Sept. 16, 1958 H. KOLLING ET AL 2,852,546

CONVERSION OF HARD PARAFFIN OBTAINED BY THE CATALYTIC HYDROGENATION OF CARBON MONOXIDE

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Fig. 1

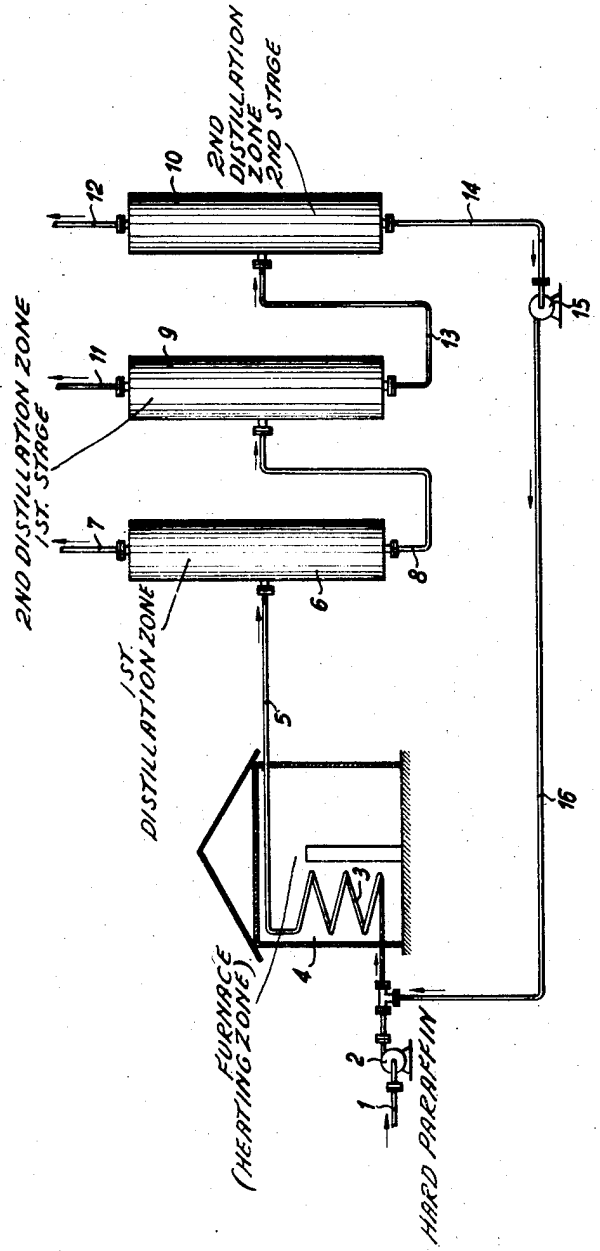

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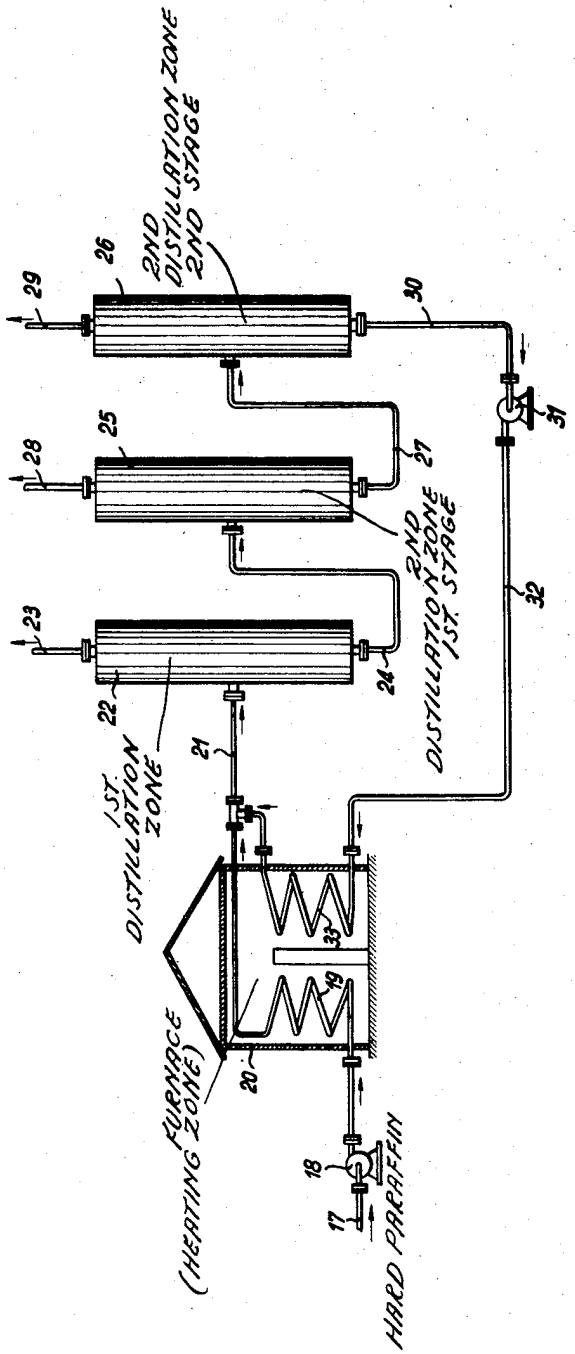
FIG. 2



