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PROCESS OF BLEACHING SULPHONATED OILS

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This invention relates to a process of bleaching sulphonated oils and more particularly to a process of bleaching sulphonated castor oil.

Sulphonated castor oil, which is prepared commercially by the sulphonation of castor oil, is a standard article of commerce and is used in the textile, leather, cosmetic and other industries. In many of these industries, a light colored oil is necessary and desirable but unfortunately the product usually obtained by treating castor oil with concentrated sulphuric acid is relatively dark colored.

However, in some industries, such as the cosmetic industry, a light colored product is practically essential. Accordingly, it is now the practice to select various fractions of sulphonated castor oil and class them in various grades depending on the color. The oil which is first pressed from the castor bean is relatively light in color and this results in a relatively light colored sulphonated product. Later pressing yields darker colored oil and of course darker colored sulphonation products. The present practice is to select the lighter colored fractions for sale to the industries which will pay a somewhat higher price for the lighter colored products.

If some method of satisfactory bleaching the sulphonated oils were available it would constitute a distinct contribution to the industry since a sufficient supply of the lighter colored sulphonated oils has never been entirely available. However, strong bleaching agents, elevated temperatures and prolonged treatment periods which have been used in attempts to bleach the material have deleterious and destructive effects on the sulphonated oil. Moreover, the expense is a very important factor since bleached oils, if satisfactorily bleached without injury to the desirable properties of the oil, have to compete on the market with the lighter colored unbleached fractions.

We have accordingly developed a process which does not use a prolonged treatment period and does not necessitate the application of an extremely elevated temperature. Moreover, large amounts of chemical bleaching agents are not necessary since the bleaching agent that we utilize, hydrogen peroxide, is employed in its most effective and efficient manner.

Accordingly, one of the objectives of our invention is to develop a process which will satisfactorily bleach sulphonated oils and in particular sulphonated castor oil in an economical and efficient manner. Moreover, another object of the invention is to develop a process which will not injure or deleteriously affect the quality of the bleached sulphonated oil. It is still another object of our invention to develop a process which will utilize a bleaching promoter or catalyst and thereby employ the bleaching agent in its most efficient economical and effective manner.

For the bleaching of sulphonated oils, such as sulphonated castor oil we have found it preferable to utilize a solution of hydrogen peroxide. Solutions of hydrogen peroxide in water of high concentration are now sold commercially and are readily obtained. They are of a relatively high degree of stability and do not substantially deteriorate upon storage. The standard solution sold for bleaching is ordinarily 100 volume which means that one volume of the solution at 25° C. will liberate 100 volumes of oxygen gas measured under standard conditions, i. e., at 0° C. and 76 Omm. pressure. While the use of 100 volume hydrogen peroxide solution is to be preferred, and the amounts of bleaching agents specified in this application are based on the 100 volume solutions it is also within the purview of our invention to utilize hydrogen peroxide solutions of other concentrations. Thus, a 50 volume solution may be used, the amount of the bleaching agent utilized being, of course, twice that amount which would be used if the 100 volume solution were employed. Similarly, solutions of a higher concentration may be occasionally obtainable commercially and these may also be satisfactorily used in our process. Solutions of low concentration such as 10 volume or 25 volume are also effective but, of course, the amount of the solution used in these cases must be correspondingly larger.

It is also possible to employ in lieu of a solution of hydrogen peroxide such as that sold commercially, any solution which yields hydrogen peroxide under the conditions of the bleaching. Thus, we might use a solution of a metal peroxide or a solution containing an alkali metal peroxide such as sodium peroxide and an acid such as sulfuric or hydrochloric. Similarly, we might use a solution of a metal persalt such as an alkali metal percarbonate, alkali metal perborate or an alkali metal pursulphate. In brief, any solution which yields hydrogen peroxide under the conditions of the process, or is equivalent to hydrogen peroxide under these conditions, comes within the scope of our invention.

We have found that hydrogen peroxide solutions are most effectively used for bleaching sulphonated oils generally, and sulphonated castor oil particularly, which sulphonated oils are

classed as water soluble, if employed in conjunction with a bleaching promoter or catalyst. The promoter which we have found to be most effective is a cobalt compound such as cobalt salt. Thus we have found that the water soluble cobalt salts of high solubility such as cobalt chloride, cobalt nitrate, cobalt sulphate and cobalt acetate are very effective as bleaching promoters. However, we may also use the less soluble cobalt compounds such as cobalt oxide and cobalt carbonate, since the presence in solution of but a very small amount of our bleaching promoter or catalysts is necessary.

