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PROCESS FOR THE BLEACHING OF WAXES OR OTHER WAX-LIKE MATERIALS BY OXIDATION AND THE NEW COMPOSITIONS OF MATTER THUS OBTAINED

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The present invention relates to a process for the bleaching of waxes or other wax-like materials by oxidation and the new compositions of matter thus obtained.

It is known that crude montan wax or other natural or synthetic waxes or wax-like substances can be freed from the staining impurities by treating them with substances evolving oxygen, such as nitric acid, chromic acid or potassium permanganate. In each of these cases, a considerable amount of oxidizing agents is necessary in order to obtain a satisfactory bleaching. Many proposals have been made to reduce the consumption of oxidizing agents without affecting the degree of bleaching. Nevertheless, to obtain a clear product there is still consumed, e.g. when montan wax is bleached with chromic acid, nearly the double amount of CrO_3 calculated upon the weight of the crude wax used.

There has already been described a bleaching process which is especially suitable for crude montan wax and which makes use of the possibility to produce wax mixtures prior to raffination. The subject of said process is the manufacture of bright hard waxes. It is a process wherein mixtures consisting of crude montan wax which, if desired, is deresinified, and of macro paraffins obtained by a synthesis according to Fischer-Tropsch and which, in general, contain less than 35 percent of crude montan wax are refined by treating them with hot concentrated sulphuric acid in the absence of oxidizing agents whereby asphalt substances and other constituents both imparting a dark coloration are extracted. Clear refined products are obtained in this manner by a supplementary treatment with solvents serving for the removal of soft waxes. The decisive drawback of these refined products is, however, that their content of ester wax actually constitutes the smallest portion of the substances they contain. Hence, the properties of these products are chiefly determined by their content of hard paraffin.

Now, I have found that it is possible to bleach waxes and/or fatty acids with a good result by oxidation by treating a homogeneous mixture of these substances and partially oxidized products of hydrocarbons that are solid at room temperature in known matter at an elevated temperature with chromosulphuric acid. There may also be used mixtures of different waxes and different, partially oxidized products of hydrocarbons. As fatty acids, there may be used such acids as are solid in usual conditions, i.e. chiefly those containing at least 14 carbon atoms. It is of special advantage to prepare the homogeneous mixture in the form of a molten mass. This form may be replaced, if necessary, by the form of suspensions of the material to be bleached and the partially oxidized products in an aqueous solution. In general, it will be suitable to provide for a good mixture of the material to be bleached and the bleaching agent during the bleaching process, e.g. by stirring.

As materials for admixing, there may be used e.g. products obtained by partially oxidizing soft paraffins, hard paraffins (i.e. paraffins with a melting point which lies in general above 80° C.) or polyethylene. It is convenient to use oxidation products in which the oxygen is

mainly present in the form of hydroxy groups. The acid and hydroxylic numbers of such oxidation products of hydrocarbons are generally between 10 and 80. It is not necessary to use products which had been freed from the unsaponifiable substances; it suffices to use products obtained on a commercial scale. The quantity of oxidation products of paraffins that may be admixed to the waxes or wax-like substances suitably amounts to 10 to 70 percent of the mixture consisting of waxes and partially oxidized products. In special cases the quantity may, however, be even larger and amount e.g. to 80 percent. There may also be obtained essential effects by the addition of smaller quantities e.g. of quantities amounting to 5 percent of the above-mentioned mixture. Furthermore, it is not necessary to remove the small amount of unsaponifiable substances contained in the final product when commercial oxidation products are used. In general, they may be left in the final products. If desired, however, they can be separated in known manner, e.g. they can be extracted with suitable solvents. By the admixture of partially oxidized solid hydrocarbons as suggested in the present invention the characteristic values of the final product obtained are only immaterially modified as compared to the characteristic values of an unblended refined product of montan wax. The consumption of oxidizing agents may, however, be reduced by the fourth part and the duration of the reaction may generally be lessened by one half or even more. Another advantage of the process according to the present invention is that large amounts of valuable crude waxes, particularly of crude montan wax may be saved. Last, but not least, the shortening of the reaction time involves a greater protection of the valuable waxes and thus diminishes the losses occurring during the bleaching process.

The method of the invention may be carried out as described in the following for the case of crude montan wax:

Deresinified or if desired, not deresinified crude montan wax is melted together in the proportion desired with partially oxidized soft paraffin, partially oxidized hard paraffin or partially oxidized polyethylene having e.g. an acid number of 20, a saponification number of 51 and a hydroxylic number of 31. It is caused to run either after cooling and in a finely pulverized form or at once while still in a molten state, into chromosulphuric acid which is generally heated to 90 to 130° C. or when pressure is applied to even higher temperatures. The chromosulphuric acid contains 90 to 120 grams of CrO_3 and 300 to 600 grams of concentrated sulphuric acid per litre. In particular circumstances, there may also be used larger or smaller quantities of CrO_3 and sulphuric acid. It is of advantage to have half of the amount of chromosulphuric acid that will probably be necessary, ready for the wax to run into and to add the rest of the acid subsequently in proportion to the consumption, while stirring and further heating. There are generally used about 0.6 to 1.3 kilograms of CrO_3 per kilogram of the mixture of wax and partially oxidized hydrocarbons. It is, of course, also possible to have the chromosulphuric acid run proportionately into the material to be bleached which is in a molten state. According to the quantity of the material to be treated, the reaction takes half an hour to three hours. When the reaction is finished, the wax is allowed to settle, the sulfuric acid containing solution of chromic sulfate is removed and the wax is washed, first with dilute sulphuric acid of 10 to 30 percent strength until it is free from chrome and then with water until it is free from acid. The product obtained has a yellowish white shade. It may be esterified without difficulty and yields ester waxes with excellent properties. Such esters may e.g. be obtained by esterification under known conditions, e.g. at temperatures of 100 to 150° C., suitably in the presence

of catalysts. As alcohol components there may be used the known monohydric or polyhydric alcohols e.g. monohydric alcohols containing at least 15 carbon atoms such as cetylic alcohol, stearyl alcohol, oleyl alcohol, montanyl alcohol (the latter is used especially with reaction products obtained from fatty acids of medium molecular weight), furthermore bihydric or polyhydric alcohols, such as ethylene glycol, propylene glycol, butylene glycol, hexane glycol, glycerol, trimethylol propane, pentaerithrite or sorbitol. If necessary, such esterification products may partly be neutralized in known manner with hydroxides of alkaline earth metals and/or zinc oxide. By this operation the hardness of the products is further increased.

The method of the invention is not only applicable to the bleaching of crude montan wax but it may also be applied for the bleaching of other waxes as well as of fatty acids of medium or high molecular weight and of synthetic or natural origin. The process is e.g. convenient for the bleaching of carnauba wax, ouricury wax, candelilla wax, beeswax, cane wax, peat wax, stearic acid, behenic acid, or arachinic acid. When carrying out the process it is often suitable to adapt to the wax or the fatty acid the molecular size of the oxidation product of hydrocarbons to be admixed. For the bleaching of fatty acids of medium molecular weight, there are used e.g. softer paraffins than for the bleaching of fatty acids of an elevated molecular weight. Furthermore, the properties of the reaction products may be influenced by the choice of the partially oxidized product of hydrocarbons in so far as the use of partially oxidized hydrocarbons with longer chains increases and the use of partially oxidized hydrocarbons with shorter chains diminishes hardness. For the bleaching of synthetic fatty acids generally containing 15 to about 20 carbon atoms, paraffin 52/54 in the form of plates, partially oxidized to an acid number of 60 to 100 may be used in quantities adequate to the special conditions.

The following examples serve to illustrate the invention but they are not intended to limit it thereto:

Example 1

100 grams of a mixture consisting of 50 grams of a deresinified crude montan wax and 50 grams of partially oxidized hard paraffin (acid number 35, saponification number 75, hydroxylic number 26) are added in a molten state to 590 cc. of a solution heated to 110° C. and containing 65 grams of CrO_3 and 300 grams of concentrated sulphuric acid. The mixture is heated while stirring until the CrO_3 is completely consumed. This will take about 30 minutes. Then the product is allowed to settle. It is then washed, first with sulphuric acid of 10 percent strength and then for several times with water. There is obtained a hard wax which is almost white and has the following characteristic values: Acid number 95, saponification number 130, hydroxylic number 2.5, flowing point/dropping point 90.1–90.5° C. (according to Ubbelohde). The yield amounts to 91 percent.

By corresponding reactions there may be obtained very hard ester and amide waxes from the product.

Example 2

1 kilogram of a mixture of 900 grams of deresinified crude montan wax and 100 grams of partially oxidized hard paraffin (acid number 25, saponification number 69, hydroxylic number 33) is added in the molten state while stirring in the course of about 5 minutes to 11 litres of a solution of CrO_3 heated to 110° C. and having the same composition as the solution described in Example 1. The mixture is then stirred for one hour at a temperature of about 110° C. At the end of this time the CrO_3 that had been introduced is completely consumed. After washing as usual with dilute sulphuric acid and water a product is obtained which is nearly white and an analysis of which yields the following result:

Flowing point/dropping point	° C.	84.5/85
Acid number		120
Saponification number		149
Hydroxylic number		2.3
Unsaponifiable substances	percent	9.8
Of these there are alcohols	do	5.8

The other 4 percent of the unsaponifiable substances mainly consist of ketones (carbonyl number 40).

The ceric acids thus obtained may be worked up into ester waxes showing an excellent applicability.

