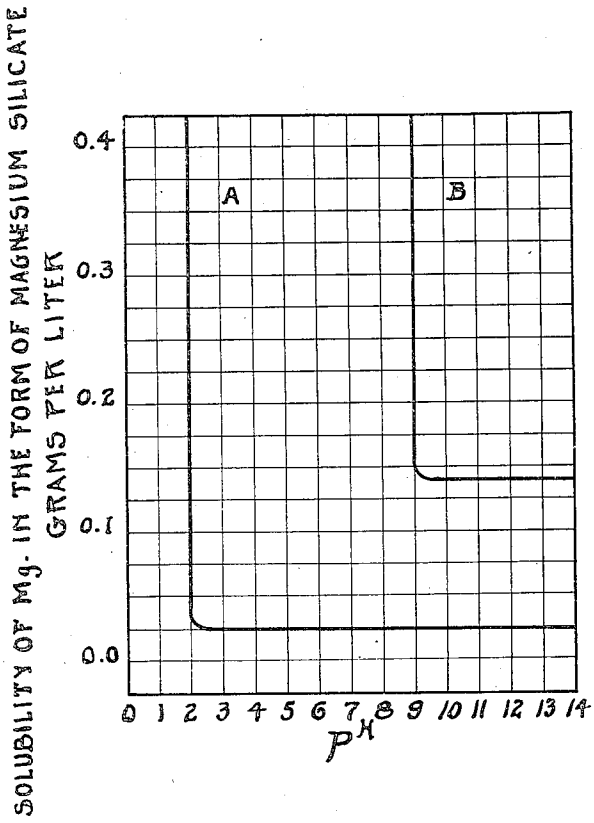

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BLEACHING PROCESS AND COMPOSITION

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This invention relates to a process of bleaching and to bleach baths containing certain stabilizers. More particularly, it relates to the preparation and use of bleach baths which contain magnesium compounds as stabilizers.

Magnesium compounds have been used as stabilizers for bleach baths consisting essentially of dilute solutions of hydrogen peroxide or similar oxygen-yielding compounds such as perborate or other peroxides for a considerable period of time. Such bleach baths usually contain, in addition to the magnesium compounds, a soluble silicate such as sodium silicate. Ordinarily in the bleaching of cotton and other materials by the use of dilute hydrogen peroxide solutions the presence of a soluble silicate such as sodium silicate is considered essential.

Due to the low solubility of magnesium silicate in solutions which are alkaline in reaction the magnesium compounds present in the solutions now used for bleaching purposes have been insoluble. In the bleaching of cotton and, indeed, in the bleaching of most other materials bleached commercially with the exception of wool, bleach baths comprising dilute solutions of hydrogen peroxide which are alkaline in reaction are employed. Due to the limited solubility of magnesium silicate which is formed in the solution when it contains a soluble silicate, these bleach baths have usually contained the stabilizing agent in the form of an insoluble precipitate.

The presence of undissolved solid salts in bleach baths is generally undesirable. The finely divided insoluble particles usually settle on the goods which are being bleached. This interferes considerably with subsequent operations such as dyeing unless the particles are removed, and the removal of these particles is ordinarily a difficult problem. Various procedures have been used to remove solid particles but, nevertheless, the presence of insoluble particles in bleach baths has been regarded as distinctly unsatisfactory and undesirable.

Commercial bleaching solutions consisting essentially of dilute hydrogen peroxide solutions usually have a pH falling between about 9.0 and 13.0. For most commercial uses the pH of such solutions is about 10.0 or 10.5. At these pH values we have found that the solubility of magnesium in the form of magnesium silicate is quite limited and, at room temperature, does not exceed about 0.025 g. magnesium metal per liter. Ordinarily amounts of magnesium silicate greater than an amount equivalent to 0.025 g. per liter are necessary for efficient stabilizing action and the bleach baths in use prior to our discovery have usually operated with precipitated magnesium silicate therein.

