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COMPLETE SPECIFICATION

Process for softening hard paraffin wax by cracking

We, RUHRCHEMIE AKTIENGESELLSCHAFT, a German Company of Oberhausen-Holten, Germany, 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 invention relates to a process for the conversion or softening of hard paraffin wax, obtained as a product of the catalytic hydrogenation of carbon monoxide, into waxes having melting points in the range 40°-80°C. by cracking.

The normally solid hydrocarbons formed by the catalytic hydrogenation of carbon monoxide have, for the greater part, more than 30 carbon atoms in the molecule, corresponding to a minimum boiling point of 460°C. at a pressure of 760 mm. Hg. These hydrocarbons from the catalytic hydrogenation of carbon monoxide boiling above 460°C. are generally referred to as hard paraffin wax or simply as hard wax. When the hydrogenation of carbon monoxide is effected with an iron catalyst, the average number of carbon atoms in the molecules of this hard wax lies between about 45 and 50.

Hard wax has a setting point of about 90°-100°C. as measured on the rotating thermometer, and penetration numbers of about 1. It is used to a small extent for hardening slab wax and increasing the pour point thereof. The utilization of larger quantities of hard wax involves considerable difficulties. In the production of polishing waxes and shoe polishes difficulties are caused, for example, by the relatively poor oil absorbability and the insufficient retention power of the hard wax. Moreover, the pastes prepared with the addition of larger quantities of hard wax have little temperature-resistance, that is to say, the hardness of the pastes is insufficient at temperatures of as low as about 30°C. For the electrical industry, the hard wax is too brittle and has too high a contraction, although its electrical properties are satisfactory. In spite of its high setting point, the hard wax is unsuitable for paper impregnation owing to its extreme brittleness. It cannot, therefore, be used as a blending component for slab wax with the same success as microcrystalline, petroleum waxes.

For this reason, hard wax has been separated by solvent extraction into fractions of different melting points or ranges. Wax fractions obtained in this manner and having melting points of 70°-80°C. are referred to as "Ozokerite" and are used, for example, as blending materials in the production of polishing waxes and shoe polishes, in electrical engineering in the manufacture of condensers (capacitors) and for paper impregnation.

The solvent extraction of hard wax, which is operated in a non-continuous manner, is extremely complicated and also very costly due to the large quantities of solvent which have to be circulated. A further disadvantage of this method of processing consists in that the extract fractions only comprise a relatively small part of the hard wax. The residue of the extraction is even more brittle than hard wax and, therefore, is still more unsuitable for use on a large scale.

No processes suitable for use on a commercial scale are known at present which permit the separation of hard wax by distillation into fractions of different melting points and different properties. Vacuum distillation, which has hitherto been the usual process, only permits a fractionation up to a temperature, recalculated to normal pressure, of about 460°C. By this process, hard wax can only be recovered as a residual or bottoms fraction. Although references are made in the literature to the molecular distillation of hard wax, on a

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laboratory scale, which permits hydrocarbons boiling above 460°C. to be obtained as distillate fractions, processes of this kind are completely unsuitable for the processing of hard wax on a commercial scale.

It is an object of the invention to provide a simple process whereby the hard wax obtained as a product in the catalytic hydrogenation of carbon monoxide may be converted into waxes having far greater utility.

According to the invention, the hard wax obtained as a product of the catalytic hydrogenation of carbon monoxide is converted by a process which comprises subjecting the hard wax to cracking at atmospheric pressure or at a slight superatmospheric pressure, for example, up to 20 kg./sq. cm., at a temperature in the range 370°-450°C. for a period of from 3 to 20 minutes, subjecting the products of cracking to distillation in a first distillation zone at about atmospheric pressure to remove the hydrocarbons boiling up to 340°C., subjecting the residue from the first distillation zone to flash vaporisation in a second distillation zone operated at an absolute pressure in the range 1-3 mm. Hg. so that the constituents boiling between 340°C. and about 550°C. at atmospheric pressure are removed overhead whilst the constituents boiling above 550°C. and forming a bottoms product are recycled to the process, and separating one or more wax fractions having melting points in the range 40°-80°C. from the overhead product of the second distillation zone.

The temperature at which the hard wax is cracked is preferably not less than 390°C. and is advantageously within the range 420°-450°C. The residence time of the hard wax in the cracking zone is preferably from 6 to 15 minutes, the cracking being advantageously effected in a tubular system.

