Patented Feb. 26, 1952

2,586,780

UNITED STATES PATENT OFFICE

2,586,780

TREATMENT OF MONTAN WAX

Frederick W. Breuer, Lititz, and David T. Zentmyer, Lancaster Township, Lancaster County, Pa., assignors to Armstrong Cork Company, Lancaster, Pa., a corporation of Pennsylvania

No Drawing. Application August 18, 1949, Serial No. 111,089

12 Claims. (Cl. 106—271)

1

This invention relates to the treatment of montan wax. More particularly the invention relates to the production of hard gel-free waxes from montan wax by a process including partial esterification of montan wax with a dihydric alcohol followed by esterification of the remaining free carboxyl groups by means of a higher polyhydric alcohol such as one containing from 3 to 8 hydroxy groups.

Montan wax is a product which is generally obtained from brown coal. One method of producing this material includes granulating brown coal and drying the resulting granulated material to a moisture content of about 10% to 12%. The granules are then sieved to remove any powder therefrom, and the powder-free granules are extracted with a mixture containing about 85% benzol and 15% unrefined wood alcohol containing methyl and isopropyl alcohols. This extraction is normally carried out at a temperature of about 90° C. to 100° C. The alcohols dissolve the cell walls of the brown coal granules and free the wax therefrom, thereby enabling the wax to be dissolved by the benzol. The wax solution is separated; and the solvent distilled off, leaving the crude montan wax as a residue.

This crude montan wax is comprised essentially of resin acids, fatty acids, and wax esters similar to those contained in carnauba wax. The similarity to carnauba wax is due to the presence of a mixture of esters of acids of high molecular weight containing 26 to 29 carbon atoms, primarily carboceric and montanic acid with 27 and 29 carbon atoms respectively with alcohols such as triacontyl ($C_{30}H_{61}OH$) and the like. We prefer to employ a wax which has been partially deresinified.

The crude montan waxes are somewhat limited in their utility because of the dark color which characterizes these materials.

Various methods have been proposed and used to produce a montan wax of sufficiently light color to enable its use in those instances where light color is required. These bleaching processes are well known and are typified in such patents as U. S. Patent 1,699,250, U. S. Patent 1,737,975, U. S. Patent 1,767,886, and U. S. Patent 1,777,766.

Although the various methods of bleaching montan wax result in a product of light color, the bleached waxes so produced tend to crystallize under certain conditions of use. This tendency is believed to be caused by the presence of considerable quantities of fatty acids in the material. Methods have been proposed for treating bleached montan wax to esterify the fatty acid content thereof, but considerable difficulty has been experienced in producing a desirable material by following these methods.

2

Among the methods which have been proposed is one involving the esterification of bleached montan wax with a dihydric alcohol, such as ethylene glycol, butylene glycol, polyethylene glycol, and the like. The esterified products show a hardness as measured by the Sward rocker method which is substantially below carnauba wax. When penterythritol and similar high polyhydric alcohols are used to esterify bleached montan wax, the products contain a substantial amount of gelled material. While we do not intend to be limited to any theories expressed herein, it is believed that the production of gels in the esterification of montan wax with pentaerythritol is due to the formation of dibasic acids during the bleaching of the montan wax by means of oxidizing agents. These dibasic acids form polycondensation products of network structure with the higher polyhydroxy alcohols such as pentaerythritol.

In order to overcome the tendency toward gel formation in the treatment of montan wax, mixtures of higher polyhydroxy alcohols and glycols were tried; but the products either contain a substantial amount of gel or are comparatively soft materials and cannot be used in formulations wherein a hardness such as that of carnauba wax is required.

We have found that hard and gel-free readily dispersible waxes can be obtained from bleached montan wax by means of a process in which the bleached wax is first treated with a glycol to partially esterify the monocarboxylic acids and to convert a substantial quantity of the dibasic acids to mono-esters and thereafter esterifying the remaining free carboxyl groups with a higher polyhydric alcohol containing, for example, 3 to 8 hydroxy groups, such as pentaerythritol. The resulting waxes show a hardness about equal to that of carnauba wax and, in addition, are free from gelled products.

In the initial esterification step of our process we may employ any of a number of dihydric alcohols to accomplish the partial esterification of the dicarboxylic acid content of the bleached montan wax. Typical of the dihydroxy alcohols are ethylene glycol, butylene glycol, diethylene glycol, propylene glycol, and the like. Generally speaking, we find it advantageous to utilize unsubstituted dihydroxy alcohols in carrying out this phase of our process. However, it will be ap-

parent to those skilled in the art that the dihydroxy alcohol may contain any substituents which do not interfere with the esterification of the dicarboxylic acid groups contained in the montan wax or the desired properties of the final product.