It is one of the objects of this invention to overcome the objectionable defect of insolubility when magnesium silicate is utilized as the stabilizing agent for bleach baths comprising dilute hydrogen peroxide solutions. It is a further object of this invention so to treat dilute solutions of hydrogen peroxide used as bleach baths or equivalent active oxygen yielding solutions, that the solubility of magnesium silicate in these solutions will be considerably increased. Moreover, it is still another object of this invention to prepare solutions of hydrogen peroxide so that much larger amounts of magnesium salts can be added thereto, in the presence of sodium silicate, without any danger of magnesium silicate being precipitated. In short, one of the principal objects of this invention is the solubilizing of magnesium compounds in bleach baths. These and still further objects of this invention will be apparent from the ensuing disclosure which is the best method known to us of practicing the improved process and preparing the improved compositions.

In the attached drawing curve A represents the solubility at room temperature of magnesium as magnesium silicate in dilute solutions of hydrogen peroxide ranging in volume concentration from about 0.25 volume to 10 volume under various conditions of acidity or alkalinity. As will be apparent, the solubility of this salt varies with the pH and the salt is most insoluble in the pH range extending from 2 to 14. Curve B represents the solubility of magnesium as magnesium silicate at room temperature over the same pH range when solutions of hydrogen peroxide of 0.25 to 10 volume concentration are prepared in accordance with the method of our invention. The volume concentration of a dilute solution of hydrogen peroxide is, of course, the number of volumes of oxygen gas, measured at 0° C. and 760 mm. of mercury pressure, which will be evolved from one volume of the solution at 25° C.

As will be apparent from curve A the solubility of magnesium, as magnesium silicate, at room temperature, in dilute solutions of hydrogen peroxide having a pH of 2 or below is in excess of 0.4 gram magnesium per liter. In the pH range 2 to 14, however, the solubility of magnesium as magnesium silicate is only about 0.025 gram magnesium per liter.

Referring now to curve B it will be noted that when the process of this invention for solubilizing magnesium silicate in bleach baths is em-

ployed, the solubility is in excess of 0.4 gram Mg per liter of solution over the much broader pH range 9 or below. In the pH range 9 to 14, which is the range ordinarily employed in cotton bleaching, the solubility of magnesium as magnesium silicate is increased to about 0.14 gram Mg per liter of solution. It will therefore be apparent that in this pH range our process results in increasing the solubility of magnesium silicate about sixfold. Since ordinarily not over about 0.14 gram Mg as magnesium silicate will be present in bleaching solutions for stabilizing purposes it is obvious that the use of our process permits the obtainment and use of bleach baths which are free from any insoluble precipitate.

In the foregoing discussion the solubility of magnesium silicate has been indicated in terms of grams of magnesium, as magnesium silicate, per liter, for the reason that magnesium silicate is ordinarily a salt of complex, variable and changing constitution and under these circumstances greater accuracy results from treating the solubility on the basis of the Mg content of the bath. In the preparation of bleach baths containing magnesium silicate as a stabilizing agent ordinarily a soluble salt of magnesium such as magnesium chloride, magnesium nitrate, magnesium acetate, or magnesium carbonate, is caused to react in situ with a soluble silicate, usually sodium silicate, present in the bath.

By following the method which we have developed for solubilizing magnesium compounds in bleach baths comprising dilute hydrogen peroxide solutions or solutions of other per-compounds such as peroxide, percarbonates, and perborates, it is possible to employ any soluble magnesium salt. Any of the salts previously indicated as suitable, i. e., magnesium sulfate, magnesium carbonate, magnesium nitrate, magnesium citrate, etc., may be used.

We have also found it possible to use freshly prepared magnesium silicate. When using magnesium silicate it is necessary to prepare a solution in which the silicate is completely dissolved. This may be done by preparing a bath containing hydrogen peroxide or other per-compound in the desired concentration, treating the solution in accordance with our solubilizing step and then dissolving magnesium silicate in the desired amount in this solution. Or, if desired, magnesium silicate may be brought into solution in a separate sample using our solubilizing step and this solution then added to the bleach bath containing the soluble silicate.