In practice we have found it most desirable to treat the sulphonated oil with a solution of hydrogen peroxide in the presence of the cobalt compound at an elevated temperature. Thus, a cobalt salt, such as cobalt sulphate, may first be added to the sulphonated oil in relatively small amounts. We have found 5 parts per million of cobalt (as a compound of cobalt) entirely satisfactory. However, we do not wish to be restricted to any specified amount of cobalt as amounts ranging from one part per million to ten parts per million have been found to yield very satisfactory results. It may be said that by the use of small amounts of cobalt, such as 0.5 part per million, the time required for the bleaching is longer than with larger amounts of cobalt such as amounts of the order of 10 or 15 parts per million.

After the cobalt compound is thoroughly incorporated in the sulphonated oil by stirring, we next add the hydrogen peroxide solution to the mixture. We have found when using 100 volume hydrogen peroxide solution that amounts of the order of 1% based on the weight of the oil are entirely suitable. When using other hydrogen peroxide solutions the amount utilized should be regulated, based on the ratio of the concentration of the solution used to that of 100 volume. While 1% of 100 volume hydrogen peroxide solution has been found best for general use, we may utilize amounts ranging from 0.5 to 5% by weight based on the weight of the sulphonated oil. For the relatively smaller amounts, longer bleaching periods and higher temperatures may be necessary, while for amounts of the order of 5% by weight the bleaching will occur rapidly and without the necessity of maintaining an elevated temperature.

While the bleaching will occur at room temperature, ordinarily when using about 1% of 100 volume hydrogen peroxide solution we prefer to maintain a temperature of approximately 120° F. However, any temperature ranging from 90° to 120° F. will also be found satisfactory. Above 120° F. darkening of the oil as a result of heat may occur and we therefore prefer to avoid temperatures above this value. When using relatively large amounts of the promoter and a relatively high concentration of the peroxide the bleaching may occur rapidly at room temperature, but ordinarily in commercial operations it is desirable to use an elevated temperature of the order specified. For some oils temperatures in excess of 120° F. may be entirely suitable and may not result in any darkening of the oil.

During the bleaching, agitation of the mixture is constantly carried out by stirring or by some other means. It will ordinarily be found that the bleaching will be complete in 24 hours or less and we prefer to continue the treatment until a test of the mixture shows but little undecomposed free hydrogen peroxide. In commercial practice the bleaching will very frequently be complete at the conclusion of an overnight treatment. We have found that a somewhat better bleach will be obtained with the lower cobalt concentrations, of the order of 1 to 3 parts per million, than when using a higher concentration of the promoter. However, with amounts of cobalt ranging from 1 to 3 parts per million a somewhat longer treatment period is required than when greater amounts (5 parts per million or above) are employed. Ordinarily since in commercial practice a period of over 24 hours is objectionable we prefer to use about 5 parts per million of cobalt. These values are, of course, parts by weight, based on the weight of the sulphonated oil. For this reason we also prefer to use an elevated temperature of the order of 120° F. since at room temperature the bleaching occurs more slowly, thereby requiring a longer treatment period.

As examples of our improved process for the bleaching of sulphonated oils the following may be given:—

Example 1

One kg. of sulphonated castor oil was produced in a 2 liter beaker. To this oil, 5 cc. of a solution of cobalt sulfate, $CoSO_4.7H_2O$, prepared by dissolving 4.769 grams of the salt in 1 liter of water, were added. This is equivalent to adding 5 parts per million of cobalt to the oil. The oil and cobalt sulphate solution were thoroughly stirred to disperse the promoter throughout the sulphonated castor oil. Ten grams of 100 volume hydrogen peroxide solution were then added. The mixture was thoroughly stirred and allowed to stand for about 24 hours at room temperature. At the end of this period the oil was found to be bleached to a satisfactory light color. The small amount of cobalt salt was permitted to remain in the oil, since its presence was not objectionable.

Example 2

One kg. of sulphonated castor oil was placed in a 2 liter beaker and 3 cc. of a solution of cobalt sulphate, prepared by dissolving 4.769 grams of $CoSO_4.7H_2O$ in 1 liter of water, were added to the oil. This results in 3 parts per million of cobalt. The cobalt salt and the oil were thoroughly stirred to disperse the promoter thoroughly throughout the mass. To the sulphonated oil, 100 grams of 10 volume hydrogen peroxide solution were now added. Thorough agitation was maintained for a period of about 30 hours. At the end of this time the oil was bleached to a satisfactory light color. The degree of bleaching was somewhat better than that obtained by following the procedure described in Example 1, although the time required was somewhat longer.

Example 3

One kg. of 75% sulphonated castor oil was placed in a 2 liter beaker. To this oil 5 cc. of a solution prepared by dissolving 4.769 grams of cobalt sulphate, $CoSO_4.7H_2O$ in 1 liter of water, were added. This addition yields 5 parts per million of cobalt in the oil. The mixture was thoroughly stirred to disperse the promoter throughout the sulphonated oil to be bleached. Ten grams of 100 volume hydrogen peroxide were then added and the oil warmed to 120° F. This temperature was maintained for approximately 3 hours during which time the mixture was

thoroughly stirred. At the end of this period the oil was bleached to a satisfactory light color.