As to higher polyhydric alcohol, we have advantageously employed pentaerythritol which may be in a highly purified form or which may be a commercial product containing some dimers and trimers of pentaerythritol. Of course, other polyhydric alcohols, such as glycerol, dipentaerythritol, tripentaerythritol, sorbitol, mannitol, and the like may be used. In this phase of our process we have obtained advantageous results by utilizing unsubstituted polyhydric alcohols containing 3 to 8 hydroxy groups; but if desired, we may employ polyhydric alcohols having 3 to 8 hydroxy groups and containing substituents which do not interfere with the esterification of the remaining free carboxyl groups in the montan wax. These substitute materials are well known to those skilled in the art.

While the bleached montan wax may be obtained by any of a number of well-known bleaching processes, we prefer to employ a bleached wax obtained by heating the wax with sulfuric acid to obtain a wax emulsion and thereafter treat the emulsion with a mixture of chromic acid and sulfuric acid or with chromic acid alone. The resulting product is quite light in color; and hence, its field of use when treated in accordance with our invention is widened.

In order to more fully understand our invention, reference may be had to the following specific examples which are given by way of illustration and not by way of limitation.

In Example I we describe our preferred method of obtaining the bleached wax which is treated in accordance with our invention.

Example I

100 grams of montan wax were placed in a 2-liter, 3-neck round bottom flask seated in an electrically heated mantle and fitted with a mechanically operated stirrer, dropping funnel, and thermometer. To this were added 400 ml. of a 47% aqueous sulfuric acid solution, and the whole was heated to 105° C. Stirring was begun as soon as the wax became molten. The mixture formed a homogeneous, emulsified mass within 15 minutes. There was then added dropwise over a 30-minute period a solution of 100 grams of chromium trioxide in 100 ml. of water. During this time the temperature of the reaction mixture was maintained at 110° C. to 112° C. (The heat of reaction was sufficient to maintain this temperature during the first 20 minutes.) After the addition of the oxidant was complete, stirring was continued for another 30 minutes at 110° C. to 112° C., and 100 ml. of boiling water were added to break the emulsion. Heating was discontinued and the contents of the flask were allowed to stand and cool. Upon separation and subsequent solidification of the wax layer, the dark, green aqueous phase was poured off. The wax was then washed with 400 ml. of 47% sulfuric acid by stirring vigorously at 95° C. to 100° C. for 20 minutes. Upon cooling and separation of the wax, the wash acid was removed, and the wax washed with two 1 liter portions of water at boil for 20 minutes each. After removal of the wash water, the wax was dried by heating with stirring at a temperature of 90° C. to 95° C. and a pressure of 160 mm. until all foaming ceased; the wax became clear, and the temperature began to rise sharply. The cooled product was brown colored and showed a reflectance of 6% at 600 mu. as determined on a General Electric recording spectrophotometer. It had a melting point of 79° C. to 84° C. and an acid number of 123. The yield was 62.8 grams or 62.8%. A further bleaching treatment of the product obtained using the same amounts of reactants and the same procedure gave a light-colored product (36% reflectance), having an acid number of 170 and a melting point of 76° C. to 80° C. The overall yield was 54.2%.

With larger quantities of reactants higher yields can be obtained.

The following examples are illustrative of the process of our invention. The esterification reactions described in the examples given below were carried out in a 4-neck round bottom flask fitted with a mechanically operated stirrer, thermometer, and gas inlet tube. During the reaction of glycols with wax acids an electrically heated reflux condenser was also attached. The temperature of this condenser was maintained at a level sufficient to prevent condensation of water vapor, but well below the boiling point of the glycol, and served to reduce the loss of glycol. After completion of the glycol esterification the condenser could be removed. The gas inlet tube served to permit the constant introduction of an inert gas such as carbon dioxide or nitrogen. The use of these gases effected the dual function of acting to sweep out the water of reaction and to provide a nonoxidizing atmosphere to reduce coloration.

