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METHOD OF BLEACHING

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This invention relates to an improved process for effecting color improvement or bleaching of non-cellulosic organic materials. The invention is applicable to the treatment of a wide variety of such materials including the following: Carbohydrates such as sugar and starch; synthetics such as acetate rayon and nylon; sponges; walnut shells; resins such as shellac; oils, fats, waxes, soaps and the like and fatty acids, such as oleic acid or red oil.

The application of my present process to the bleaching of cellulosic materials is described and claimed in my copending application Serial No. 414,139, filed October 8, 1941, granted January 23, 1945, as Patent No. 2,367,771, of which my present application is in part a continuation.

In accordance with the process of my present invention, the material to be bleached is subjected to simultaneous action of a chlorite and an aldehyde in the presence of water. Advantageously, the material being treated is admixed with the chlorite and aldehyde in aqueous solution, the pH of the solution during the bleaching operation generally being maintained at not less than about 7.

Various methods have heretofore been proposed for the bleaching of organic materials. Many of such methods have involved the use of acids and other strong chemicals which have a tendency to injure the material being bleached or require very careful, critical control to avoid such injury.

Many of these previously proposed bleaching methods, especially those involving the use of acid solutions, tend to char or cause an undesirable reaction between the organic material and the acid constituent of the solution and are not applicable to the treatment of many materials of this type, particularly soaps or other alkaline reacting materials.

I have discovered that a wide variety of organic materials, including organic substances such as previously mentioned, can economically be bleached to an exceptionally high degree without substantial degradation or danger of deleteriously affecting their desirable characteristics by subjecting them to the action of a chlorite in an alkaline or substantially neutral aqueous solution in the presence of an aldehyde, as herein-after more fully described.

The function of the aldehyde in my improved bleaching process appears to be that of activating the chlorite rather than a direct action upon the organic material itself. Thus activated, the chlorites, or reaction products thereof, are enabled to effect the bleaching of the organic ma-

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terial either in an alkaline or substantially neutral environment.

Chlorites useful in my process are those sufficiently soluble in water to provide an adequate concentration to effect the desired bleaching. When the bleaching requirement is relatively low, less soluble chlorites may be used. However, for most purposes, I prefer the chlorites of the alkali and alkaline earth metals, such as sodium chlorite, NaClO_2 , and calcium chlorite, $\text{Ca}(\text{ClO}_2)_2$.

Various aldehydes may be used, including the aliphatic aldehydes, aromatic aldehydes, other carbocyclic aldehydes and heterocyclic aldehydes. For example, I have found formaldehyde, acetaldehyde, paraformaldehyde, furfural, benzaldehyde, and 5 and 6 carbon atom aldose sugars and inverted sugars to be particularly useful. All of these compounds are characterized by the CHO group. In addition to those highly soluble in water, the relatively insoluble aldehydes have been found to function satisfactorily in most instances.

Temperatures and concentrations are not usually critical and may be varied over a wide range. Increasing the temperature has generally been found to increase the rate of bleaching. Also, the ratio of chlorite to aldehyde may be widely varied. However, a molar ratio of chlorite to aldehyde of about 1:1 has been found generally useful.

The optimum operating conditions, with respect to temperature, concentration and ratio of chlorite to aldehyde, are to a considerable extent interdependent and will vary with the particular material being bleached, the degree of bleaching required, the length of the period of treatment and, to some extent, with the particular chlorite and aldehyde employed.

The temperature best suited for a particular operation will, to a considerable extent, depend upon the nature of the material being treated. Ordinary room temperature may frequently be employed with advantage but higher temperatures are usually desirable when treating a material normally solid where it is desired to effect the melting or solution thereof. Temperatures at which the material being treated becomes unstable or at which the material is deleteriously affected are to be avoided.

Though the hydrogen ion concentration of my improved bleaching solution may be varied over a considerable range, a decided acid condition of the solution is generally to be avoided, as previously noted. Where the material being treated has an acid reaction, I have found it usually de-

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sirable to employ a buffer to maintain the solution substantially neutral or on the alkaline side. The use of a buffer having the characteristics and in sufficient quantity to maintain the solution at a pH of about 7 is generally desirable in the treatment of material such as oils and waxes. In the bleaching of soap a higher pH is usually desirable and no buffer need be employed.

Generally satisfactory results have been obtained where the pH is maintained at about 7 or higher, for instance within the range of about 7 to about 11. While solutions having a pH slightly lower than 7 may be used in the treatment of acid materials such as fatty acids and of various other materials with good results, a pH substantially on the acid side should generally be avoided.

