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PROCESS FOR THE MANUFACTURE OF HARD WAXES RICH IN ESTER FROM MIXTURES OF MONTAN WAX ACIDS AND PARAFFINS

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The present invention relates to a process for the manufacture of hard waxes rich in ester from mixtures of montan wax acids and paraffins.

Various methods are known for converting paraffin hydrocarbons of high molecular weight into ester waxes. In all these processes it is necessary that the paraffin be previously converted into an oxygen-containing compound in order to be rendered partially or completely susceptible to an esterification. For this purpose, the paraffin may be subjected, for example, to an oxidation. As oxidizing agents there are generally used oxygen, air or compounds yielding oxygen, for example nitric acid or nitrous gases. Oxidation products having a particularly high acid content are obtained by a combination of the aforesaid oxidation method with a chromosulfuric acid oxidation. It is also possible to convert paraffin into carboxylic acids by chlorination, dehydrochlorination, oxo-reaction and subsequent oxidation or alkali melt or direct oxidation of the paraffin dehydrochlorination products. The wax acids so obtained are, however, seldom used per se for the manufacture of high-grade ester waxes, since their hardness is only relatively low and they are often too expensive. As acid components for the esterification there are therefore often used mixtures of montan wax acids and paraffin oxidation products as they are obtained, for example, by treating montan wax and high molecular weight paraffin hydrocarbons oxidized with air, separately or simultaneously with chromosulfuric acid. In all cases, the paraffin is at least partially converted into carboxylic acids in a separate stage prior to the esterification.

Now we have found that hard waxes rich in ester can be obtained in a simple and direct manner from high molecular weight paraffin hydrocarbons having a solidification point above 70° C. by oxidizing said paraffin hydrocarbons together with montan wax acids in the molten state at temperatures up to 200° C., advantageously within the range of 130 to 170° C., with oxygen or gases containing oxygen, advantageously in the presence of a catalyst. It was surprising to see that the oxidation proceeds in a manner substantially contrary to what would be expected from the oxidation of paraffin with air. Whereas the acid number and ester number increase continuously in the oxidation of paraffin with air, the ester number increases in the oxidation according to the invention while the acid number decreases or remains unchanged and increases only insignificantly in rare instances.

As paraffin components for the compositions to be oxidized by the process of the invention there may be used natural, or advantageously synthetic, paraffin hydrocarbons of high molecular weight whose solidification point is above 70° C., advantageously above 90° C., for example well refined petroleum paraffins or hydrocarbon mixtures obtained in the catalytic carbon monoxide hydrogenation or mixtures containing at most about 40% of wax-like high pressure polyolefins or low pressure polyolefins, for example from ethylene and/or propylene, which generally have a molecular weight within the

range of about 1000 to about 20,000, advantageously 5000 to 10,000.

The montan wax acids used in the manufacture of ester waxes are commercially available wax acid mixtures as they are obtained, for example, by the oxidation of montan wax with chromic acid. By oxidizing such montan wax acids under the reaction conditions of the present invention, the characteristic values are only insignificantly changed while the oxidation products are strongly discolored.

Paraffin and montan wax acids, mixed in a desired proportion, can be oxidized with oxygen or gases containing oxygen, for example air or air enriched with oxygen. With extreme mixing proportions, the result of the oxidation is influenced by the component constituting the major portion of the mixture. When, for example, 90% and more of the mixture is paraffin, the oxidation substantially proceeds like a normal paraffin oxidation. The mixtures suitably contain about 20 to 80% by weight, advantageously 30 to 70% by weight, of paraffin, the percentage figures being calculated on the total weight of the mixture to be oxidized. In many cases, the mixing proportion depends on the desired acid number of the end product. If it is intended to obtain low acid numbers, a large proportion of paraffin may be used. For high acid numbers, a larger proportion of wax acids must be added. The following table shows how the acid number of the starting mixture decreases as the paraffin content increases, the montan wax acid having an acid number of 150.

Percent paraffin.	0	10	20	30	40	50	60	70	80	90	100
Acid number of mixture.....	150	135	120	105	90	75	60	45	30	15	0

The oxidation conditions are also variable. The lower limit of the temperature is determined by the melting range of the mixture and the upper limit by the rate of discoloration which increases with the oxidation temperature. At extremely low temperatures, for example immediately above the melting range of the mixture, in which case longer reaction times are needed, the acid number is sometimes slightly increased. The oxidation is therefore advantageously carried out at a temperature within the range of 100 and 200° C., advantageously 130 and 170° C.

The laws known from the paraffin oxidation apply also to the oxidation according to the invention. For a fast oxidation, the following factors are of importance: fine distribution of oxidizing agent; quantity of oxidizing agent used per hour and unit of weight of starting material; contact time; pressure. For example, 200 to 1000 liters of air may be blown in per kilogram of wax.