Example II

100 grams (0.28 equivalent of wax acids) of bleached montan wax (acid number 160), 8.7 grams (0.28 equivalent) of ethylene glycol, and 0.50 gram p-toluene sulfonic acid were melted together in the apparatus described above and heated at 110° C. to 112° C. with constant agitation in a stream of nitrogen gas (about 0.4 liter per minute) until (four hours) successive acid number determinations indicated substantially all of the glycol had been esterified. The acid number of this partially esterified wax was 34.1. 50 grams (0.031 equivalent of wax acids) of this material were then allowed to react with 1.1 grams (0.030 equivalent) of technical grade pentaerythritol (commercially available as "Pentek") by heating to 170° C. until the pentaerythritol was dissolved. This took about 5 to 10 minutes. The reaction was continued at 150° C. to 160° C. with stirring, and nitrogen gas was passed through the reaction zone in the manner indicated above. After six hours the esterification was substantially complete, and the acid number of the product was 4.2. The wax was hard, light brown colored, and had a melting point of 75° C. to 80° C. as determined on a Fisher-Johns melting point determination stage. The Sward hardness of a molded sample of the wax was 15.

Example III

The flask was charged with 50.0 (about 0.15 equivalent of wax acids) of bleached montan wax (acid number 170), 2.4 grams (0.077 equivalent) of ethylene glycol, and 0.25 gram of p-toluene sulfonic acid. The mixture was heated slowly to melt the wax and then heated at 150° C. to 160° C. with continual stirring and passage of nitrogen gas through the reaction zone at a rate

of about 0.4 liter per minute. After 1.5 hours the acid number of the melt was 101. There were then added 2.10 grams (0.058 equivalent) of pentaerythritol, and the mixture was heated at 160° C. to 180° C. for four hours. The final product was a light brown hard wax with a melting point of 69° C. to 73° C., and an acid number of 32.8. The Sward hardness was 17.

Example IV

150.0 grams (0.43 equivalent of wax acids) of bleached montan wax (acid number 160), 15.1 grams (0.49 equivalent) of ethylene glycol, and 0.75 gram p-toluene sulfonic acid were heated at 108° C. to 112° C. with constant stirring under nitrogen gas for five hours. The acid number leveled off at 24.4. To 50 grams of this material there was added 0.80 gram (0.022 equivalent) of pentaerythritol and the temperature raised to and maintained at 170° C. to 180° C. After six hours acid number determinations indicated that substantially all of the pentaerythritol had been esterified. The product was a light brown colored wax with a melting point of 75° C. to 80° C. and had a Sward hardness of 18. The final acid number was 16.0.

In another embodiment of our invention the bleached montan wax may be treated with a dihydric alcohol as above described to esterify the dibasic acids and thereafter treated with pentaerythritol or other higher polyhydric alcohols. After substantially all of the carboxylic acids have been esterified, minor portions of an unsaturated dicarboxylic acid or anhydride thereof may be added. The unsaturated dicarboxylic acid may be maleic acid or its anhydride and any other unsaturated dicarboxylic acid or anhydride thereof similar to maleic acid may be used, for example, itaconic acid, fumaric acid, phthalic acid, and the like. We prefer to employ unsubstituted unsaturated dicarboxylic acids; but if desired, any substituted acid may be used which does not contain substituents which would interfere with the desired reaction. Waxes obtained by this embodiment of our invention are particularly suitable for use in the preparation of emulsion floor polishes. This embodiment of our invention is illustrated in the following specific examples.

Example V

50 grams (0.141 acid equivalent) of bleached montan wax (acid number 170) were partially esterified by treating with 4.8 grams (0.155 equivalent) of ethylene glycol in the presence of 0.25 gram of p-toluene sulfonic acid at 110° C. to 115° C. for five hours. Nitrogen gas and agitation were utilized as described in Example II. The acid number reached 14.8. There was then added 0.65 gram (0.019 equivalent) of pentaerythritol and the mixture heated to 175° C. and held there until the pentaerythritol dissolved. This occurred in about 10 minutes. The contents of the flask were then cooled to 110° C. and the reaction continued at 110° C. to 115° C. for 1.5 hours. 0.44 gram (.009 equivalent) of maleic anhydride was then added, and the mixture heated for eight more hours. The product was a light brown colored wax with acid number of 9.28, a melting point of 73° C. to 80° C., and a Sward hardness of 19.

Example VI

50 grams of partially esterified bleached montan wax (acid number 24.4) prepared as described in Example IV and 1.0 gram (0.027 equivalent) of pentaerythritol were allowed to react. The temperature of the reaction mixture was raised to 170° C. and the reaction continued at that temperature for thirty minutes (acid number 18.1). To the mixture there was then added 0.5 gram (0.01 equivalent) of maleic anhydride. Heating was continued at 170° C. to 180° C. for six hours. The product was a hard, light brown wax with an acid number of 4.35, a melting point of 77° C. to 80° C., and a Sward hardness of 17.

