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METHOD OF TREATING MONTAN WAX

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This application is a continuation in part of our application Ser. No. 497,596, filed November 22, 1930.

This invention relates to the production of waxy materials and more particularly to the production of highly valuable, pale colored esters from Montan wax.

It is known that pale colored products can be obtained by bleaching crude or deresinified Montan wax or their saponification products with oxidizing agents in neutral, acid or alkaline solutions. Especially an oxidizing treatment of Montan wax with chromic acid in a solution containing mineral acid as described in the U. S. Patent No. 1,767,886, filed by Theodor Hellthaler on July 18th, 1927, has proved very efficient. This method is, however, attended by certain disadvantages which result from the chemical constitution of the crude Montan wax. The impurities which cause its dark color, can be oxidized only comparatively difficultly, and, therefore, the oxidizing agents also act on other, highly valuable constituents of the Montan wax, in particular on the alcohols of wax which may be present in the wax in the esterified state, or in the free state after saponification, and oxidize them to fatty acids. Therefore, in the bleaching of the crude or deresinified Montan wax, or their saponification products, by an oxidizing agent a comparatively unduly high consumption of oxidizing agent takes place, and the chemical constitution and the properties of the bleached products do not correspond any longer to those of the initial material, but they consist mainly of fatty acids.

It has also been suggested to purify the crude or deresinified Montan wax by a treatment with decolorizing powders such as active carbon, fuller's earth or the like, if desired, in the presence of solvents, such as benzine or ethyl acetate. This treatment does not involve a chemical conversion of the waxy constituents, but nevertheless, it requires a great quantity of decolorizing agent and of solvent and is therefore very expensive.

We have now found that Montan wax may be converted into valuable, pale colored waxy materials mainly consisting of wax esters by excluding all disadvantages adhering to the known process, by first subjecting the initial material in any known manner to the saponification, whereupon the saponified carboxylic acids are separated from the unsaponified constituents mainly consisting of the alcohols of the wax. The unsaponified products are separately

bleached by means of decolorizing powders having an adsorbing action, such as active carbon or fuller's earth, if desired in the presence of solvents, while the carboxylic acids, if desired after converting them into the free acids, are decolorized by a treatment with solutions of oxidizing agents as described for example in the U. S. Patent No. 1,767,886. The single components of the original esters thus purified are esterified with each other in any known manner, if desired, with the addition of alcohols from other natural waxes and/or of fatty acids of fats, fatty oils or waxes. For the sake of brevity the fatty acids of fats, fatty oils or waxes will be defined in the following and in the appended claims as "high-molecular fatty acids". The terms "alcohols from natural waxes" and "high-molecular fatty acids", are to be understood to cover all alcohols, which are present as the main constituents in the known different kinds of natural waxes containing esters of alcohols of high molecular weight, and the fatty acids, respectively, of such waxes or of fats, either in the free or combined state, as well as synthetic equivalents of these substances, obtained by chemical processes. Such fatty acids are for example those of tallow, palm kernel oil, olive oil, soy-bean oil, sperm oil, train oil or of hardened fats or oils of the said nature and the single acids of such fats and oils as for example stearic, palmitic or oleic acids and the fatty acids from the oxidation of paraffin and like hydrocarbons. The process according to this invention consists in decomposing the Montan wax by saponification into its components, either with the aid of strong acids, such as sulphuric acid or, preferably, with the aid of strong alkalies and liberating the fatty acids of the wax from the resulting soaps, bleaching the single components separately, each in the manner most convenient therefor, that is the unsaponified matter, defined in the following as "alcohols of Montan wax", by means of adsorptive agents and the carboxylic acids by solutions of oxidizing agents, and, finally, esterifying the bleached components with each other, if desired, with the addition of similar, light colored alcohols of natural waxes and/or similar fatty acids of high molecular weight. By treating Montan wax in the above described manner, the oxidizing agents employed for the removal of the dark colored constituents are utilized more economically than in the oxidation processes hitherto known. Consequently, the consumption of oxidizing agent is lower and

the valuable alcohols of Montan wax remain unchanged, since they remain unattacked by the detrimental action of oxidizing agents. The new process further requires lower quantities of decolorizing powder than the treatment of unsaponified Montan wax, because the coloring substances contained in the Montan wax, which are only difficultly attacked by a simple treatment with adsorptive decolorizing agents mainly adhere to the carboxylic acids of the wax. By re-esterifying the purified alcohols of Montan wax and the carboxylic acids in the proportion in which they are present in the initial material, a pale colored waxy material or purified Montan wax is obtained, the valuable properties of which correspond to those of the dark colored initial material. In the place of crude Montan wax, a product enriched in the esters in the usual manner or de-resinified Montan wax may be employed, in which cases the purification according to the present invention is facilitated.