It is of advantage to proceed in the presence of a catalyst as it is used in the paraffin oxidation carried out with air, for example a metal salt, heavy metal oxide, organic peroxide or acid. By the use of such catalyst, the oxidation is considerably accelerated and the discoloration of the oxidation product shifted towards high degrees of oxidation, as desired. Heavy metal soaps such as the stearate or naphthenate of cobalt or manganese are very effective, especially in the ester formation; they are generally used in an amount of less than 1%. In the absence of a catalyst, longer oxidation times and/or higher temperatures, within the indicated temperature range, are necessary to obtain the same result as in the presence of a catalyst. The oxidation time depends on the paraffin content of the mixture and the desired de-

gree of oxidation. The latter is defined in a very simple manner by the content of unchanged paraffin. The higher the proportion of paraffin, the longer is the time of oxidation. The oxidation time is limited by the tendency of the oxidation product to deepen in color, since fairly light oxidation products are desired.

As already mentioned above, the process of the invention enables waxes that are rich in ester to be directly obtained by air oxidation of mixtures of high molecular weight paraffin hydrocarbons and montan wax acids. The conversion of the paraffin to oxygen-containing products increases with the oxidation time, the paraffin being incorporated with the wax in the form of ketones and alcohols and predominantly in the form of esters.

The composition of the end products can be varied within wide limits. In mixtures having a high content of paraffin, for example, only a part of the paraffin may be oxidized, whereby especially the long chain paraffin molecules are reacted. Alternatively, the paraffin may be reacted almost completely, this method being particularly advantageous when mixtures containing a small proportion of paraffin are used. The oxidation products obtained by the process of the invention are somewhat softer than the starting mixture, have a lower melting point and a light yellow to brown coloration depending on the degree of oxidation. They may be used directly or if desired after complete or partial conversion of the free acid groups still present into soaps, amides or esters, for the manufacture of floor polishes and leather dressing agents. Products containing lime soap may also be used as lubricating waxes for the work-up of plastics, the unchanged oxidation products make agents favoring the emulsification of soft paraffins and the amidation products thereof may be used as cable sealing compounds in the electrical industry. It is also possible to admix the products obtained by the process of the invention subsequently with other substances commonly used in wax preparations, for example ester waxes, amide waxes and/or hydrocarbon waxes.

The following examples serve to illustrate the invention but they are not intended to limit it thereto. The acid number, saponification number, ester number, hydroxyl number and carbonyl number were determined according to the methods usually applied in the analysis of waxes. The flow point/drop point was determined according to Ubbelohde, the solidification point was determined at a rotating thermometer and the paraffin content of the oxidation products was determined by chromatography. The hardness was measured as penetrometer hardness (load 100 g.; 5 seconds; 25° C.).

Example 1

A mixture of 240 grams of montan wax acid (acid number 150, saponification number 175, flow point/drop point 80.0/80.5° C.) which had been obtained by subjecting montan wax to an oxidizing bleaching with chromosulfuric acid and 160 grams of a hard paraffin of high molecular weight which had been obtained by synthesis and had a solidification point of 98° C., was oxidized for 9 hours at 150° C. with 200 liters/hour of air in the presence of 1 gram of cobalt stearate as catalyst in an oil-heated frit tube 500 mm. high and 50 mm. in diameter. The following table indicates the characteristic values of the starting mixture and the oxidation products obtained after 4 hours and 9 hours respectively.

	Starting mixture	oxidation product after 4 hours	oxidation product after 9 hours
acid number.....	92	80	73
saponification number.....	107	117	133
ester number.....	15	37	60
hydroxyl number.....	0	16	14
carbonyl number.....	10	32	40
flow point/drop point, °C.....	112.0/112.5	101.5/102.0	95.0/95.5
penetrometer number.....	1	4	4
paraffin content, percent.....	40	20	30

300 grams of the yellow oxidation product were subsequently reacted within 7 hours at 140 to 160° C. with 15 grams of ethylene diamine. A brown, very hard wax was obtained which had the following characteristic values: acid number 10, saponification number 50, flow point/drop point 102.6/103.0° C., penetrometer hardness 2.

Example 2

A mixture of 160 grams of the montan wax acid described in Example 1 and 240 grams of the hard paraffin described in Example 1 was oxidized at 165° C. for 3.5 hours with 200 liters/hour of air in the presence of 1 gram of cobalt stearate as catalyst in an oil-heated frit tube. The following table indicates the characteristic values of the starting mixture and the oxidation product obtained.

	starting mixture	oxidation product
acid number.....	61	52
saponification number.....	72	115
ester number.....	11	63
hydroxyl number.....	0	11
carbonyl number.....	3	38
flow point/drop point, °C.....	114.0/114.5	99.2/99.5
penetrometer number.....	1	3.5
paraffin content, percent.....	60	14

250 grams of the dark yellow oxidation product were saponified, while stirring vigorously, within 20 minutes at 110 to 120° C. with 8 grams of calcium hydroxide under a nitrogen atmosphere. The light brown, tough reaction product containing lime soap had the following characteristic values: acid number 15, saponification number 75, flow point/drop point 99.5/100.5° C.