Example VII

360 grams (1.09 equivalents) of bleached montan wax (acid number 170), 24.6 grams (0.79 equivalent) of ethylene glycol, and 2.0 grams p-toluene sulfonic acid were heated at 108° C. to 112° C. (with mechanical agitation and a stream of carbon dioxide gas at the rate of 0.7 liter per minute) for 1.5 hours (acid number 72.3). 10.28 grams (0.28 equivalent) of pentaerythritol were added and the temperature of the mixture was raised to 200° C. and held there for 25 minutes. The temperature was then raised to 250° C. and held there for 5 minutes. The mixture was cooled to 145° C., and 3.52 grams (0.072 equivalent) of maleic anhydride were added. The reaction was continued at 170° C. to 180° C. for three hours (acid number 20.5). The wax produced was light brown in color and had a Sward hardness of 16 and a melting point of 71° C. to 75° C.

Example VIII

50 grams of bleached montan wax partially esterified (acid number 24.2) with ethylene glycol as described in Example IV and 2.29 grams (0.052 equivalent) of dipentaerythritol ("Dipentek") were added. The mixture was heated at 200° C. to 210° C. for one hour while being stirred. A stream of carbon dioxide gas was passed through at the rate of 0.4 liter per minute. The acid number dropped to 9.40. At this point the reaction mixture was cooled to 150° C., and 1.47 grams (0.030 equivalent) of maleic anhydride were added. Heating was continued at 200° C. for two hours. The product was brown in color and hard, showing a Sward hardness of 16. The acid number was 5.52 and the melting point was 76° C. to 82° C.

The waxes obtained in accordance with our invention may be emulsified by any of the methods known to the art. A typical formulation is illustrated in the following example:

Example IX

10 grams of the wax obtained in accordance with Example VII, 1.4 grams of oleic acid, and 1.4 grams of triethanolamine were heated on a steam cone until the temperature was 92° C. With constant stirring 80 grams of boiling water were slowly added. The emulsion was then cooled to room temperature with stirring. A bright drying emulsion was obtained which was adapted for use as a floor polish.

While our invention may be practiced utilizing various quantities of dihydric alcohol and higher polyhydric alcohol, we have found that in order to definitely avoid gel formation the ratio on a stoichiometrical equivalent basis of polyhydric alcohol to dihydric alcohol should be in the range of about 0.2 to about 0.8 part of higher polyhydric alcohol to about 1 part of dihydric alcohol. Within these limits of 0.2 to 0.8 equivalent of higher polyhydric alcohol to 1 equiva-

lent of dihydric alcohol, the higher ratio will apply to the minimum allowable percentage of wax acids esterified in the first step and the lower ratios will apply in those instances where higher percentages of wax acids are esterified in the first step. In other words, when a higher percentage of wax acids is esterified in the first step, lesser quantities of higher polyhydric alcohol are required for substantially complete esterification; and when a lower percentage of esterification is obtained, greater quantities of higher polyhydric alcohol are required in the second step. When maleic anhydride or equivalent dicarboxylic acid material is employed in conjunction with glycol and higher polyhydric alcohol, the ratio is advantageously 0.01 to 0.07 part maleic anhydride, 0.14 to 0.4 higher polyhydric alcohol, and about 1 part of dihydric alcohol. In the three-stage process, we have found it advantageous to use approximately a twenty-five percent excess of polyhydric alcohol to provide sufficient hydroxyl groups for subsequent esterification with dicarboxylic acid. Although materials having some desirable characteristics may be prepared utilizing the reactants in proportions outside of the ranges set forth, products having less desirable properties are obtained. In our two-stage process gel formation is overcome by reacting at least 38% of the wax acid with dihydric alcohol and reacting the remaining groups with higher alcohol. We have obtained hard gel-free waxes in a three-stage process by reacting the dihydric alcohol with bleached montan wax until at least 55% of the wax acids have been reacted as evidenced by the acid number. The resulting material is then reacted with the higher alcohol until substantially all of the acid groups have been esterified. Maleic anhydride or its equivalent is added after the higher alcohol in this embodiment.

Generally speaking, in the practice of our invention the esterification reactions are advantageously carried out at a temperature between about 105° C. and about 225° C. Ordinarily we prefer to employ temperatures of about 105° C. to 140° C. as the lower temperatures within this range yield lighter colored products. If desired, the pressure may be reduced to speed up the reaction by more rapid removal of the water of reaction. It is also within the scope of our invention to carry out the reaction in the absence of an inert gas at temperatures up to 140° C. without the development of excess color. This is generally practiced when a substantially completely pure higher polyhydric alcohol is utilized. When technical grade materials are employed, it is generally desirable, if not necessary, to heat at higher temperatures in order to get these materials in solution. For example, using a technical grade pentaerythritol we find operation at temperatures of about 170° C. would be desirable.

