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COMPLETE SPECIFICATION

Wax Processing

We, SOUTH AFRICAN COAL, OIL AND GAS CORPORATION LIMITED, a South African Limited Liability Company, of P.O. Box 1, Sasolburg, Orange Free State, Union of South Africa, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the production of improved wax acids.

It has already been proposed to catalytically oxidize paraffin waxes, and especially those obtained by synthesis from gases containing carbon monoxide and hydrogen (hereinafter referred to for the sake of brevity as "Fischer-Tropsch" paraffin waxes) by means of air or other gas comprising free oxygen to products comprising wax carboxylic acids and esters. The higher the degree of oxidation, the softer do these products become and the more does their colour change from white to yellow and even brown. These waxes comprise, according to their degree of oxidation, besides the wax carboxylic acids and esters aforesaid, aldehydes together with more or less or little or no original hydrocarbon material. Due to their complicated composition, they are useful only in a limited field of application and therefore cannot compete with the much purer and more uniform natural waxes such as carnauba wax, bees wax and the like.

It is an object of the present invention to produce well defined wax acids which are adapted to serve as intermediates for the production of improved wax products.

In accordance with the present invention, such wax acids are produced by the catalytic oxidation in a molten state of a paraffin wax having a melting point exceeding 75° C. and a mean molecular weight of at least 650 with a gas comprising free oxygen at a temperature below 145° C. and for so short a time as to produce an intermediate oxidized wax product comprising carboxylic wax acids and wax esters and having an acid number between 5 and 25 and a saponification number between 10 and 60, and hydrolyzing the said wax esters to carboxylic wax acids and alcohols and oxidizing the said alcohols in the mixture by means of a solid or liquid oxidising agent to carboxylic wax acids.

The melting points referred to herein are based on determinations by the rotating thermometer method, but any other method of melting point determination may be employed provided the values obtained are corrected to the basis herein specified.

It is advantageous to conduct the said oxidation so as to produce intermediate products having acid numbers between 5 and 20 and saponification numbers between about 10 and 45. As will be explained in greater detail below, the degree to which the oxidation is carried out for optimal conditions depends on the nature and molecular weight of the paraffin waxes oxidized. It will be noted that in the intermediate products, in accordance with the invention, even with low degrees of oxidation, the saponification number is usually twice as great as their acid number. This indicates that an amount of carboxylic acid approximately equal to that present as free acid is converted to esters with alcohols of higher molecular weight. The formation of oxy-acids which occurs on over-oxidation should be suppressed as far as possible.

The melting point of the intermediate product is usually between about 95° and 75° C.

The initial paraffin wax preferably has a melting point of about 86° to 105° C., advantageously of at least 100° C., and excellent intermediate products of higher molecular weight are also obtained by the oxidation of paraffin waxes having melting points of 105—117° C. The initial materials are preferably hard paraffin waxes having a mean molecular weight above about 700, say between about 700 and 830 or between 830 and 1100 for products of higher molecular weight. They are preferably substantially free from constituents having a molecular weight below 500.

Particularly advantageous results are obtained when using as initial materials Fischer-Tropsch hard paraffin waxes of the aforesaid type.

Depending, more especially, on the catalysts employed, paraffin waxes of various general types are produced by the Fischer-Tropsch type synthesis.

Thus hard paraffin waxes are produced by a Fischer-Tropsch synthesis with cobalt or iron Fischer-Tropsch type catalysts.

Paraffin waxes of this origin, having melting points above 80° C. and preferably above 85° C. usually consist substantially of straight chain normal paraffins with a molecular weight of over 500 and those with a mean molecular weight above 650 may be employed as initial materials in accordance with the invention. The percentage of branched chain hydrocarbons present varies between 10 and 20 per cent, alpha-methyl branching being predominant. The olefin, aromatics, alcohol and aldehyde content of such waxes is usually very low, usually below 1—2 per cent, at any rate in so far as the paraffin waxes produced with cobalt catalysts are concerned. With paraffin waxes containing olefins and possibly some oxygen-containing compounds, which may be the case when they have been produced with iron catalysts, it is usually desirable to eliminate the olefins and the like by hydrogenation, sulphonation or the like. Such hydrogenated hard waxes even when derived from iron catalyst operation have a content of olefins, aldehydes, and alcohols well below 1 per cent. Initial paraffin waxes containing some olefins, however, also give interesting intermediate products which, however, may lead to processed products with a higher oxidation number.