The new purifying process also offers the possibility of obtaining final products, which, besides their pale color, can be substantially improved in comparison to the initial material. This is attained by esterifying with each other the resulting purified alcohols of the wax and the carboxylic acids in proportions other than those in which they are present in the initial material. An esterification in a proportion, by weight, of about 1 part of carboxylic acid to 1 part of alcohol and of about 1 to 1.5 has proved of special advantage. By such esterification the disadvantage of the formation of waxes containing free acids due to the alcohols and acids being not present in the original Montan wax in equivalent proportions so that the less valuable carboxylic acids are present in great excess can be avoided. In order to obtain waxy materials with special properties, the esterification of the bleached alcohols and acids of Montan wax may also be effected, according to the present invention, by the said addition of alcohols of natural waxes or of high-molecular fatty acids which are not present in Montan wax. Thus for example, myricyl alcohol, alcohols of wool fat, alcohols of shellac wax, and/or stearic acid, palmitic acid, carnaubic acid, cerotic acid and one or more like alcohols and/or fatty acids may be added before the esterification.

Moreover, before or after the esterification, paraffin wax, ceresine and other solid aliphatic hydrocarbons may be added to the mixtures of alcohols and acids. Thus, the properties of the final products may be influenced to a great extent.

The present invention is applicable to crude Montan wax as well as to deresinified Montan wax, and also to fractions rich in Montan wax, which have been isolated from crude Montan wax in any known manner by the usual extraction with solvents.

In carrying out the process according to our invention we proceed, for example, as follows:

100 kilograms of crude Montan wax are heated in the molten state in an autoclave for 3 hours, while vigorously stirring, to about 250° C. with a concentrated aqueous solution of caustic soda, prepared from 12 kilograms of caustic soda. The product thus saponified is dried until it can be comminuted to pieces having about the size of walnuts which are then subjected to extraction with a solvent of low boiling point such as low boiling fractions of petroleum, acetone or the

like. Both the extract and the residue resulting from the extraction are freed from the solvent by distillation. The extract amounting to about 30 kilograms has a yellow-brown color and mainly contains the alcohols of the Montan wax, while the residue consists of the sodium salts of the carboxylic acids. From the latter are liberated and separated the dark brown fatty acids by heating with a quantity of a dilute aqueous mineral acid solution, such as of aqueous sulphuric acid, slightly exceeding that equivalent to the quantity of caustic soda employed. The yield amounts to about 70 kilograms.

The alcohols are taken up in hot ethyl acetate and are boiled, while continuously stirring, for about one hour with 10 per cent, by weight of the alcohol, of active carbon. The solution is then freed from the carbon by filtration and is evaporated. About 27 kilograms of alcohols having a light yellow color are thereby obtained.

The dark brown carboxylic acids are melted and mixed with a solution of 170 kilograms of concentrated sulphuric acid in 100 kilograms of water. While vigorously stirring, a solution of 63 kilograms of sodium bichromate in 63 kilograms of water is gradually introduced within 3 hours. The temperature is controlled in such a manner, that the mixture is kept weakly boiling. After the solution has assumed a dark green color, stirring is stopped, whereupon the bleached product separates out at the top of the aqueous liquor and is separated therefrom. It is washed in the molten state with a dilute aqueous sulphuric acid solution and finally with water. The yield of purified acids amounts to about 64 kilograms. The solution of the alcohols of Montan wax obtained in subjecting the saponification products to extraction with solvents, may, of course, be treated directly with a decolorizing powder, without the solvent being previously removed by distillation. Similarly, the soaps freed from the alcohols of the wax can be directly subjected to an oxidizing treatment as described above, without previously separating the acids, which have been precipitated by acidifying the soaps, from the salt solution.

Esterifications of the resulting purified acids and alcohols, may be carried out for example as follows though the specific methods and compositions of the initial materials may be varied without departing from the scope of the present invention, the following examples being merely illustrative:

1. 30 parts by weight of the bleached alcohols of Montan wax are stirred for 3 hours with 70 parts by weight of the bleached acids in the presence of about 0.5 per cent, by weight of the alcohols and acids, of an 8 per cent aqueous sulphuric acid solution at a temperature of 130° C. in a vessel the free space of which is filled with nitrogen. The reaction product is washed with hot water and then treated, if desired, with decolorizing carbon if a coloration should have occurred in the esterification. The product is a hard wax having a yellowish color, an acid value of 38 and a saponification value of 102.