The separation of the vacuum distillate into the particular fractions desired, for example, into a fraction of 340°-460°C. boiling range at atmospheric pressure and a fraction boiling above 460°C. at atmospheric pressure with the fraction boiling above 460°C. remaining as the residue, may be effected in a manner known *per se* by distillation. The individual fractions can be freed from oil-containing constituents in known manner by means of extractive deoiling processes or, if necessary or desired, by sweating processes. It is possible in this manner to obtain oil-free waxes having the particular melting points or ranges desired. It is of advantage if the fractions, prior to the deoiling, are hydrogenated in a manner, known *per se*, for example, in the presence of a nickel catalyst, at temperatures of about 250°C. By this step, an increased yield of oil-free waxes is obtained.

It is also possible to avoid separation by distillation of the distillate boiling between about 340°C. and 550°C. In this case, the overall fraction, preferably after hydrogenation, is separated into paraffin waxes having melting points of, for example, about 70°C., about 50°-60°C. and about 40°-45°C. and an oily fraction, by subjecting the overall fraction to a stagewise deoiling at decreasing temperatures, such as at temperatures of between 20°C. and 0°C.

It is also possible, however, to separate the entire vacuum distillate by solvent extraction at increasing temperatures, the extraction being effected in known manner with the use, for example, of heptane or other low boiling solvents. In this extraction, the low melting constituents are obtained first and the high melting constituents last.

The flash vaporisation in the second distillation zone may be carried out with particular advantage in two or more series-connected vacuum columns operating with decreasing absolute pressure. In this manner, several vacuum distillates are directly obtained rather than a single vacuum distillate and the necessity of a subsequent separation by distillation is eliminated, a simple deoiling of the different vacuum distillates being sufficient.

An increased yield of valuable waxes having melting points of between 60°C. and 80°C. may be obtained by cracking the hard wax in a tubular system heated to 370°-410°C., the residence time of the hard wax in the tubular system being preferably between 6 and 15 minutes, whilst the residue boiling above about 550°C. from the vacuum or second distillation zone is cracked in a second tubular system which is heated to temperatures of between 410°C. and 450°C., and preferably between 420°C. and 430°C. the residence time of the residue in the second tubular system being advantageously from 6 to 15 minutes, the cracked products from the two tubular systems being then processed together in the first and second distillation zones.

With this modification of the invention in which the residue from the second distillation zone is cracked in one zone whilst the hard wax is cracked in another zone, a further embodiment of the process may be carried out if not only the hard wax, but all of the hydrocarbons from the catalytic hydrogenation of carbon monoxide boiling above approximately 340°C. are charged as feedstock in the process of the invention. In this case also, the feed boiling above 340°C. is passed through the first tubular system maintained at a temperature in the range 370°-410°C. whilst the residue from the vacuum or second distillation zone is passed through the second tubular system maintained at a temperature in the range 410°-450°C. The cracked products from the two tubular systems are then passed together through the first and second distillation zones.

It is also possible, of course, to adjust the initial boiling point of the residue from the vacuum or second distillation zone to temperatures lower than about 550°C. such as 500°C. Thus, for example, all of the hydrocarbons boiling above 500°C. are recycled for cracking. In this case, the reaction product contains less waxes having melting points of 60°-80°C. and more waxes having melting points of between 40°C. and 60°C.

The process of the invention can be operated on a commercial scale without difficulty. The formation of undesirable residual products or of carbon causing obstructions or blockages in the apparatus, has not been observed. It is possible by means of the process of the invention to convert the hard wax into valuable waxes having melting points within the range 40°-80°C. approximately with a yield of about 70-80% and with 80-90% of these waxes being of particular value by virtue of their having melting points within the range 70°-75°C. approximately.

It is already known to subject carbon monoxide hydrogenation products boiling above 450°C. to thermal cracking to produce therefrom fractions boiling between 320°C. and 450°C. which have been converted into fatty acids by oxidation. In this cracking process, however, quite considerable quantities of gases and low boiling hydrocarbons are obtained so that the yield of waxes having melting points of about 45°-60°C. is very low, whilst waxes having melting points above 60°C. cannot be obtained at all.

It has also been proposed to treat hard waxes from the carbon monoxide hydrogenation at 400°-450°C. until the hard wax has turned into a salve-like product similar to a jelly. In this method, the treatment is carried out for 2-18 hours. In contrast to this process, the process according to the invention yields no jelly-like products at all, but solid, oil-free waxes.