Example 3

A mixture of 840 grams of the montan wax acid of Example 1 and 3,360 grams of a hard paraffin of high molecular weight which had been obtained by synthesis and had a solidification point of 101° C. was oxidized at 140° C. for 23 hours with 4 cubic meters/hour of air in the presence of 12 grams of cobalt stearate as catalyst in an electrically heated frit tube 1000 mm. high and 100 mm. in diameter. The following table indicates the characteristic values of the starting mixture and the oxidation product obtained.

	starting mixture	oxidation product
acid number.....	30	43
saponification number.....	38	123
ester number.....	6	80
hydroxyl number.....	0	15
carbonyl number.....	2	68
flow point/drop point, °C.....	112.5/113.0	89.5/90.0
penetrometer number.....	1	6
paraffin content, percent.....	80	6

Example 4

A mixture of 160 grams of the montan wax acid of Example 1, 204 grams of the hard paraffin of Example 1 and 36 grams of a low pressure polyethylene having a melting point of 118° C. and an average molecular weight of about 2000 was oxidized at 150° C. for 8.5 hours with 200 liters/hour of air in the presence of 1 gram of cobalt stearate as catalyst in the oil-heated frit tube described in Example 1. The following table indicates the characteristic values of the starting mixture and the oxidation product obtained.

	starting mixture	oxidation product
acid number.....	60	50
saponification number.....	81	96
ester number.....	21	46
hydroxyl number.....	0	15
carbonyl number.....	4	31
flow point/drop point, °C.....	113.2/113.5	103.0/103.5
penetrometer number.....	0.5	1.5
paraffin content, percent.....	60	18

Example 5

A mixture of 240 grams of the montan wax acid of Example 1 and 160 grams of a well refined hard micro-crystalline petroleum residue of a solidification point of 75° C. was oxidized at 145° C. for 4 hours with 300 liters/hour of air in the presence of 1 gram of cobalt stearate as catalyst in the oil-heated frit tube described in Example 1. The following table indicates the characteristic values of the starting mixture and the oxidation product obtained.

	starting mixture	oxidation product
acid number.....	86	82
saponification number.....	100	117
ester number.....	14	35
hydroxyl number.....	0	1
carbonyl number.....	9	23
flow point/drop point, °C.....	81.0/81.3	80.6/81.0
penetrometer number.....	1	1.5
paraffin content, percent.....	40	28

Instead of cobalt stearate, the corresponding naphthenate or the manganese salts of these acids may be used as catalysts.

We claim:

1. A process for the manufacture of a hard wax rich in ester which comprises contacting a molten mixture consisting essentially of (1) a high molecular aliphatic hydrocarbon having a solidification point above 70° C. and (2) a montan wax acid at a temperature up to 200° C. with free oxygen, until at least about 30 percent of the said high molecular aliphatic hydrocarbon is oxidized to form an aliphatic alcohol which reacts with the wax acid to form the ester, the high molecular aliphatic hydrocarbon being contained in the starting mixture in an amount from 20 to 80 percent by weight.

2. A process for the manufacture of a hard wax rich in ester which comprises contacting a molten mixture consisting essentially of (1) a high molecular aliphatic hydrocarbon having a solidification point above 90° C. and (2) a montan wax acid at a temperature in the range

between 130 and 170° C. with free oxygen, until at least about 30 percent of the said high molecular aliphatic hydrocarbon is oxidized to form an aliphatic alcohol which reacts with the wax acid to form the ester, the high molecular aliphatic hydrocarbon being contained in the starting mixture in an amount from 20 to 80 percent by weight.

3. The process of claim 2, wherein the free oxygen is applied in the form of air.

4. The process of claim 2, wherein the free oxygen is applied in the form of air enriched with oxygen.

5. A process as claimed in claim 2, wherein the high molecular aliphatic hydrocarbon contains up to 40 percent of a polymer having a molecular weight in the range between about 1000 and about 20,000, said polymer being a polymer of at least one olefin selected from the group consisting of ethylene and propylene.

6. A process as claimed in claim 2, wherein the starting mixture to be oxidized contains from 30 to 70 percent of a high molecular aliphatic hydrocarbon.

7. A process for the manufacture of a hard wax rich in ester which comprises contacting a molten mixture consisting essentially of (1) a high molecular aliphatic hydrocarbon having a solidification point above 90° C. and (2) a montan wax acid at a temperature in the range between 130 and 170° C. with free oxygen in the presence of less than 1 percent of an oxidation catalyst, until at least about 30 percent of the said high molecular aliphatic hydrocarbon is oxidized to form an aliphatic alcohol which reacts with the wax acid to form the ester, the high molecular aliphatic hydrocarbon being contained in the starting mixture in an amount from 20 to 30 percent by weight.

8. A process for the manufacture of a hard wax rich in ester, which comprises contacting a molten mixture consisting essentially of 20 to 80 percent by weight of a high molecular aliphatic hydrocarbon having a solidification point above 90° C. and the balance of a montan wax acid at a temperature in the range from 130 to 170° C. with 200 to 1000 liters, calculated per kilogram of the starting mixture, of air, until at least about 30 percent of the said high molecular aliphatic hydrocarbon is oxidized to form an aliphatic alcohol which reacts with the wax acid to form the ester.

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