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BLEACHING OF ORGANIC MATERIAL

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The present invention relates to the decolorization of organic materials.

An object of the invention is the provision of a process for bleaching organic compounds.

A further object of the invention is the provision of a chlorite bleaching process resulting in improved color stability of product.

Another object of the invention is the provision of a process for bleaching polyhydric compounds and ester derivatives thereof.

Many organic compounds, which are colorless in the pure state, when prepared by practical procedures become contaminated by color bodies. Since some technological applications require the use of materials low in color, it is often desirable to employ decolorizing procedures in connection with organic preparations. Several such procedures have been available for some time. Absorption processes, such as are obtained by the use of decolorizing carbon, are quite efficacious, and bleaching treatments with agents such as hydrogen peroxide, hypochlorous acid or chlorite materials have been found advantageous. In many cases, however, these procedures have not produced as permanent decolorization as might be desired.

Chlorite bleaching by reaction of the material to be bleached with a soluble chlorite such as sodium chlorite or chlorine dioxide has recently found particular favor in the art. Chlorite bleaching procedures are disclosed, for example, by Woodward and Vincent in "Soap and Sanitary Chemicals," volume 22 No. 9 (September 1946) page 40, and by Isbell in "Research Paper R. P. 1436" of the National Bureau of Standards.

The present invention is particularly directed to an improvement of chlorite bleaching whereby increased stability of final color is obtained.

According to the present invention, treatment with an easily oxidized, polybasic, organic acid is employed in conjunction with the chlorite bleaching of organic materials.

Many different organic materials may be chlorite bleached and hence are amenable to the present process. For example, it has been successfully applied to such materials as hexitan and hexide partial esters, poly olefine oxide ethers of sorbitan partial esters, esters of poly olefine oxide ethers of polyhydric materials, and polyglycol esters of organic acids.

Because of its ready availability and ease of use, sodium chlorite is the preferred soluble chlorite material. However, other chlorite salts and chlorine dioxide gas are chlorite bleaching materials which may also be used.

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Citric acid, oxalic acid, and tartaric acid are examples of easily oxidized polybasic organic acids which may be used in the present process in conjunction with chlorite bleaching. Citric acid is often productive of particularly good results.

Usually both the chlorite material and the easily oxidized acid are most conveniently employed in aqueous solutions. The presence of some water appears to aid the bleaching reaction, and the somewhat explosive properties exhibited by dry chlorite salts provide an added reason for their use in solution. When chlorine dioxide gas is used as a chlorite material, it is usually simply bubbled with a carrier gas into the material to be bleached. The order of use of the chlorite and the easily oxidized acid is not generally important to the obtention of good results. In the bleaching of some materials, however, it will be found preferable to use the easily oxidized acid after the addition of the chlorite.

It is often desirable to perform the reaction at elevated temperatures. However, temperatures so high that they of themselves produce rapid darkening of the materials being bleached should be avoided. For many products temperatures as high as about 120° C. are often satisfactory. In general, the reaction should be conducted at temperatures above about 70° C. to obtain practicable reaction rates.

The amount of chlorite employed should depend upon the amount of decolorization desired, and also somewhat on the particular material being bleached. Usually sufficient chlorite to provide an amount equivalent to at least about 0.05% by weight of sodium chlorite should be employed, and amounts greater than that equivalent to about 2% by weight of sodium chlorite are usually found unnecessary or undesirable.

The color stability of the bleached product is usually improved as the amount of easily oxidized, polybasic, organic acid that is employed is increased up to about 2% by weight of the material being bleached. However, not so much acid should be used that the properties of the material being bleached are adversely affected. For example, unduly large amounts of easily oxidized, polybasic, organic acid are often deleterious to emulsifiability, and when emulsifying agents are to be bleached usually not more than 0.5% of easily oxidized acid should be used. Sometimes as little as 0.05% of easily oxidized, polybasic, organic acid is sufficient.

The invention will be further described by

means of the following examples which illustrate specific embodiments.