Alkali metal phosphates such as the monosodium and disodium orthophosphates have been found to be particularly advantageous buffers for the purpose of the present invention, though other buffers may be used with advantage. I have found that in the presence of such phosphates the consumption of chlorite in the bleaching operation is materially reduced. In some instances a saving of 50% of chlorite has been effected by the use of these phosphates, in conjunction with the other constituents of my bleaching solution previously noted.

As applied to the bleaching of oils, fats, waxes, soaps and the like, my invention is particularly useful in the treatment of either natural or synthetic materials of this type, including unsaponifiable petroleum waxes and saponifiable oils and waxes such as beeswax, carnauba wax, candelilla wax, corn oil and soya bean oil. It is especially applicable to the bleaching of soaps and similar alkaline reacting materials.

The consumer market of sugar requires a highly bleached product. Also, in numerous commercial uses of starch, current trade requirements necessitate bleaching and the attainment of a high degree of white while at the same time precluding any substantial chemical reaction with the starch. By my improved process, sugars and starches may be bleached without deleteriously affecting the product or imparting thereto objectionable tastes or odors.

It will be recognized that in a strictly scientific sense there is a great variety of so-called sponges. Some of these are composed of hard, calcareous or siliceous substances. However, the familiar bath sponges which are the remains of marine animals belonging to species of the genera *Euspongia* and *Hippispongia* are made up of horny fibers closely resembling silk in composition. It is to the bleaching of the familiar bath sponges which the present invention relates.

In their natural stage these sponges are of a dark color and unattractive appearance. The desirability of bleaching sponges to improve their appearance and salability has heretofore been recognized. Though sponges have been bleached to a greater or less degree, such color improvement has generally been accomplished at the expense of durability of the sponge if excessive bleaching is effected.

By my improved bleaching method, such sponges may be bleached to an exceptionally high degree with no substantial tendering or weakening of their fiber structure so that their normal resistance to tearing apart in use is not substantially impaired.

The bleaching of starch, in accordance with my present invention, is with advantage effected by

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subjecting the starch to the action of the chlorite and the aldehyde while in aqueous suspension. The bleaching of sugar, oils, fats, waxes, soaps, shellac, fatty acid and the like is with advantage effected by treating the material while in a liquid condition, i. e., either molten or in aqueous solution, depending upon the characteristics of the particular material being treated.

For example, such materials, either molten or in aqueous solution, may be admixed with a chlorite in the presence of water and the aldehyde thereafter added or the material to be treated may be admixed with the aldehyde in the presence of water and the chlorite added to this mixture. The resultant mixture is maintained at a temperature usually ranging from room temperature to about 100° C., for a period of time sufficient to effect the desired bleaching and is thereafter cooled and separated.

In the bleaching of soap, for instance, the soap may be melted by heating in water, the soap solution admixed with an aqueous chlorite solution and the desired amount of aldehyde thereafter added gradually or as a series of small proportions during agitation.

In the treatment of wax or the like, which is solid at normal temperatures, the material is with advantage melted and an aqueous solution of the chlorite and the aldehyde admixed therewith or the chlorite and aldehyde may be separately added.

My invention and its application to the bleaching of various types of non-cellulosic organic materials thereby contemplated will be further illustrated by the following specific examples:

Example I

An aqueous solution was prepared by admixing 50 c. c. of pH 7 sodium phosphate buffer solution, 50 c. c. of an aqueous sodium chlorite solution containing 10 grams of available chlorine and 100 c. c. of a dilute aqueous formalin solution containing 2.2 grams of HCHO. 100 grams of soybean oil was then admixed with the resultant solution and allowed to stand for 2 hours, at the end of which time much of the original yellow color of the oil had been removed and, upon separation from the solution, a superior product was obtained. During the admixing of the oil with the solution and during the following 2 hour period a pH of about 7 and a temperature of about 25° C. were maintained.

Example II

Beeswax was not only bleached but the texture thereof was made smoother by the following treatment: To 50 grams of beeswax melted in a water bath there was added 50 c. c. of an aqueous pH 7 sodium phosphate buffer solution, 100 c. c. of an aqueous sodium chlorite solution containing 5 grams of available chlorine as chlorite and 1.9 c. c. of furfural. After admixing the solution and the melted beeswax, the admixture was permitted to stand for 1 hour at a temperature of 60° C. Thereafter, the wax was separated and allowed to solidify. The resultant product was found to have a much lighter color than the original wax.