While we have illustrated and described our invention with reference to certain particular embodiments and with reference to certain specific examples, it is to be understood that the invention is not limited thereby. Therefore, changes, omissions, substitutions, and/or additions may be made without departing from the spirit of the invention as defined in the appended claims which are intended to be limited only as required by the prior art.

We claim:

1. A process of producing a hard waxy material from bleached montan wax comprising esterifying a portion of the acid content of the bleached wax using dihydric alcohol, and thereafter esterifying substantially all of the remaining free carboxyl groups with a higher polyhydric alcohol.

2. The product of the process of claim 1.

3. A process of producing a hard readily dispersible wax from bleached montan wax comprising esterifying at least a portion of the acids of said wax with a dihydric alcohol, heating the resulting material in the presence of a higher polyhydric alcohol to esterify substantially all of the remaining free carboxyl groups, and thereafter reacting the resulting material by heating in the presence of an unsaturated dicarboxylic acid.

4. The product of the process of claim 3.

5. A floor wax preparation comprising an aqueous emulsion of the product of claim 4.

6. A process of producing hard readily dispersible waxes from bleached montan wax comprising esterifying the dicarboxylic acid groups in said wax with ethylene glycol, and thereafter esterifying substantially all of the remaining free carboxyl groups with pentaerythritol.

7. A process of producing a hard readily dispersible wax from bleached montan wax comprising heating said wax in the presence of ethylene glycol to esterify the dicarboxylic acid groups in said wax, heating the resulting material in the presence of pentaerythritol to esterify substantially all of the remaining free carboxyl groups, and thereafter reacting the resulting material with maleic anhydride by heat in the presence thereof.

8. A process of producing a hard waxy material from bleached montan wax comprising esterifying a portion of the dibasic acid content of the bleached wax by means of a dihydric alcohol, and thereafter esterifying the remaining free carboxyl groups with a polyhydric alcohol containing 3 to 8 hydroxy groups.

9. A process of producing a hard waxy material from bleached montan wax comprising heating said bleached wax in the presence of a dihydric alcohol to esterify a portion of the dibasic acid content thereof, and thereafter esterifying the remaining free carboxyl groups with a polyhydric alcohol containing 3 to 8 hydroxy groups, the ratio of polyhydric alcohol to dihydric alcohol being in the range of about .2 to about .8 parts of higher polyhydric alcohol to about 1 part of dihydric alcohol on a stoichiometrical equivalent basis.

10. A process of producing hard waxy material from bleached montan wax comprising heating said bleached wax in the presence of a dihydric alcohol until at least 38% of the wax acids have reacted with said alcohol, and thereafter heating the resulting material in the presence of a polyhydric alcohol containing 3 to 8 carbon atoms to esterify the remaining free hydroxyl groups, the ratio on a stoichiometrical equivalent basis of polyhydric alcohol to dihydric alcohol being in the range of about .2 to about .8 parts of polyhydric alcohol to about 1 part of dihydric alcohol.

11. A process of producing a hard readily dispersible wax from bleached montan wax comprising heating said wax in the presence of a dihydric alcohol to esterify a portion of the dibasic acid content thereof, heating the resulting material in the presence of a polyhydric alcohol containing 3 to 8 carbon atoms, and thereafter reacting the product with an unsaturated dicarboxylic acid, the ratio of the additives being 0.01

to 0.07 part maleic anhydride, 0.14 to 0.4 of polyhydric alcohol, and about 1 part of dihydric alcohol on a stoichiometrical equivalent basis.

12. A process of producing a hard readily dispersible wax from bleached montan wax comprising heating said wax in the presence of a dihydric alcohol until at least 55% of the wax acids have been reacted, heating the resulting material in the presence of a polyhydric alcohol having 3 to 8 hydroxy groups to esterify substantially all of the remaining free carboxyl groups, and thereafter reacting the resulting material by heating in the presence of an unsaturated dicarboxylic acid, the ratio of dihydric alcohol, polyhydric alcohol, and dicarboxylic acid on a stoichiometrical equivalent basis being 0.01 to 0.07 part

maleic anhydride, 0.14 to 0.4 polyhydric alcohol, and about 1 part of dihydric alcohol.

FREDERICK W. BREUER.
DAVID T. ZENTMYER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,834,056	Guthke et al.	Dec. 1, 1931
2,025,612	Rodman	Dec. 24, 1935

OTHER REFERENCES

Bennett—Commerical Waxes, 1944, Chem. Pub. Co., Brooklyn, N. Y., page 499.