Example 1

1200 grams of commercial sorbitan monostearate were charged into an agitated vessel. The charge was heated to 79° C. and 1.8 gram of citric acid contained in a 60% aqueous solution was added. After 6 minutes, the temperature had risen to 80° C. and 6.0 grams of sodium chlorite contained in a 50% aqueous solution were added. After 15 more minutes, the temperature had reached 85° C. and a vacuum of about 27 inches of mercury was applied to the charge to remove water. The reaction was continued for 1 hour and 26 minutes in which time the temperature was 86° C. and the product was then filtered in the presence of a diatomaceous earth filter aid. Before bleaching, the sorbitan monostearate had a color of 36 units; after bleaching, the color was 3 units; and after storing at 100° C. for 4 hours, the color had increased to 7 units. When another sample of the same material was similarly bleached, but without the addition of citric acid, the final color was again 3 units, but after storing for 4 hours at 100° C. the color had risen to 14 units.

The colors of material in this and the subsequent examples are expressed in terms of the modified units for the Hess-Ives Tintphotometer proposed by Sanders in "Chemical and Metallurigical Engineering," volume 28, pages 541 and 542 (1923), the cell length being 6 millimeters.

Example 2

3000 grams of commercial sorbitan sesquioleate were charged into an agitated vessel. The charge was heated to 76° C. and 7.5 grams of citric acid contained in a 50% aqueous solution were added. After five minutes the temperature had reached 78° C. and 30.0 grams of sodium chlorite contained in a 50% aqueous solution were added. After 15 more minutes, the temperature had reached 83° C. and a vacuum of about 27 inches of mercury was applied to the charge to remove water. The reaction was continued for one hour and 5 minutes more after which time the temperature was 84° C. The product was then filtered in the presence of a diatomaceous earth filter aid. Before bleaching, the material had a color of 44 units; after bleaching the color was 3 units; and after storing at 100° C. for 4 hours, the color had risen to 4.5 units. When another sample of the same material was similarly bleached, but without the addition of citric acid, the color after bleaching was 5 units and the color, after storing at 100° C. for 4 hours, was 19 units.

Example 3

3000 grams of commercial sorbitan trioleate were charged into an agitated vessel. The charge was heated to 75° C. and 7.5 grams of citric acid contained in a 50% aqueous solution and 30.0 grams of sodium chlorite contained in a 50% aqueous solution were added. After 10 minutes the temperature had risen to 85° C. and a vacuum of about 27 inches of mercury was applied to the charge to remove water. The reaction was continued for 30 more minutes after which time the temperature was 84° C. and the product was then filtered in the presence of a diatomaceous earth filter aid. Before bleaching, the sorbitan trioleate had a color of 36 units; after bleaching it had a color of 6 units; and after storage for 205 days at room temperature, the color had risen to 8 units.

Example 4

1000 grams of commercial sorbitan monooleate were charged into an agitated vessel. The charge was heated to 83° C. and 5 grams of tartaric acid contained in a 50% aqueous solution were added. After 2 minutes, the temperature was still 83° C. and 10 grams of sodium chlorite contained in a 50% aqueous solution were added. After 26 more minutes, the temperature was 86° C. and a vacuum of about 27 inches of mercury was applied to the charge to remove water. The reaction was continued for 35 more minutes, at which time the temperature was 82° C., and the product was then filtered in the presence of a diatomaceous earth filter aid. Before bleaching, the product had a color of 75 units; after bleaching the color was 8 units; and after storing for about 5 hours at 100° C., the color had risen to 18 units.

Example 5

1000 grams of the reaction product of 5 molecular equivalents of ethylene oxide with 1 molecular equivalent of commercial sorbitan mono-oleate were melted and charged into a 2000 milliliter flask. The charge was heated to 100° C., and deodorized by heating under an absolute pressure of from about 4 to 10 millimeters of mercury for 1 hour and at a temperature between about 100° C. and 110° C. The vacuum was then released and 1.0 gram of sodium chlorite contained in 5 grams of water was added. The temperature was 102° C. at this point. Two minutes later the temperature was 104° C. and 1.0 gram of citric acid contained in 1.0 gram of water was added. Ten minutes after the addition of the sodium chlorite a vacuum of about 27 inches of mercury was applied. After 40 minutes, the vacuum was released and the charge was then filtered in the presence of a diatomaceous earth filter aid. The color of the bleached product was 4 units, whereas the color before bleaching had been 10 units. After 3½ hours at about 95° C., the color had risen to 6 units.