Example III

Cocoabutter was saponified by treatment with caustic soda and 200 grams of the resulting soap was melted with 200 grams of water. 1 gram of sodium chlorite dissolved in an equal weight of water was then added and admixed with the soap

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solution. This was followed by the addition of 10 c. c. of aqueous formaldehyde solution prepared by dissolving 0.53 gram of 36% formalin in 100 c. c. of water. The addition of 10 c. c. of this aqueous formaldehyde solution was repeated at 10 minute intervals until a total of 100 c. c. of the solution had been added. During this period, the pH of the solution was approximately 9.3, no buffer being used, and the mixture was kept hot (about 100° C.) by the passage of steam there-through. Thereafter, the bleached soap was cooled and separated. Its color was very white.

Example IV

A further batch of the cocoabutter soap was bleached, as described in Example III, except that a reduced amount of formaldehyde was used. In this operation the formaldehyde solution was prepared by dissolving 0.4 gram of 30% formalin in 100 c. c. of water. The color of the bleached soap was found to be even superior to that resulting in Example III.

Example V

A still further batch of cocoabutter soap was bleached, as described in Example III, except that the 10 c. c. portions of the formaldehyde solutions were added at 15 minute intervals. Results comparable with those of Example III were obtained, indicating that the time factor is not critical.

Example VI

200 grams of yellow laundry soap was melted with an equal weight of water containing 0.48 gram of 36% formalin. At 15 minute intervals, 10 c. c. portions of an aqueous solution of commercial sodium chlorite, each containing 0.1 gram of chlorite, were added until a total of 100 c. c. of the chlorite solution had been added. During this period, the pH of the solution was about 9.3, no buffer being used. A temperature of about 100° C. was maintained during this period, and thereafter until all of the available chlorite had disappeared, by the passage of steam through the solution. Thereafter the soap was salted out and was found to be of a very good white color.

Example VII

For the purpose of illustrating the advantages derived from the use of the aldehyde in my process, results of the following experiments are presented:

To 500 grams of the yellow laundry soap of Example VI, maintained at its melting point, about 100° C., there was added and admixed therewith 2.5 grams of sodium chlorite in 3 c. c. of water. After being maintained at this temperature for about 2 hours, the soap was only slightly bleached. The mixture was then allowed to cool and stand for 2 days at the end of which time all available chlorine had been exhausted. The color of the soap was thereby somewhat improved though it still exhibited a slightly yellow cast. It will be observed that no aldehyde was used in this operation.

To 500 grams of the same soap, maintained at its melting point, there was added 2.5 grams of sodium chlorite and 0.932 gram of 36.6% formalin solution. After stirring the mixture for 20 minutes, all available chlorine had disappeared and the soap was well bleached. After removing a 100 gram sample of the soap, an additional 1.25 grams of sodium chlorite and 0.466 gram of formalin was added. After 15 minutes of stirring, the available chlorine had disappeared

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and a still further bleaching of the soap obtained. During these tests, the pH of the soap solution was about 9.3, no buffer being used.

Example VIII

A 25 gram piece of acetate rayon fabric was immersed in an aqueous solution prepared by admixing 250 c. c. of pH 7 phosphate buffer solution, 100 c. c. of aqueous sodium chlorite solution containing 5 grams of available chlorine and 150 c. c. of diluted formalin containing 2.2 grams of CH_2O . After an hour's treatment at 60° C., the fabric was removed, rinsed and dried. The color of the fabric was found to be considerably improved and the original fine texture thereof was completely unaffected.

Example IX

To 50 parts of crude brown sugar dissolved in 100 parts of water there was added 20 parts of a solution of sodium chlorite containing 1 part of available chlorine and 0.78 part of a formaldehyde solution containing 0.22 part of CH_2O . The mixture was buffered at pH 7 by the presence of a phosphate buffer and was held at 40° C., for 1 hour. At the end of this period the solution was found to be bleached to a substantially water-white color. A check test, under the identical conditions and using the same quantities of the same reagents except that the formaldehyde was omitted, gave no bleaching whatever. In fact the solution appeared to be slightly darker after the treatment than before.

Example X

118 parts of dark, reddish-brown shellac was dissolved in 11.8 parts of soda ash and 1000 parts of water. To 100 parts of this solution there was added 1 part of available chlorine as sodium chlorite in 20 parts of aqueous solution and 0.78 part of a formaldehyde solution containing 0.22 part of CH_2O . The solution was maintained at a temperature of 40° C. for one hour. No buffer was used and the pH of the solution was between 7 and 8.2. By the end of this period of treatment, the original dark purple colored solution had been bleached to a light tan.