The molecular weight distribution of such waxes varies considerably. All the hard wax collected from a Fischer-Tropsch synthesis reactor run over several months or from a plurality of synthesis reactors operated with catalyst of different ages, which is herein termed "total hard wax product", has the widest range. The average molecular weight of such wax is usually the higher, the higher the total wax yield from a given quantity of synthesis gas. Hard waxes from catalysts giving a yield below 25 per cent hard wax with respect to total yield in C_3+products in the Fischer-Tropsch synthesis usually do not contain wax constituents having more than 60 carbon atoms per molecule or wax constituents melting above 180° C. in the total hard wax. Their average of carbon atoms in the molecule is between 40 and 50. On the other hand, total hard wax from a catalyst giving a yield higher than 25 per cent of hard wax with respect to C_3+products increases in average molecular weight considerably. Catalysts giving e.g. a hard wax yield near 40 per cent with respect to all C_3+products contain wax constituents with more than 100 carbon atoms in the molecule to the extent of 10—30 per cent. If the reactor wax is taken from the very first period of the Fischer-Tropsch synthesis at medium pressure, this percentage of high molecular weight paraffin waxes is even larger and the molecular weights go even higher, so that constituents with more than 150 carbon atoms per molecule may be present in a substantial percentage.

From this it is obvious that the initial paraffin wax material and also the intermediate products obtained vary considerably within the limits herein specified.

Examples of suitable initial materials are the following:—

1a) It may be a total mix from a plant where, usually in a plurality of reactors, catalysts of different ages and production characteristics are employed. This total mix may have a melting point of about 90° C., an average molecular weight of about 650 and have on the average about 46 carbon atoms in the molecule. Solvent fractionation shows that the total mix has e.g. 10 to 15 per cent of C30—34 wax, 10 to 15 per cent in the C35—39 range, 70—55 per cent wax content in the range C40—C50, and only 10 to 15 per cent of waxes of a molecular weight higher than 800 (C50+).

1b) It may be a selected paraffin wax from initial periods of single reactors. This selected product contains much higher molecular paraffin wax than that referred to in 1a, e.g. with a maximum proportion at C60, or C80 or even higher, e.g. at C100.

1c) It may be fractionated paraffin wax as is obtained by fractional crystallisation or extraction. Such narrower range fractions may predominantly contain C40, C60, C80, C100 or C150 waxes.

As will be shown in the following table, the degree to which the oxidation is carried out namely the acid numbers and saponification numbers desired for the intermediate product is dependent *inter alia* on the molecular weight of the hard paraffin wax selected as an initial material, as will be shown in the table below. The intermediate product usually contains over 50 per cent of non-oxidized paraffin wax.

	Intermediate product		Crude improved wax acid	
Initial hard wax	Acid number	Saponification number	Acid number	Saponification number
A. about C_{55}—C_{65}	15—25	25—60	45—100	45—100
B. 1. Max. about C_{60}	10—15	17—35	30—50	30—50
B. 2. Max. about C_{80}	6—12	10—28	18—40	18—40
C. Product rich in over C_{80} hydrocarbons	5—10	10—25	15—40	15—40

The catalytic oxidation of the paraffin wax with air or the like is usually carried out at temperatures of about 120°—140° C., say at about 130° C.

A thorough distribution of the oxidizing gas in the material being oxidized is a factor in favour of obtaining good results.

Fatty acid salts of manganese, cobalt, copper and the like, or oxides and salts, such as potassium permanganate, manganese dioxide, iron oxide or silver oxide are examples of the catalysts that may be employed for the oxidation to yield oxidized waxes. The catalysts are preferably dissolved or suspended in a finely divided condition in the molten paraffin wax undergoing oxidation, depending on their solubility.

The said oxidation is usually carried out at substantially atmospheric pressure, but may be carried out at any other suitable pressure, e.g. elevated pressure, if desired or required.