However, when preparing commercial bleach baths it is usually more desirable to use a soluble salt of magnesium such as magnesium sulfate and a soluble silicate such as sodium silicate. These components result in the formation of magnesium silicate in the bleach bath, which, if prepared in accordance with our improved solubilizing step, will be soluble in amounts equivalent to 0.125 pound of magnesium per 100 gallons of solution.

In making up our improved bleach baths we have found it essential that the solubilizing step, which will hereinafter be described more fully, be employed before the soluble silicate and magnesium salt are brought into contact under conditions wherein precipitation might occur. In other words it is necessary to avoid any opportunity for the precipitation of magnesium silicate prior to the use of our solubilizing step. Once precipitated in the bath the solubility of magnesium silicate cannot be increased by the use of our process. Accordingly the exact order of steps is important and we have found it essential in preparing our solutions first to add the magnesium salt to the bleach bath, then to adjust the pH in accordance with our solubilizing step, and finally add the sodium silicate or other soluble silicate, this final step serving at the same time to adjust the alkalinity to the desired pH value.

A commercial solution of hydrogen peroxide such as one of 100 volume concentration sold commercially under the trade-mark name "Albone C" may be first diluted with water until a solution of the desired volume concentration is obtained. For most bleaching applications this will be a concentration somewhere between 0.25 volume and 10 volumes. Next a soluble magnesium salt, which may be any one of the magnesium salts previously specified or may be magnesium silicate in solution, is added. The amount of magnesium salt should be sufficient so that the amount of magnesium in the form of magnesium silicate in the bleach bath after the addition subsequently of the soluble silicate, will be from 0.1 to 0.125 lb. of Mg per 100 gallons of solution. In practice we have used as little as 0.2 to 0.3 ounce of magnesium per 100 gallons of solution with entirely satisfactory results although, ordinarily, the more magnesium present in a bleach bath in the form of magnesium silicate up to about 0.125 lb. per 100 gallons, the more stable is the solution. For these reasons we prefer to add enough of a soluble magnesium salt to adjust the magnesium concentration of the bath to about 0.1 to 0.125 lb. per 100 gallons of solution. An added reason for using amounts of this order is that frequently goods to be bleached are introduced into the bleach baths while in the wet condition and their water content tends to dilute the bath somewhat and to lower the magnesium concentration.

The amounts which should be added are specified as amounts of Mg in the form of its salts. If the relatively inexpensive magnesium salt, magnesium sulfate, $MgSO_4.7H_2O$, is used, it is necessary for a magnesium content of from 0.1 to 0.125 lb. per 100 gallons to add approximately 1 to 1.25 lbs. of magnesium sulfate. When other magnesium salts are utilized the amount of salt necessary can be calculated from its magnesium content.

It should be understood that amounts up to as high as 0.125 lb. of magnesium per 100 gallons of solution are not necessary in order that the solution be stabilized, nor are they necessary in carrying out the process which constitutes our invention. However, it is an object of this invention to permit the use of larger quantities of magnesium silicate in soluble form and as a result of our novel solubilizing step we can use these larger amounts without any insoluble precipitate forming in the bleach bath.

After the addition of the magnesium compound in the requisite amount to the dilute hydrogen peroxygen solution we next carry out a solubilizing step. This step, which is an essential element of our invention, involves the addition of an inorganic acid such as hydrochloric, nitric or sulfuric acids to the solution in amount sufficient to render it distinctly acid in reaction. We have discovered the surprising fact that by the use of this solubilizing step the solubility of magnesium as magnesium silicate in bleach baths is changed as indicated by curves A and B on the drawing. By distinctly acid in reaction

is meant that the pH of the solution should be about 2.5 or below. This pH value is given merely as illustrative, however, as in practice enough acid would be added to make the solution distinctly or even strongly acid. While a pH of 2.5 cannot be termed strongly acid it may be regarded as distinctly acid.

Instead of mineral acids various inorganic salts equivalent to mineral acids may be used. Thus we have found that sodium acid sulfate,

$$NaHSO_4.H_2O$$

is suitable. Other inorganic salts may also be used, and as they are exactly equivalent to the acids they should be added in sufficient amount to render the hydrogen peroxide solution containing magnesium distinctly acid in reaction. In other words the pH should be adjusted to about 2.5 or below by the addition of the salt.