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United States Patent Office 2,852,546 Patented Sept. 16, 1958

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CONVERSION OF HARD PARAFFIN OBTAINED BY THE CATALYTIC HYDROGENATION OF CARBON MONOXIDE

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Application February 7, 1955, Serial No. 486,584

Claims priority, application Germany February 10, 1954

12 Claims. (Cl. 260—450)

This invention relates to improvements in the conversion of hard paraffin obtained by the catalytic hydrogenation of carbon monoxide into paraffins having melting points between 40° and 80° C.

By far the greatest part of the normally solid hydrocarbons formed by the catalytic hydrogenation of carbon monoxide has more than 30 carbon atoms in the molecule corresponding to a boiling temperature 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. For the carbon monoxide hydrogenation effected with iron catalysts, the average number of carbon atoms of this hard paraffin ranges between about 45 and 50.

Hard paraffin has a setting point of about 90–100° C. as measured with a rotating thermometer, and penetration numbers of about 1. It finds use to a small extent for hardening slab paraffin and increasing the pour point thereof. The use of the major quantities of the hard paraffin is very restricted. The use of hard paraffins in the production of polishing waxes and shoe polishes presents difficulties, for example, due to their relatively poor oil-absorbability and insufficient retention power. Moreover, the pastes prepared with the addition of larger quantities of hard paraffin have little temperature-resistance, i. e., the hardness of the pastes are insufficient even at temperatures of as low as about 30° C. For the electrical industries the hard paraffin is too brittle and has too high a contraction, although the electrical properties are satisfactory. In spite of its high setting point, the hard paraffin is hardly suitable for paper impregnation, due to its extreme brittleness. It can, therefore, not be used as a blending component for slab paraffin with the same success as microcrystalline petroleum waxes.

For this reason, in the past hard paraffin was separated into fractions of different melting points by extraction with solvents. Paraffin 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 for fabricating precipitators, and for paper impregnation.

The discontinuously operating solvent extraction of hard paraffin is extremely complicated and also very costly, due to the large circulating quantities of solvent. A further disadvantage of this processing method consists in that the extract fractions utilize only a relatively small part of the hard paraffin. The remaining extraction residue is even more brittle than hard paraffin, and, therefore, still less suited for use on a large scale.

No commercially suitable processes have been known up to the present which permit the separation of hard paraffin by distillation into fractions of different melting points and different properties. The usual vacuum distillation only permits a fractionation up to a temperature, recalculated to normal pressure, of about 460° C. By this process, hard paraffin can only be recovered as a residual fraction. Although statements are contained in the literature on molecular distillations of hard paraffin carried out on a laboratory scale and permitting the obtaining of hydrocarbons boiling above 460° C. as distillate fractions, processes of this kind are completely unsuited for a commercial processing of hard paraffin.

One object of this invention is a process for converting hard paraffins into paraffins preferably melting between about 40 and 80° C. without the above-mentioned difficulties and in an extremely simple manner. This, and still further objects, will become apparent from the following description:

In accordance with the invention, the starting hard paraffins obtained from the catalytic hydrogenation of carbon monoxide are passed through a heating zone and thermally treated in this zone. The heating zone is preferably defined by a tubular system. The paraffins are passed through the zone so that they have a residence time of about 3 to 20 and preferably 6 to 15 minutes in the zone. The heating in the zone is effected to a temperature of about 390 to 450 and preferably 420 to 450° C. while the pressure is maintained at atmospheric pressure or pressures up to 20 kilograms per square centimeter.