EXAMPLE 1

Hydrogenated molten hard wax having an average molecular weight of about 840, an acid number 0, saponification number 0, iodine number 2, and a melting point (rotating thermometer) 103° C. is charged into a thermostatically heated cylindrical glass vessel and 0.2% manganese stearate is added as catalyst. The air for oxidation of the wax is introduced into the molten wax with the aid of a fritted disc at the lower end of the vessel. The vessel should be approximately half filled with the paraffin wax. The temperature is regulated to about 130° C. and air flow is adjusted to about 120 normal litres of air per litre of wax. The oxidation is stopped after 6 to 8 hours when an intermediate product having an acid number of 15 and a saponification number of 32 has been produced.

In accordance with the present invention, the intermediate products are subjected to an oxidative treatment in which the esters contained in the intermediate product are hydrolyzed to wax acids and wax alcohols and the alcohols split off are oxidized mainly to the corresponding carboxylic wax acids, either at the time when they are produced by hydrolysis or in a subsequent operation.

The hydrolysis of the esters may be carried out in various ways, e.g. by treatment with hot water under pressure, by treatment with hot sulphuric acid, by a Twitchell type of reaction or the like.

The oxidation of the alcohols split off from the esters to carboxylic acids is carried out with any suitable oxidizing agent, e.g. alkali metal bichromate in sulphuric acid, chromic acid or hydrogen peroxide. If desired the spent oxidising agent may be regenerated, e.g. electrolytically or in the case of chromium salts, by means of hydrogen peroxide.

The following example illustrates a de-esterifying hydrolysis and the almost simultaneous oxidation of the wax alcohols thus split off predominantly to the corresponding carboxylic wax acids.

EXAMPLE 2

The intermediate product is produced from a Fischer-Tropsch hard paraffin wax having an average molecular weight of about 870, a softening point (ring and ball) of 102° C. and containing 2—3 per cent of olefins by catalytic oxidation under conditions similar to those employed according to Example 1.

The initial paraffin wax is not previously hydrogenated, which constitutes the main difference from Example 1. The intermediate product thus produced has an acid number of 10 and a saponification value of 22. 100 parts of this intermediate product are placed in a round bottom flask and melted. 200 parts of hot 50 per cent sulphuric acid are slowly added during about 15 minutes, and during a further 15 minutes 100 parts of hot 40 per cent sodium bichromate solution are slowly added, keeping the liquid under constant stirring at near boiling temperature (about 105° C.), the entire reaction being completed in about 2 hours. After washing the crude wax acid thus produced with boiling water, sample analysis shows that the acid number is about 46 and the saponification number approximately 48 and the softening point 100.2° C. The increase in acid number is somewhat higher than in the case of hydrogenated wax which may be attributed to the presence of small amounts of olefins. It can be seen from this that the wax esters have been practically entirely converted to carboxylic wax acids.

If desired or required, the carboxylic acids produced in accordance with the invention may be subjected to a refining treatment by any suitable method, e.g. for the removal of low molecular weight acids. For example, they may be subjected to solvent extraction, preferably with mixed solvents. Mixtures of an aromatic hydrocarbon, such as benzene, toluene and xylene, with an alcohol such as methanol, ethanol, propanol, isopropanol, butanol and the like in various ratios are suitable. Alternatively the carboxylic acids may be refined by vacuum distillation.

Examples 3 and 4 illustrate the purification of the crude wax acids to remove low molecular weight acids by solvent extraction and vacuum distillation respectively.

EXAMPLE 3

A sample of the crude wax acid produced in accordance with Example 2 is powdered and extracted in a Soxleth apparatus with an ethanol-toluene mixture (68 per cent+32 per cent) for about 2 hours. A residue of about 50 per cent is recovered from the thimble which on analysis gives an acid number of 32. It has a penetration of 30 units at 58° C. (the original has 55 units), hence it is considerably harder. The softening point (ring and ball) is 102° C. (2° higher than the original). The extracted wax has an acid number of 55 and a softening point of 78° C. Penetration at 58° C. cannot be carried out as the wax is too soft.