2. A mixture of 40 parts by weight of the purified alcohols of Montan wax and 60 parts by weight of the purified acids of Montan wax are esterified in the same manner as described above. The resulting wax melts at 80° C. and has a saponification value of 79.

3. By esterifying a mixture of equivalent amounts of purified alcohols and of purified acids

of Montan wax under the same conditions as described above, a light colored wax is obtained, having an acid value of 7, a saponification value of 69.5 and a melting point of 79.5° C.

4. By esterifying a mixture of 50 parts by weight of the purified acids of Montan wax, 20 parts by weight of the purified alcohols of Montan wax and 30 parts by weight of alcohols of carnauba wax under the same conditions as described above, a hard wax is obtained, having a melting point of 82° C., an acid value of 3 and a saponification value of 65.

5. By esterifying a mixture of the purified alcohols of Montan wax with a mixture of 50 per cent of the bleached acids of Montan wax and 50 per cent of the bleached acids of carnauba wax in the proportion, by weight, of 1 part of alcohols to 1 part of the mixture of acids under the same conditions as described above, a hard wax is obtained having a light yellow color, the melting point of the crude Montan wax (79° C.) and properties similar to those of carnauba wax.

6. A mixture consisting of 33 parts by weight of the purified alcohols of Montan wax, 23 parts by weight of stearic acid, 10 parts by weight of the bleached acids of Montan wax and 34 parts by weight of soft paraffin wax having a melting point of 41° C. is stirred for 2 hours at 140° C. with an addition of 1 per cent by weight of concentrated sulphuric acid, then washed with water until neutral and finally heated to boiling. A soft wax is obtained having a melting point of 60° C., an acid value of 38 and a saponification value of 75.

The process according to this invention is not restricted to the specific manner of carrying out the saponification process as described in the above examples. Thus, the saponification of the Montan wax may be effected, for example, with caustic alkali metal hydroxides in alcoholic solution or with a caustic alkaline earth, these means being preferred to the hydrolysis by means of strong mineral acids.

The treatment with sodium bichromate in sulphuric acid solution may be replaced by any other similar oxidizing treatment, as for example by means of nitric acid, hydrogen peroxide solution or solutions of a permanganate and sulphuric acid.

The treatment with active carbon can also be effected in the absence of solvents or can be replaced by a treatment with fuller's earth. Similarly the conversion of the bleached alcohols into esters may be carried out according to any known esterification process.

Various modifications may be made in the details disclosed in the foregoing specification without departing from the invention or giving up the advantages thereof.

This is a continuation-in-part to our copending application Ser. No. 497,596, filed November 22nd, 1930.

What we claim is:—

1. The process for the production of light-colored waxy materials which comprises saponifying Montan wax, separating fatty acids from the alcohols of Montan wax, bleaching the said alcohols with a decolorizing powder having an adsorbing action, bleaching the fatty acids with a solution of an oxidizing agent and esterifying alcohols thus bleached with fatty acids thus bleached.

2. The process for the production of light-colored waxy materials which comprises saponifying Montan wax, separating the fatty acids from the alcohols of Montan wax, bleaching the said alcohols with a decolorizing powder having an adsorbing action, bleaching the fatty acids with a solution of an oxidizing agent and esterifying the resulting bleached alcohols with the bleached fatty acids in the same proportion as they are contained in the initial material.

3. The process for the production of light-colored waxy materials which comprises saponifying Montan wax, separating the fatty acids from the alcohols of Montan wax, bleaching the said alcohols with a decolorizing powder having an adsorbing action, bleaching the fatty acids with a solution of an oxidizing agent and esterifying the bleached alcohols with the bleached fatty acids in the proportion by weight of about 1 to about 1.

4. The process for the production of light-colored waxy materials which comprises saponifying Montan wax, separating the fatty acids from the alcohols of Montan wax, bleaching the said alcohols with a decolorizing powder having an adsorbing action, bleaching the fatty acids with a solution of an oxidizing agent and esterifying the bleached alcohols with the bleached fatty acids in the proportion of about 1 to 1.5.

5. The process for the production of light-colored waxy materials which comprises saponifying Montan wax, separating fatty acids from the alcohols of Montan wax, bleaching the said alcohols with a decolorizing powder having an adsorbing action, bleaching the fatty acids with a solution of an oxidizing agent and esterifying the resulting bleached alcohols and light colored alcohols of other natural waxes with the bleached fatty acids.

6. The process for the production of light-colored waxy materials which comprises saponifying Montan wax separating fatty acids from the alcohols of Montan wax, bleaching the said alcohols with a decolorizing powder having an adsorbing action, bleaching the fatty acids with a solution of an oxidizing agent and esterifying the bleached alcohols with the bleached fatty acids and other light colored high-molecular fatty acids.

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