After the treatment in the heating zone, gasoline and diesel oil hydrocarbons formed, boiling up to about 340° C., are distilled off in a first distillation zone, as, for example, in a distilling column operated under about atmospheric pressure. After the distilling off of this fraction boiling up to about 340° C., the distillation residue from the first distillation zone is distilled under reduced pressure of about 1 to 3 millimeters mercury absolute in a second distillation zone. The fraction of the material boiling between about 340 to 550° C. is distilled off in this second distillation zone, while the fraction boiling above about 550° C. is retained as distillation residue. The distillation in the second distillation zone is effected by depressurizing the hot distillation residue from the first distillation zone to thereby utilize its heat content. The paraffins having a melting point between about 40 and 80° C. are recovered from the distillate from the second distillation zone, while the distillation residue is preferably recycled to the process, as, for example, by being mixed with fresh hard paraffins to be passed through the heating zone. In this manner, 10–60% of fresh hard wax may be mixed with 90–40% of residues which remain in the vacuum distillation, i. e., in the second distillation.

The equipment diagrammatically shown in Fig. 1 may be used for carrying out this process on a commercial scale.

The hard paraffin to be processed is admitted through line **1**. The molten hard paraffin is forced by pump **2** through the tubular coil **3** which is located within the furnace **4** where it is heated to the temperatures required in accordance with the invention. After a sufficiently long residence time, the heated hydrocarbon mixture passes through line **5** into the column **6** which is operated at about normal atmospheric pressure. The constituents to be distilled off are led off through line **7** while the bottom products are passed through line **8** and into a vacuum distillation section which comprises the two columns **9** and **10**. The evaporated portions are led off from the top of the columns through lines **11** and **12**. The bottom product from column **9** passes through line **13** and into column **10** where it is further heated under a sufficient vacuum.

The bottom product of column **10** is led off through line **14** and, by means of pump **15**, passed through line **16** and admixed to the entering hard paraffin at a point before the furnace **4**.

The dimensions of the lines and distilling columns required are adapted to the capacity intended of the unit,

it being possible to use commercially known installations as a pattern.

The distillate obtained under vacuum in the second distillation zone may then be separated in the known manner with the usual commercial equipment into the particular fractions desired, such as into fractions of 340–460° C. and above 460° C. with the fraction boiling above 460° C. remaining as the residue. The individual fractions can be freed from oil-containing portions in the conventional manner by means of extractive de-oiling processes, or, if necessary or desired, by sweating processes. It is possible in this manner to obtain oil-free paraffins having the particular melting points desired. It is of advantage if the fractions, prior to the de-oiling, are hydrogenated in the conventional manner, such as with nickel catalysts at temperatures of about 250° C. By this measure, an increased yield of oil-free paraffins is obtained.

A further separation by distillation of the distillate boiling between about 340° and 550° C. may possibly be dispensed with. In this case, the over-all fraction, preferably after hydrogenation, is separated into paraffins having melting points of, for example, about 70° C., about 50–60° C., and about 40–45° C., and an oily fraction by subjecting it to a stage-wise de-oiling at decreasing temperatures such as at temperatures of between 20 and 0° C. The principle of this working method may be seen, for example, from German Patent No. 850,044.

It is also possible, however, to separate the entire vacuum distillate by a solvent extraction at increasing temperatures effected in the conventional manner, such as with heptane or other low-boiling solvents. In this extraction, the low-melting portions are obtained at first and the high-melting portions at last.

It is also possible to subject the reaction product obtained in the first distillation zone under normal pressure to an extraction with hydrocarbons or other solvents with the elimination of the vacuum distillation and to recover the different paraffins at increasing extraction temperatures. This working method, however, sacrifices a substantial advantage of the process of the invention, i. e., the elimination of the complicated separation by extraction.

The process of the invention may also be carried out with particular advantage in depressurizing the reaction product after the first distillation stage, in two or more series-connected vacuum columns operating with decreasing absolute pressure. In this manner, several distillates are directly obtained rather than a single distillate, and the necessity of a subsequent separation by distillation is eliminated, a simple de-oiling of the different vacuum distillates being sufficient.

An increased yield of valuable paraffins having melting points of between 60 and 80° C. is obtained by passing the hard paraffin first through a tubular system heated to 370–410° C. with the residence periods being expediently between 6 and 15 minutes. The paraffin is then passed through a normal pressure distilling column and one or several vacuum distilling columns in the manner described above. The distillation residue boiling above about 550° C. is then passed through a second tubular system which is heated to temperatures of between 410 and 450° C. and preferably between 420 and 430° C. with the residence times in this tubular system being expediently 6–15 minutes. The reaction product from the second tubular system is then processed in the same subsequent distilling columns together with the reaction product obtained from the first tubular system.