Example 6

2500 grams of polyethenoxy tall oil prepared by the reaction of 20 molecular equivalents of ethylene oxide, and 1 molecular equivalent of tall oil, were charged into an agitated reaction vessel. The charge was heated to 80° C. and 25 grams of sodium chlorite contained in a 45% aqueous solution were added. After 5 minutes the temperature had risen to 86° C. and 2.5 grams of citric acid contained in a 50% aqueous solution were added. After 10 more minutes, the temperature had risen to 88° C. and a vacuum of about 27 inches of mercury was applied to the vessel to dry the charge. The reaction was continued for 30 more minutes at which time the temperature was 85° C., and the product was then filtered in the presence of a diatomaceous earth filter aid. Before treatment, the polyethenoxy tall oil had a color of 68 units, and the bleached product had a color of 18 units. After storage at room temperature for 88 days, its color was found to be 21 units.

Example 7

2500 grams of a polyethenoxy rosin prepared by reacting 14 molecular equivalents of ethylene

oxide with 1 molecular equivalent of rosin were charged into an agitated vessel. The charge was heated to 77° C. and 25 grams of sodium chlorite contained in a 45% aqueous solution were added. After 5 minutes the temperature had risen to 81° C. and 2½ grams of citric acid contained in a 50% aqueous solution were added. After 10 more minutes, at which time the temperature had risen to 86° C., a vacuum of about 27 inches of mercury was applied to the charge to remove water. The reaction was continued for 30 more minutes at which time the temperature was 85° C., and the product was then filtered in the presence of a diatomaceous earth filter aid. Before bleaching, the polyethenoxy rosin had a color of 120 units; after bleaching, the color was 45 units. After storage at room temperature for 88 days the color was 59 units.

Example 8

619 pounds of the alcoholysis product of lanolin and the ether of sorbitol with 40 mols of ethylene oxide per mol of sorbitol were charged into an agitated jacketed kettle and heated to 85° C. 1% by weight of sodium chlorite contained in a 50% aqueous solution was then added, and heating was continued for 5 minutes at 85° C. Then 0.25% of citric acid contained in a 50% aqueous solution was added, and heating was continued for 30 minutes, the temperature rising to about 100° C. The hot charge was then filtered in the presence of a diatomaceous earth filter aid. The color of the filtered product was 26 units, whereas the color of the unbleached product had been 96 units. After storage at room temperature for 35 days, the color of the bleached product was 29 units.

Example 9

400 grams of commercial sorbitan tetra-ester of linseed oil fatty acids were charged into an agitated reaction vessel. The charge was heated to 85° C. and 4 grams of sodium chlorite contained in a 45% aqueous solution were added. After 2 minutes the temperature had risen to 84° C. and 1 gram of citric acid contained in 1 gram of water was added. After 17 more minutes, a vacuum of about 27 inches of mercury was applied to the vessel to dry the charge. The reaction was continued for 12 more minutes, and the product was then filtered in the presence of a diatomaceous earth filter aid. Before treatment, the sorbitan tetra-ester had a color of about 60 units and the bleached product had a color of 19 units. After storage at room temperature for 130 days, its color was found to be 27 units.

What is claimed is:

1. A process for bleaching an ester of sorbitan which comprises reacting said ester with between about 0.05% and about 2% of sodium chlorite contained in an aqueous solution, and between about 0.05 and about 0.5% of citric acid contained in an aqueous solution, at a temperature above about 70° C. and no greater than about 120° C.

2. A process for bleaching a polyethenoxy ether of an ester of sorbitan which comprises reacting said ether ester with between about 0.05% and about 2% of sodium chlorite contained in an aqueous solution and between about 0.05% and about 0.5% of citric acid contained in an aqueous solution, at a temperature above about 70° C. and no greater than about 120° C.

3. A process for bleaching an ester of a polyethenoxy ether of sorbitol which comprises reacting said ester with between about 0.05% and about 2% of sodium chlorite contained in an aqueous solution and between about 0.05% and about 0.5% of citric acid contained in an aqueous solution, at a temperature above about 70° C. and no greater than about 120° C.

4. A process for bleaching organic materials selected from the group consisting of esters of sorbitan, polyethenoxy ethers of esters of sorbitan and esters of polyethenoxy ethers of sorbitol which comprises reacting said organic material with between about 0.05% and about 2% of sodium chlorite contained in an aqueous solution and between about 0.05% and about 0.5% of citric acid contained in an aqueous solution at a temperature above about 70° C. and no greater than about 120° C.

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