The process of the invention, which may be termed the "Paraforming" process, now makes possible the conversion of hard wax from the catalytic hydrogenation of carbon monoxide into waxes melting between about 40°C. and 80°C. with high yields, and particularly into waxes having melting points of 60°-80°C., which waxes may be widely used in the production of polishing waxes and shoe polishes, in electrical engineering and in paper impregnation. Moreover, the waxes produced in accordance with the invention and having melting points of about 70°C. are suitable for the manufacture of candles. Heat-resistant candles particularly suitable for use in the tropics and having excellent combustion properties can be produced from, for example, 1 part of wax having a melting point of about 68°-75°C. and, for example, one part of wax having a melting point of about 56°-62°C.

By the process of the invention, the hard wax from the catalytic hydrogenation of carbon monoxide, which hitherto had little use, is converted into valuable products having an almost unlimited market. This is of particular importance since by far the greatest part of the normally solid paraffin hydrocarbons obtained in the products of the catalytic hydrogenation of carbon monoxide consists of hard wax and the lack of opportunity for the sale of this hard wax has hitherto had a very disadvantageous effect on the Fischer-Tropsch synthesis from the economic standpoint.

The invention is illustrated by the following Examples:

EXAMPLE 1

A mixture consisting of 35 parts by weight of a hard wax boiling above 460°C., obtained by the hydrogenation of carbon monoxide in the presence of an iron catalyst and having an average molecular weight of 630, and 65 parts by weight of a distillation residue boiling above 550°C. and derived from the process cycle, was passed at normal pressure through a tube heated to 425°C., the residence time of the mixture within the tube being 8 minutes. After the passage through this tube, the gaseous reaction products formed in the tube and the liquid constituents boiling up to about 340°C. were separated from the reaction product in a first distillation column operated at atmospheric pressure. The bottoms product or residue from the first distillation column was depressurized or subjected to flash vaporisation in a second distillation column operated at an absolute pressure of 1 mm. Hg and from which, while utilizing the heat content of the said bottoms product, the reaction products boiling between 340°C. and 550°C. (at atmospheric pressure) were taken off overhead while the residue boiling above 550°C. was, after admixture with fresh hard wax, recycled to the cracking zone, that is, to the tube heated to 425°C.

The head temperature in the vacuum or second distillation column was 275°C. and the bottom temperature was 375°C.

Based on the hard wax charged to the process, the following reaction products were obtained:

Overhead products in the first distillation:

1.0% by weight of gas
3.7% by weight of a fraction boiling in the range 30°-160°C.
11.0% by weight of a fraction boiling in the range 160°-340°C.

Overhead products in the second distillation:

84.7% by weight of a fraction boiling in the range 340°-550°C.

The fraction boiling in the range 340°-550°C. was separated in a conventional commercial vacuum distillation until at an absolute pressure of 3 mm. Hg into a distillate boiling in the range 340°-460°C. at atmospheric pressure and a residue boiling in the range 460°-550°C. at atmospheric pressure. Based on the hard paraffin charge, the yield was as follows:

19.2% by weight of a fraction boiling in the range 340°-460°C.
65.5% by weight of a fraction boiling in the range 460°-550°C.

These two fractions, after the addition of 5% by weight of a hydrogenation catalyst (100 Ni, 15 MgO, 50 kieselguhr), were separately stirred for 1 hour in an autoclave at 250°C. and under a hydrogen partial pressure of 50 atmospheres and subsequently separated from the catalyst by filtration. The hydrogenated fractions were processed as follows:

One part by weight of the fraction boiling in the range 340°-460°C. was admixed by stirring at 60°C. with three parts by weight of a solvent consisting of 35% of benzene and 65% of isopropanol, cooled to 20°C. and filtered at this temperature. The filtration residue was washed with small amounts of the same solvent mixture. After evaporation of the solvent, an oil-free slab paraffin wax having a pour point of 57.5°C. was obtained.

The filtrate obtained was further cooled to 5°C. and again filtered at this temperature. The filtration residue was washed and then freed from the solvent. This resulted in an oil-free soft paraffin wax having a pour point of 44°C. The solvent mixture was separated from the filtrate by distillation. The residue consisted of an extraction oil having a pour point of 25°C.

The yield, based on the hard wax charge, was as follows:

9.7% by weight of slab paraffin wax
3.9% by weight of soft paraffin wax
5.6% by weight of extraction oil

One part by weight of the fraction of 460°-550°C. boiling range was stirred at 80°C. with 3 parts by weight of the benzene-isopropanol solvent mixture hereinbefore referred to, cooled to 5°C. and filtered at this temperature. The filtration residue was washed with small amounts of the solvent. After evaporation of the solvent, an oil-free wax having a pour point of 73.5°C. was obtained. The solvent was separated from the filtrate by distillation. The residue consisted of an extraction oil having a pour point of 27°C. The yields were as follows:

59.0% by weight of paraffin wax having a pour point of 73.5°C.
6.5% by weight of extraction oil.