This embodiment of the process of the invention may be realized by means of the arrangement of apparatus shown in Fig. 2.

The molten hard paraffin is admitted through line **17** and forced by means of pump **18** through a tubular coil **19** which is located within the furnace **20** where it is heated to the temperature required. After a sufficiently long residence time, the heated hydrocarbon mixture passes through line **21** and into the column **22** operated under normal atmospheric pressure. The overhead products from this column are withdrawn through line **23** while the bottom product passes through line **24** to the vacuum distillation section comprising the two columns **25** and **26** which are connected by line **27**. The overhead products from the vacuum distillation section are withdrawn through lines **28** and **29** while the bottom product of column **26**, by means of line **30**, pump **31**, and line **32**, is forced through a tubular coil **33** which is also located in furnace **20**. After the passage through line **33**, the heated bottom product is returned into the process cycle through line **21**.

With this arrangement, a further embodiment of the process may be carried out with not only the hard paraffin, with with all of the hydrocarbons of the catalytic carbon monoxide hydrogenation boiling above approximately 340° C. being charged. Also, in this case the feed product boiling above 340° C. is passed through the first tubular system maintained at somewhat lower temperatures, and the residue from the last vacuum distillation is passed through the second tubular system maintained at higher temperatures. The processing of the reaction products is effected with the same subsequent distillation equipment.

It is also possible, of course, to adjust the initial boiling point of the residue from the last vacuum distillation to temperatures lower than about 550° C. such as 480 or 500° C. Thus, for example, all of the hydrocarbons boiling in excess of 500° C. are returned to the heater system. In this case, the reaction product contains less paraffins having melting points of 60–80° C. and more paraffins having melting points of between 40° and 60° C.

The process of the invention is commercially operated without any difficulty. A formation of undesirable residual products or of carbon causing obstructions of the apparatus does not occur. It is possible with the process of the invention to convert all of the hard paraffin into valuable paraffins having melting points of about 40–80° C. with the yield being about 70–80%, and with 80–90% of these paraffins being particularly valuable, due to their melting point ranging between about 70 and 75° C.

It is already known to thermally crack products from the carbon monoxide hydrogenation boiling above 450° C. to produce therefrom fractions boiling between 320 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 paraffins having melting points of about 45–60° C. is very low and paraffins having melting points in excess of 60° C. cannot be obtained at all.

It has also been suggested to treat hard paraffins from the carbon monoxide hydrogenation at 400–450° C. until the hard paraffin has turned into salve-like products similar to jelly. In this method, the treatment is effected for 2–18 hours. In contrast to this process, the process of the invention yields no jelly-like products at all, but solid, oil-free paraffins.

The process of the invention makes possible the conversion of hard paraffin from the catalytic carbon monoxide hydrogenation into high yields of paraffins melting between about 40 and 80° C., and preferably into paraffins having melting points of 60–80° C., which may widely be used in the production of polishing waxes and shoe polishes, in electrical engineering and in paper impregnation. Moreover, the paraffins produced in accordance with the invention and having melting points of about 70° C. are suitable for the manufacture of candles. Particularly heat-resistant candles for the tropics with excellent combustion properties can be produced from, for example, 1 part of paraffin having a melting

point of about 68–75° C., and, for example, 1 part of paraffin having a melting point of about 56–62° C.

The process of the invention processes the hard paraffins from the catalytic hydrogenation of carbon monoxide, which previously had little use, into valuable, almost unlimitedly saleable products. This is of particular importance, since by far the greatest part of the normally solid paraffin hydrocarbons from the catalytic carbon monoxide hydrogenation consists of hard paraffin, and the hitherto non-existing sales opportunities for this hard paraffin may be very disadvantageous for the Fischer-Tropsch synthesis from the economical point of view.

Example 1

A mixture consisting of 35 parts by weight of a hard paraffin boiling above 460° C., obtained by carbon monoxide hydrogenation with iron catalysts and having a 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 at 425° C. with the residence time within the tube being 8 minutes. After the passage through this tube, the gaseous reaction products formed in the tube and the liquid portions boiling up to about 340° C. were removed from the reaction product in a first distilling column. The residue was depressurized in a second distilling column operating under an absolute pressure of 1 mm. Hg and from which while utilizing the heat content of the reaction products, the reaction products boiling between 340 and 550° C. were drawn off overhead while the residue boiling above 550° C. was mixed with fresh hard paraffin and returned into the tube heated to 425° C.