EXAMPLE 4

A crude wax acid, obtained as hereinbefore described, is washed with hot water and dried in a fatty acid still and subjected to vacuum distillation in order to remove the lower boiling acids and lower boiling hydrocarbons. This treatment yields similar results to the solvent extraction, but the product is not as white but is more yellow in colour.

Depending on the raw material used and the further treatment and how much material is taken off, or removed by solvent extraction, a large variety of raw wax acids can be obtained, so that in this way the varieties of further derivatives obtainable therefrom are manifold. In many cases, the hard wax acids thus obtained can be used directly for commercial purposes (textile auxiliaries) and as raw materials for further chemical reactions as mentioned below.

However, for obtaining still purer wax acids, unsaponifiable matter may be removed partly or substantially completely from the crude wax acids.

The removal of unsaponifiable matter can be achieved in several ways; e.g., by neutralisation of the acid with alkali and solvent extraction of wax from the crude soap.

It is a particular feature of the invention that this purification of raw wax acids is much easier than that of paraffin wax oxidation products.

The amount of lower molecular weight acid which has to be removed by extraction or the like in order to obtain the higher molecular weight fatty acids and unreacted wax is the greater, the higher the degree of oxidation of the intermediate product. When the crude acids listed in the table are refined by solvent extraction, the refined acids remaining as residue are from:—

Crude acid from wax A	C30—C40
,, ,, ,, ,, B	C40—C60
,, ,, ,, ,, C	C60+

With the wax acids obtained in accordance with the invention, it is now possible to prepare valuable wax derivatives by the esterification of crude or refined wax acids e.g. with crude or refined wax alcohols. These ester waxes, as has been explained previously, can be prepared with a large variety of properties, ranging from soft wax types to hard and brittle waxes, similar to natural waxes. Considerably improved products are thus obtained of great value for all industries where similar natural waxes have found application.

EXAMPLE 5

From the hard wax acids of Example 3, which contains about 50 per cent of pure C30—C50 fatty acids, a cetyl ester is prepared in the following way: 100 parts of hard wax acid are melted in a round bottom vessel, about 1 part of zinc dust is added as a catalyst and then 10 parts of cetyl alcohol are added. The mixture is heated to about 200° C. for 3 hours, a CO_2 stream being bubbled through to remove water. The wax is then decanted from the remaining zinc dust and filtered over an activated clay while still molten. Analysis of the cetyl ester wax thus obtained gives an acid number of 6, which is satisfactory for a commercial wax type. It is very hard, of white colour and has a softening point (ring and ball) of 103° C.

The surface of the sample gives excellent gloss when rubbed with a cloth. The product can be used as a hard, gloss-giving wax constituent in polish compositions.

A similar product is obtained using cholesterol as the alcohol constituent.

When using lower molecular weight alcohols such as *n*-butanol for esterification with the hard wax acids, waxes are obtained with properties approaching those of bees wax.

The esterification of the crude and refined wax acids, with glycols and similar bi-functional or poly-functional compounds, e.g. glycerol or pentaerythritol yields valuable products. These esterifications are carried out in accordance with known practice. Valuable waxes are obtained, e.g. with glycols, of more than double the molecular weight of the acids. Monoesters of this type are valuable as emulsifiers.

Salts of the crude wax acids or refined wax acids may be formed with alkali, alkaline earths or amines and the like, e.g. with calcium hydroxide, harder products being thus obtained. These salts prove of particular value in wax preparations, e.g. where emulsions have to be prepared and the like.

Total or partial neutralisation of the aforesaid hard wax acids with alkali or alkaline earth and other oxides, such as of earth metals or of the fifth, sixth, seventh or eight column of the periodical system gives a series of interesting soaps and salts which prove useful as additives to soaps, lubricating oils and greases, and for cosmetic and pharmaceutical preparations.

What we claim is:—

1. A process for the production of wax acids, which comprises the catalytic oxidation in a molten state of a paraffin wax having a melting point exceeding 75° C. and a mean molecular weight of at least 650 with a gas comprising free oxygen at a temperature below 145° C. and for so short a time as to produce an intermediate oxidized wax product comprising carboxylic wax acids and wax esters and having an acid number between 5 and 25 and a saponification number between 10 and 60, and hydrolyzing the said wax esters to carboxylic wax acids and alcohols and oxidizing the said alcohols in the mixture by means of a solid or liquid oxidizing agent to carboxylic wax acids.