The total yield obtained from 100 parts of hard paraffin wax was as follows:

59.0% by weight of paraffin wax having a pour point of 73.5°C.
9.7% by weight of slab paraffin wax having a pour point of 57.5°C.
3.9% by weight of soft paraffin wax having a pour point of 44.0°C.
12.1% by weight of extraction oil having a pour point of 26.0°C.
10.7% by weight of a fraction boiling in the range 160°-340°C.
3.6% by weight of a fraction boiling in the range 30°-160°C.
1.0% by weight of gas.

EXAMPLE 2

A mixture consisting of 30 parts of the hard paraffin wax used in Example 1 and boiling above 460°C. and 70 parts of a distillation residue boiling above 550°C., was passed at normal pressure through a tube heated to 430°C., the residence time in the tube being 6 minutes. After passage through this tube, the gas and the liquid constituents boiling up to about 340°C. were separated from the treated mixture in a first distillation column operating at normal pressure. The residue or bottoms product from the first column was depressurized or subjected to flash vaporisation in a second distillation column operating at an absolute pressure of 1 mm. Hg and from which, while utilizing the heat content of the bottoms product of the first distillation column, the products boiling between 340°C. and 550°C. at atmospheric pressure were withdrawn as distillate, whilst the residue boiling above 550°C. was recycled to the heater tube.

Based on the hard wax charge, the following overhead products were obtained:

In the first distillation:

0.8% by weight of gas
3.8% by weight of a fraction boiling in the range 30°-160°C.
11.0% by weight of a fraction boiling in the range 160°-340°C.

In the second distillation:

84.4% by weight of a fraction boiling in the range 340°-550°C.

The fraction of 340°-550°C. boiling range was subsequently hydrogenated in the manner described in Example 1 and then processed as follows:

One part by weight of the fraction 340°-550°C. was stirred at 80°C. with 5 parts by weight of a solvent mixture consisting of 50% of benzene and 50% of isopropanol, cooled to 20°C. and filtered at this temperature. The filtration residue was washed with small amounts of the solvent mixture. After evaporation of the solvent an oil-free paraffin wax having a pour point of 70°C. was obtained. The resulting filtrate was subjected to distillation in which a distillate consisting of about 66% of benzene and 33% of isopropanol distilled off as an azeotropic mixture. The distillation was continued until about 60% of the solvent mixture was distilled off. The distillation residue was cooled to 20°C. and filtered at this temperature. The filtration residue was washed with small amounts of solvent mixture and then freed from the solvent. This resulted in an oil-free, slab paraffin wax having a pour point of 52°C. The filtrate was then cooled to 5°C. and filtered at this temperature. The filtration residue was washed and subsequently freed from the solvent. This resulted in an oil-free, soft paraffin wax having a pour point of 43°C. The solvent was separated from the filtrate by distillation. The residue consisted of an extraction oil having a pour point of 26°C.

The total yield obtained in this manner from 100 parts of hard paraffin wax was as follows:

61.8% by weight of paraffin wax having a pour point of 70°C.
6.9% by weight of slab paraffin wax having a pour point of 52°C.
2.8% by weight of soft paraffin wax having a pour point of 43°C.
12.9% by weight of extraction oil having a pour point of 26°C.
11.0% by weight of a fraction boiling in the range 160°-340°C.
3.8% by weight of a fraction boiling in the range 30°-160°C.
0.8% by weight of gas.

EXAMPLE 3

35 parts by weight of the hard paraffin wax mentioned in Example 1 were passed at normal pressure through a tube heated to 430°C., the residence time in the tube being 6 minutes. Through a second tube which was also heated to 430°C., 65 parts by weight of a distillate boiling above 550°., were passed, with a residence time in the tube of 8 minutes. Both of the treated products were combined and then the gaseous and liquid constituents boiling up to about 340°C. were separated in a first distillation column operating at normal pressure. The bottoms product from the first distillation column was depressurized i.e. subjected to flash vaporisation, in a second column operating at an absolute pressure of 80 mm. Hg. At a head temperature of 300°C. and a bottom temperature of 400°C. the constituents boiling in the range 340°-460°C. at atmospheric pressure were separated as distillate. The residue from the second distillation column was then subjected to flash vaporisation in a third distillation column operating at an absolute pressure of 1mm. Hg. At a bottom temperature of 375°C. and a head temperature of 290°C. the constituents boiling between 460°C. and 550°C. at atmospheric pressure were separated as distillate while the residue boiling above 550°C. was returned into the second tube heated to 430°C.