After the solubilizing step the alkalinity of the solution is next adjusted by the addition of an alkaline material. Ordinarily we prefer to add sodium silicate at this stage, as this soluble silicate serves at the same time to reduce the acidity, since it is alkaline in reaction, and to add the requisite amount of silicate to the bleach bath. Of course, other soluble silicates could be used in place of the sodium silicate, or if desired, the pH may be first adjusted by the use of some other alkaline materials such as caustic soda or soda ash. The alkalinity is adjusted so that it falls somewhere within the range desired in bleaching which, for most bleaching purposes, is somewhere between 9 and 13, and for the great majority of bleaching applications within the range 10.0 and 11.5. If the alkalinity has not been adjusted by the addition of sodium silicate a soluble silicate in sufficient amount is added at this point. However, as indicated, we prefer to adjust the alkalinity by means of sodium silicate since this is a convenient and inexpensive alkaline material and serves at the same time the purpose of supplying silicate in sufficient amount to the bath. In most bleaching operations it is usual to have a considerable quantity of sodium silicate present in the bleach bath and an excess of silicate over the amount necessary to form magnesium silicate in the bleach bath is not objectionable and, in fact, is to be desired.

When this process is followed the solubility of magnesium as magnesium silicate in the bleach bath is found to be increased in accordance with the curves indicated on the drawing. After the use of our process, Curve B represents the solubility of magnesium in the form of magnesium silicate in the bleach bath. This means that magnesium may be present in amounts as high as 0.125 lb. magnesium as magnesium silicate per 100 gallons of solution without precipitation occurring. This is attributable to the novel solubilizing step. The order of addition of the material to the hydrogen peroxide solution is also important and it is necessary to add the magnesium prior to the addition of the solubilizing agent and finally add the desired amount of soluble silicate to the solution. If the order of steps is changed precipitation will occur and it will be impossible to increase the solubility as desired.

As an example of the improved process the following may be given:

Example

To 100 gallons of water sufficient 100 volume hydrogen peroxide solution was added to yield a bath having a concentration of 25 volumes, and to this bath ⅘ lb. of magnesium sulfate, $MgSO_4.7H_2O$, was added. Approximately ⅔ pound of concentrated sulfuric acid (95.5 to 96.5% H_2SO_4) were next added. The solution was thoroughly mixed and its pH determined. The pH value was approximately 2.5 as observed by the colorimetric method.

Next 6 lbs. of 42° Baumé sodium silicate was added. The pH of the solution was finally adjusted to 10.0 to 10.4 by the addition of caustic soda. When used for the bleaching of ordinary cotton goods this bath gave excellent results and at no time during 48 hours of operation, either at room temperature or at elevated temperatures, was any insoluble precipitated matter observable therein.

It is to be understood that the various amounts and procedures previously described as illustrative are not to be regarded as restrictive. The invention is of broad general application wherever the solubilizing of magnesium in bleach baths is to be accomplished. Various changes may be made in the procedure disclosed which would still fall within the scope of our invention and which would utilize the essential element thereof, the use of a solubilizing step in order to render magnesium silicate in bleach baths more soluble. The scope of the invention is to be determined in accordance with the appended claims, as various equivalents of the disclosed steps and procedures might be utilized which would come within the purview of our invention.

We claim:

1. A process for preparing solutions of hydrogen peroxide containing large amounts of dissolved magnesium silicate which comprises the steps of adding a soluble magnesium compound to a solution of hydrogen peroxide, adjusting the pH of the solution to 2.5 or below, adding a soluble silicate thereto, and adjusting the pH so that said solution is alkaline in reaction.

2. A process for preparing solutions of hydrogen peroxide containing large amounts of magnesium silicate in solution which comprises adding a soluble magnesium compound to a solution of hydrogen peroxide, adding a mineral acid in amount sufficient to adjust the pH of said solution to 2.5 or below, subsequently adding a soluble silicate thereto, and adjusting the pH of said solution so that it is alkaline in reaction.