Example XI

A small reddish-brown sponge was immersed for 1 hour in 200 parts of an aqueous solution containing 1 part of available chlorine as sodium chlorite and 0.22 part of CH_2O . During this period the solution was held at a temperature of 50° C., and at a pH of 6.6 by the use of a buffer. Thereafter the sponge was removed from the bleaching solution, washed and dried and was found to be of a light buff color.

Example XII

To 25 parts of crude corn starch of a greenish tint suspended in water, there was added 1 part of available chlorine as sodium chlorite dissolved in 20 parts of aqueous solution and 0.22 part of CH_2O in 20 parts of aqueous solution, the entire aqueous mixture amounting to 200 parts by weight. This suspension was held at a temperature of 50° C., for 1 hour. At the beginning of this period the pH of the solution was 7 and at the end thereof the pH had dropped to about 6.5. The starch was then filtered, washed and dried and was found to be of a pure white color free from any objectionable tints.

Example XIII

To 50 parts of red oil (oleic acid), heated in

a boiling water bath to a temperature of about 100° C., and agitated by the passage of steam therethrough, there was added 0.5 part of available chlorine as sodium chlorite dissolved in 10 parts of water. A solution of 0.25 part of 36% formalin in 10 parts of water was prepared and 1 part of this solution was added at 5 minute intervals until the total had been added. A few minutes after the final addition, all available chlorine had reacted. The fatty acid was then separated and was found to be a well bleached product.

By my improved process, a high degree of bleaching may thus be accomplished with economy in time and chemicals while avoiding deleteriously affecting the material being treated and the necessity of critical control of time, temperature and concentration heretofore required to avoid injuring the material.

I claim:

1. In the bleaching of non-cellulosic organic materials, the improvement which comprises subjecting the material to be bleached to the action of a substantially non-acidic aqueous solution of a chlorite of a metal of the group consisting of the alkali and alkaline earth metals in the presence of an aldehyde.

2. In the bleaching of non-cellulosic organic materials, the improvement which comprises subjecting the material to be bleached to the action of an aqueous solution having a pH not less than about 7 and containing a chlorite of a metal of the group consisting of the alkali and alkaline earth metals and an aldehyde.

3. In the bleaching of non-cellulosic organic materials, the improvement which comprises admixing the material to be bleached with a chlorite of a metal of the group consisting of the alkali and alkaline earth metals in the presence of water and an aldehyde at a pH not less than about 7.

4. In the bleaching of non-cellulosic organic materials, the improvement which comprises admixing the material to be bleached with a chlorite of a metal of the group consisting of the alkali and alkaline earth metals in the presence of water and an aldehyde and maintaining the hydrogen ion concentration of the mixture at a pH not less than about 7 by the presence of an alkali metal phosphate buffer.

5. In the bleaching of non-cellulosic carbohydrates, the improvement which comprises subjecting the material to be bleached to the action of an aqueous solution having a pH not less than

about 7 and containing a chlorite of a metal of the group consisting of the alkali and alkaline earth metals and an aldehyde.

6. In the bleaching of sponge, the improvement which comprises subjecting the material to be bleached to the action of an aqueous solution having a pH not less than about 7 and containing a chlorite of a metal of the group consisting of the alkali and alkaline earth metals and an aldehyde.

7. In the bleaching of starch, the improvement which comprises subjecting the starch to the action of a substantially non-acidic aqueous solution of a chlorite of a metal of the group consisting of the alkali and alkaline earth metals and an aldehyde.

8. In the bleaching of starch, the process which comprises subjecting the starch to the action of a substantially non-acidic aqueous solution of a chlorite of a metal of the group consisting of the alkali and alkaline earth metals and an aldehyde at a temperature of about 50° C. for a period of about one hour.

9. In the bleaching of sugar, the improvement which comprises subjecting the sugar to the action of a substantially non-acidic aqueous solution of a chlorite of a metal of the group consisting of the alkali and alkaline earth metals and an aldehyde.

10. In the bleaching of sugar, the improvement which comprises subjecting the sugar to the action of an aqueous solution having a pH of about 7 and containing a chlorite of a metal of the group consisting of the alkali and alkaline earth metals and an aldehyde at a temperature of about 40° C. for a period of about 1 hour.

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