2. A process as claimed in Claim 1, in which the catalytic oxidation is carried out for so short a time as to produce an intermediate oxidized wax product comprising carboxylic wax acids and wax esters, which product has an acid number between 5 and 20 and a saponification number between 10 and 45.

3. A process as claimed in Claim 1 or Claim 2, in which the initial paraffin wax is a hard paraffin wax with a melting point above 80° C. substantially consisting of straight chain normal paraffins produced by a Fischer-Tropsch type synthesis with iron group Fischer-Tropsch type catalysts.

4. A process as claimed in Claim 3, in which a Fischer-Tropsch paraffin wax having a melting point above 85° C. is catalytically oxidised with air at a temperature of 120°—140° C. to an intermediate oxidized wax product having an acid number between 5 and 20 and a saponification number between 10 and 45.

5. A process as claimed in any of Claims 1 to 4, in which the wax alcohols split off from the wax esters of the intermediate product are oxidized to wax acids with a bichromate in sulphuric acid, chromic acid or hydrogen peroxide.

6. A process as claimed in any of Claims 1 to 5, in which the hydrolysis is carried out by treatment with hot water under pressure, by treatment with hot sulphuric acid or by a Twitchell type of reaction.

7. A process as claimed in any of Claims 1 to 6, in which the carboxylic wax acids produced are subjected to a refining treatment for the removal of low molecular weight acids.

8. A process as claimed in Claim 7, in which the refining treatment is carried out by solvent extraction with mixtures of an aromatic hydrocarbon with an alcohol or with other mixed solvents.

9. A process as claimed in Claim 7, in which the refining treatment is carried out by vacuum distillation.

10. A process as claimed in any of Claims 7 to 9, in which the refined higher molecular weight wax acid is esterified with cetyl alcohol, butanol, glycol, glycerol or pentaerythritol.

11. A process as claimed in any of Claims 1 to 10, in which the initial hard paraffin wax has 35 to 55 carbon atoms in the molecule, is catalytically oxidized with a gas containing free oxygen to an intermediate product containing wax esters and acids and having an acid number of 15 to 25 and a saponification number of 25 to 60, which product is hydrolyzed and oxidized to yield an improved wax acid having an acid number of 45—100.

12. A process as claimed in any of Claims 1 to 10, in which the initial hard paraffin wax has up to about 60 carbon atoms in the molecule, is catalytically oxidized with a gas containing free oxygen to an intermediate product containing wax esters and acids and having an acid number of 10 to 15 and a saponification number of 17 to 35, which product is hydrolyzed and oxidized to yield an improved wax acid having an acid number of 30 to 50.

13. A process as claimed in any of Claims 1 to 10, in which the initial hard paraffin wax has up to about 80 carbon atoms in the molecule, is catalytically oxidized with a gas containing free oxygen to an intermediate product containing wax esters and acids and having an acid number of 6 to 12 and a saponification number of 10 to 28, which product is hydrolyzed and oxidized to yield an improved wax acid having an acid number of 18 to 40.

14. A process as claimed in any of Claims 1 to 10, in which the initial hard paraffin wax has over 80 carbon atoms in the molecule, is catalytically oxidized with a gas containing free oxygen to an intermediate product containing wax esters and acids and having an acid number of 5 to 10 and a saponification number of 10 to 25, which product is hydrolyzed and oxidized to yield an improved wax acid having an acid number of 15 to 40.

15. A process as claimed in Claim 1, in which the initial paraffin wax has a molecular weight between 700 and 1100.

16. A process as claimed in Claim 1, in which the oxidation with the solid or liquid oxidising agent follows on the hydrolysis as a

separate reaction in sequence with the hydrolysis.

17. A process as claimed in Claim 1, in which the oxidation with the solid or liquid oxidising agent is carried out substantially simultaneously with and in the same reagent mixture as the hydrolysis.

18. A process for the production of wax acid products, substantially as hereinbefore described.

19. Wax acids whenever obtained by the process claimed in any of Claims 1 to 18.

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