3. A process for preparing solutions of hydrogen peroxide which when they are rendered alkaline in reaction will retain amounts of magnesium silicate up to those equivalent to 0.14 gram of magnesium as magnesium silicate per liter without precipitation developing therein which comprises the steps of adding a magnesium salt to a solution of hydrogen peroxide, adjusting the pH of said solution to a value of 2.5 or below, and adding thereto a soluble silicate.

4. A process for preparing solutions of hydrogen peroxide containing dissolved magnesium silicate in amounts up to and including 0.14 gram of magnesium as magnesium silicate per liter which when rendered alkaline in reaction to a pH falling within the range 9 to 14 will not precipitate magnesium silicate in solid form which comprises the steps of adding a soluble magnesium compound to a solution of hydrogen peroxide, adding a material selected from the group which consists of inorganic acids and acid salts of inorganic acids in amount sufficient to impart

to said solution a pH of 2.5 or below, and subsequently adding thereto sodium silicate.

5. A process for preparing bleach baths comprising oxygen-evolving compounds which will retain in solution amounts of magnesium silicate up to those equivalent to 0.14 gram of magnesium as magnesium silicate per liter without precipitation developing therein when said solutions are rendered alkaline in reaction which comprises the steps of adding a magnesium compound to a bleach bath containing an oxygen-evolving compound, adjusting the pH of said solution to a value of 2.5 or below, and subsequently adding thereto a soluble silicate.

6. A process for preparing bleach baths comprising active oxygen yielding compounds which will retain in solution amounts of magnesium silicate up to those equivalent to 0.14 gram of magnesium as magnesium silicate per liter without precipitation developing therein when said baths are rendered alkaline and used for bleaching which comprises the steps of adding a soluble magnesium salt to a bleach bath, adjusting the pH of said bath to a value of 2.5 or below, and then adding thereto a soluble silicate.

7. In a process of preparing solutions of hydrogen peroxide having a pH value within the range 9 to 14 and containing dissolved therein magnesium silicate equivalent in amount to 0.14 gram magnesium as magnesium silicate per liter of solution, said solutions being free of undissolved solid precipitates, the step which comprises adjusting the pH of said solutions to a pH value of 2.5 or below in order to render said magnesium silicate, when formed in said solutions, soluble up to said stated amount.

8. As a new composition of matter a clear active oxygen yielding bleach bath containing substantially no undissolved stabilizing agents and having a pH falling within the range 9 to 14 there being present therein dissolved magnesium silicate in amounts equivalent to from 0.025 to 0.14 gram magnesium as magnesium silicate per liter of solution.

9. As a new composition of matter a clear solution of hydrogen peroxide containing substantially no undissolved stabilizing agents, said solution having a volume concentration from 0.25 volume to 10 volume, having a pH within the range 9 to 14, and containing dissolved therein magnesium silicate in amounts equivalent to from 0.025 gram magnesium as magnesium silicate to 0.14 gram of magnesium as magnesium silicate, both of these amounts being per liter of solution.

10. A clear solution of hydrogen peroxide containing substantially no undissolved stabilizing agents, having a pH within the limits 9 to 14 and containing dissolved therein magnesium silicate in amounts ranging from that equivalent to 0.025 gram of magnesium as magnesium silicate per liter of solution to 0.14 gram magnesium as magnesium silicate per liter of solution.

11. A process for preparing solutions of hydrogen peroxide having a pH ranging from 9 to 14 and containing amounts of magnesium silicate up to and including 0.14 gram of magnesium as magnesium silicate per liter of solution which comprises the steps of adding a magnesium compound to said solution, adding to said solution an acidic material selected from the group which consists of mineral acids and sodium acid sulfate in amount sufficient to impart to said solution a pH of 2.5 or below thereby rendering magnesium silicate more soluble therein, adding a soluble silicate thereto, and then adjusting the pH of said solution to any desired value within the range 9 to 14.

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