Based on the hard paraffin wax charge, the following overhead products were obtained:

In the first distillation:
0.5% by weight of gas
2.2% by weight of a fraction boiling in the range 30°-160°C.
5.1% by weight of a fraction boiling in the range 160°-340°C.
In the second distillation:
12.2% by weight of a fraction boiling in the range 340°-460°C.
In the third distillation:
80.0% by weight of a fraction boiling in the range 460°-550°C.

The two fractions of 340°-460°C. and 460°-550°C. boiling range respectively were separately hydrogenated and de-oiled in the manner described in Example 1.

The total yield obtained from 100 parts by weight of hard paraffin wax was as follows:

71.8% by weight of paraffin having a pour point of 73.0°C.
5.7% by weight of slab paraffin having a pour point of 56.0°C.
2.5% by weight of soft paraffin having a pour point of 43.0°C.
12.2% by weight of extraction oil having a pour point of 27.0°C.
5.1% by weight of a fraction boiling in the range 160°-340°C.
2.2% by weight of a fraction boiling in the range 130° and 160°C.
0.5% by weight of gas.

What we claim is:—

1. A process for the conversion of the hard wax obtained as a product of the catalytic hydrogenation of carbon monoxide, which comprises cracking the hard wax by heating the wax at atmospheric pressure or a slight superatmospheric pressure at a temperature within the range 370°-450°C. for a period of from 3 to 20 minutes, subjecting the products of cracking to distillation in a first distillation zone at about atmospheric pressure to remove the hydrocarbons boiling up to 340°C., subjecting the residue from the first distillation zone to flash vaporisation in a second distillation zone operated at an absolute pressure in the range 1-3 mm. Hg in such a manner that the constituents boiling

between about 340°C. and about 550°C. at atmospheric pressure are removed overhead whilst the constituents boiling above about 550°C. and forming a bottoms product are recycled to the process, and separating one or more wax fractions having melting points in the range 40°-80°C. from the overhead product of the second distillation zone.

2. A process according to claim 1, in which the cracking of the hard wax is effected at a temperature of not less than 390°C.

3. A process according to claim 1 or claim 2, in which the cracking of the hard wax is effected at a pressure not exceeding 20 kg./sq. cm.

4. A process according to any one of the preceding claims, in which the cracking of the hard wax is effected at a temperature within the range 420°-450°C.

5. A process according to any one of the preceding claims, in which the hard wax is heated during cracking for a period of from 6-15 minutes.

6. A process according to any one of the preceding claims, in which the cracking of the hard wax is effected in a tubular system.

7. A process according to any one of the preceding claims, in which the wax fractions are separated by distillation from the overhead product of the second distillation zone.

8. A process according to any one of claims 1 to 6, in which the wax fractions are obtained from the overhead product of the second distillation zone by deoiling.

9. A process according to any one of claims 1 to 6, in which the wax fractions are obtained from the overhead product of the second distillation zone by solvent extraction.

10. A process according to any one of the preceding claims, in which the overhead product of the second distillation zone is subjected to hydrogenation prior to separation of the wax fractions.

11. A process according to any one of the preceding claims, in which the second distillation zone comprises two or more distillation stages, through which the residue from the first distillation zone is passed, the stages of the second distillation zone being operated at decreasing pressures in the direction of flow of the product under treatment.

12. A process according to any one of the preceding claims, in which the bottoms product from the second distillation zone is subjected to cracking by being passed through a tubular system at a temperature of 410°-450°C. at atmospheric pressure or a pressure not exceeding 20 kg./sq. cm., whilst the cracking of fresh hard wax is effected in a separate tubular system at a temperature in the range 370°-410°C., the products from both tubular systems being thereafter treated together in the first and second distillation zones.

13. A process according to claim 11, in which the bottoms product from the second distillation zone is maintained for a period of from 6 to 15 minutes at a temperature in the range 410°-450°C. during cracking.

14. A process according to claim 12 or claim 13, in which the bottoms product from the second distillation zone is cracked at a temperature within the range 420°-430°C.

15. A process for the production of a wax having a melting point in the range 40°-80°C. from hard wax, substantially as hereinbefore described.

16. A process for the production of a wax having a melting point in the range 40°-80°C., substantially as hereinbefore described in any one of the Examples.

17. Waxes having melting points in the range 40°-80°C., whenever obtained by the process of any preceding claim.

EDWARD EVANS & CO.,
53-64, Chancery Lane, London, W.C.2,
Agents for the Applicants.

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