Example 4

One kg. of 75% sulphonated castor oil was placed in a beaker and to this 1 cc. of a solution of cobalt sulphate, prepared by dissolving 4.769 grams of the salt $CoSO_4.7H_2O$ in 1 liter of water, were added. This results in 1 part per million of cobalt in the oil. The cobalt salt was thoroughly dispersed in the mixture by stirring. Then grams of 100 volume hydrogen peroxide solution were then added and the temperature maintained at 120° F. At the end of 24 hours the oil was completely bleached and tests indicated that the peroxide was completely decomposed.

Example 5

One kg. of 75% sulphonated castor oil was placed in a 2 liter beaker. To this oil 5 cc. of a solution prepared by dissolving 4.938 grams of cobalt nitrate, $Co(NO_3)_2.6H_2O$ in 1 liter of water, were added. This results in 5 parts per million of cobalt in the oil.

In all these examples we have employed a process of titration to determine when the hydrogen peroxide is completely decomposed. Ten grams of a sample of the untreated oil are titrated quickly in the presence of 20 cc. of water and 10 cc. of 20% sulphuric acid with a N/10 solution of potassium permanganate. It should require about 0.35 to 0.5 cc. of the permanganate solution to produce a faint pink tinge in the oil.

A corresponding process is carried out with a 10 gram sample of the oil which is being bleached. When it requires no greater amount of the N/10 permanganate solution to produce a perceptible color in the oil which is being bleached, than that required to produce a faint pink coloration in the sample of untreated oil, it is assumed that the hydrogen peroxide is substantially completely decomposed and that no further bleaching will result from prolonging the treatment.

It is to be understood that the various manipulations, times, and amounts specified in this application are to be considered as illustrative and not restrictive. Our invention is not limited to the selection of precise temperatures, definite amounts of reagents, or definite process steps but is one of broad general application for use wherever sulphonated oils are to be bleached. The various numerical amounts given are not to be considered as restrictive, but the scope of the invention is to be construed solely in accordance with the appended claims.

Wherever in the appended claims reference is made to hydrogen peroxide it is intended to include within the scope of these claims solutions capable of yielding hydrogen peroxide or equivalent to hydrogen peroxide under the conditions of the process. Thus, solutions of various peroxides such as sodium peroxide, and various persalts such as the alkali metal perborates and percarbonates are to be included within the scope of the expression "hydrogen peroxide."

We claim:

1. A process of bleaching a sulphonated oil of the glyceride type which comprises subjecting sulphonated oil to the action of hydrogen peroxide in the presence of a bleaching promoter comprising a cobalt compound.

2. A process of bleaching a sulphonated oil of the glyceride type which comprises subjecting sulphonated oil to the action of hydrogen peroxide in the presence of a bleaching promoter comprising a small amount of a cobalt compound at an elevated temperature.

3. A process of bleaching a sulphonated oil of the glyceride type which comprises subjecting the sulphonated oil to the action of hydrogen peroxide in amounts ranging from 0.5 to 5% by weight in the presence of a bleaching promoter comprising a cobalt compound present in amounts ranging from 1 to 10 parts per million based on the weight of the sulphonated oil.

4. A process of bleaching a sulphonated oil of the glyceride type which comprises subjecting sulphonated oil to the action of hydrogen peroxide in the presence of about 5 parts per million of a cobalt salt as a bleaching promoter, about 0.10% of 100 volume hydrogen peroxide by weight being utilized and the bleaching being carried out at a temperature of approximately 120° F.

5. A process of bleaching sulphonated castor oil which comprises subjecting said sulphonated oil to the action of hydrogen peroxide in the presence of a bleaching promoter comprising a cobalt compound.

6. A process of bleaching sulphonated castor oil which comprises subjecting said sulphonated oil to the action of hydrogen peroxide in the presence of a bleaching promoter comprising a small amount of a cobalt compound at an elevated temperature.

7. A process of bleaching sulphonated castor oil which comprises subjecting said sulphonated oil to the action of hydrogen peroxide in amounts ranging from 0.5 to 5% by weight in the presence of a bleaching promoter comprising a cobalt compound, present in amounts ranging from 1 to 10 parts per million based on the weight of the sulphonated oil.

8. A process of bleaching sulphonated castor oil which comprises subjecting said sulphonated oil to the action of hydrogen peroxide in the presence of about 5 parts per million of a cobalt salt as a bleaching promoter, about 0.10% of 100 volume hydrogen peroxide by weight being utilized and the bleaching being carried out at a temperature of approximately 120° F.

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