Example 3

20 kilograms of a mixture consisting of 16 parts of deresinified crude montan wax and 4 parts of the oxidation product of paraffins (acid number 20, saponification number 50, hydroxylic number 31) were finely pulverized and added in this form in portions, while stirring, to 135 litres of a solution of chromic acid heated to 110° C. and having the same composition as the solution described in Example 1. Then another 72 litres of chromic acid were added in proportion to the consumption. The whole bleaching process took two hours. The temperature was then reduced to 100° C. and the molten wax left to itself. The further treatment, carried out as described in Examples 1 and 2, yielded a yellowish-white wax with the following characteristic values: Acid number 111, saponification number 134, flowing point/dropping point 88/88.5° C.

From this ceric acid there could be obtained excellent ester waxes.

I claim:

1. In a process for treating an ester wax of natural origin at a temperature of at least 90° C. with chromosulfuric acid in which process dark impurities are decolorized, the ester wax is substantially hydrolyzed to yield aliphatic alcohols and aliphatic carboxylic acids and the said alcohols are oxidized to yield additional carboxylic acids, the improvement which comprises treating with the chromosulfuric acid a homogeneous mixture of the said ester wax and an oxidation product of aliphatic hydrocarbons which are solid at room temperature, the said oxidation product having an acid number between 10 and 80, the quantity of the said oxidation product ranging from 5 to 80 percent of the weight of the said homogeneous mixture.

2. A process according to claim 1, wherein the amount of the oxidation product of aliphatic hydrocarbons that are solid at room temperature is in the range from 10 to 70 percent of the homogeneous mixture.

3. The process of claim 1 in which said oxidation product of aliphatic hydrocarbon contains the oxygen as alcoholic oxygen.

4. The process of claim 1 in which a temperature of from 90 to 130° C. is employed.

5. A process according to claim 1 wherein montan wax is the ester wax of natural origin.

6. In a process for treating an ester wax of natural origin at a temperature of at least 90° C. with chromosulfuric acid in which process dark impurities are decolorized, the ester wax is substantially hydrolyzed to yield aliphatic alcohols and aliphatic carboxylic acids and the said alcohols are substantially oxidized to yield additional carboxylic acids, the improvement which comprises treating a homogeneous mixture of the said ester wax with an oxidation product of aliphatic hydrocarbons which are solid at room temperature, the said oxidation product having an acid number between 10 and 80, the quantity of the said oxidation product ranging from 5 to 80 percent of the weight of the said homogeneous mixture, the carbon chain length of the said oxidation product being the longer, the more carbon atoms are contained in the ester wax of natural origin.

7. In a process for treating an ester wax of natural origin at a temperature of at least 90° C. with chromosulfuric acid in which process dark impurities are decolorized, the ester wax is substantially hydrolyzed to yield aliphatic alcohols and aliphatic carboxylic acids and the said alcohols are oxidized to yield additional carboxylic acids, the improvement which comprises treating with the chromosulfuric acid a homogeneous mixture of the said ester wax and an oxidation product of aliphatic hydrocarbons which are solid at room temperature, the said oxidation product having an acid number between 10 and 80, wherein the oxidation product of the aliphatic hydrocarbons used has a hydroxylic number between 10 and 80 and is present in an amount between 5 and 80 percent of the weight of the said homogeneous mixture.

8. In a process for treating an ester wax of natural origin at a temperature of at least 90° C. with chromosulfuric acid in which process dark impurities are decolorized, the ester wax is substantially hydrolyzed to yield aliphatic alcohols and aliphatic carboxylic acids and the said alcohols are oxidized to yield additional carboxylic acids, the improvement which comprises treating with the chromosulfuric acid a homogeneous mixture of the said ester wax and an oxidation product of aliphatic hydrocarbons which are solid at room temperature, the said oxidation product having an acid number between 10 and 80, wherein the oxidation product used is an oxidation product of polyethylene and is present in an amount between 5 and 80 percent of the weight of the said homogeneous mixture.

9. A composition of matter comprising bleached products of homogeneous mixtures of an ester wax of natural origin and an oxidation product of aliphatic hydrocarbons that are solid at room temperature, which oxidation product has an acid number between 10 and 80 and is contained in the homogeneous mixture in a quantity of 5 to 80 percent of the weight of this mixture, said bleaching having been carried out at a temperature of at least 90° C. by means of chromosulfuric acid and said bleached

products consisting essentially of long-chain aliphatic carboxylic acids.

10. A composition of matter comprising esterification products obtained by esterifying at least one aliphatic alcohol selected from the group consisting of monohydric alcohols having at least 15 carbon atoms, polyhydric alcohols and mixtures thereof with a bleached product of a homogeneous mixture of an ester wax of natural origin and an oxidation product of aliphatic hydrocarbons that are solid at room temperature, which oxidation product has an acid number between 10 and 80 and is contained in the homogeneous mixture in a quantity of 5 to 80 percent of the weight of this mixture, said bleached product consisting essentially of long-chain aliphatic carboxylic acids and having been obtained by bleaching an ester wax of natural origin at a temperature of at least 90° C. by means of chromosulfuric acid.

11. A composition of matter obtained by the partial neutralization of a product of claim 10 by at least one hydroxide selected from the group consisting of alkaline earth metal hydroxides, zinc hydroxides, and mixtures thereof.

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