In the vacuum column, the head temperature was 275° C. and the bottom temperature 375° C.

Based on the hard paraffin charged, the following reaction products were obtained:

Overhead products in the first distillation:

1.0 wt.-percent of gas
3.6 wt.-percent of a fraction boiling between 30 and 160° C.
10.7 wt.-percent of a fraction boiling between 160 and 340° C.

Overhead products in the second distillation:

84.7 wt.-percent of a fraction boiling between 340 and 550° C.

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

19.2 wt.-percent of a fraction boiling between 340 and 460° C.
65.5 wt.-percent of a fraction boiling between 460 and 550° C.

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

One part by weight of the fraction boiling between 340 and 460° C. was stirred up 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, 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 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 paraffin charged, was as follows:

9.7 percent by weight of slab paraffin
3.9 percent by weight of soft paraffin
5.6 percent by weight of extraction oil

One part by weight of the fraction 460–550° C. was stirred up at 80° C. with 3 parts by weight of the above-mentioned solvent mixture, cooled to 5° C., and filtered at this temperature. The filtration residue was washed with smal amounts of the solvent. After evaporation of the solvent, an oil-free paraffin 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 percent by weight of paraffin having a pour point of 73.5° C.
6.5 percent by weight of extraction oil.

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

59.0 wt.-percent of paraffin having a pour point of 73.5° C.
9.7 wt.-percent of slab paraffin having a pour point of 57.5° C.
3.9 wt.-percent of soft paraffin having a pour point of 44.0° C.
12.1 wt.-percent of extraction oil having a pour point of 26.0° C.
10.7 wt.-percent of a fraction boiling between 160–340° C.
3.6 wt.-percent of a fraction boiling between 30 and 160° C.
1.0 wt.-percent of gas.

Example 2

A mixture consisting of 30 parts of the hard paraffin 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. with the residence time being 6 minutes. After the passage through this tube the gas and the liquid portions boiling up to about 340° C. were separated in a first distilling column operating at normal pressure. The residue was depressurized in a second distilling column operating at an absolute pressure of 1 mm. Hg and from which, while utilizing the heat content of the reaction product, the reaction products boiling between 340 and 550° C. were withdrawn as distillate, while the residue boiling above 550° C. was returned into the heater tube.

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

In the first distillation:

0.8 wt.-percent of gas
3.8 wt.-percent of a fraction boiling between 30 and 160° C.
11.0 wt.-percent of a fraction boiling between 160 and 340° C.

In the second distillation:

84.4 wt.-percent of a fraction boiling between 340 and 550° C.

The fraction 340–550° C. was subsequently hydrogenated in the same manner as in Example 1 and then processed as follows:

One part by weight of the fraction 340–550° C. was stirred up 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 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. This 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 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 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 was as follows:

61.8 wt.-percent of paraffin having a pour point of 70° C.

6.9 wt.-percent of slab paraffin having a pour point of 52° C.

2.8 wt.-percent of soft paraffin having a pour point of 43° C.

12.9 wt.-percent of extraction oil having a pour point of 26° C.

11.0 wt.-percent of a fraction boiling between 160 and 340° C.

3.8 wt.-percent of a fraction boiling between 30 and 160° C.

0.8 wt.-percent of gas

Example 3

35 parts by weight of the hard paraffin mentioned in Example 1 were passed at normal pressure through a tube heated to 430° C. with the residence time being 6 minutes. Through a second tube, which was also heated to 430° C., there were passed 65 parts by weight of a distillate boiling above 550° C. with the residence time being 8 minutes. Both of the reaction products were combined, and then the gaseous and liquid reaction products boiling up to about 340° C. were separated in a first distilling column operating at normal pressure. The residue was depressurized 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 portions boiling between 340 and 460° C. were separated as distillate. The residue from the second distilling column was then depressurized in a third distilling column operating at an absolute pressure of 1 mm. Hg. At a bottom temperature of 375° C. and a head temperature of 290° C. the portions boiling between 460 and 550° C. 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 charged, the following overhead products were obtained:

In the first distillation:

0.5 wt.-percent of gas

2.2 wt.-percent of a fraction boiling between 30 and 160° C.

5.1 wt.-percent of a fraction boiling between 160 and 340° C.

In the second distillation:

12.2 wt.-percent of a fraction boiling between 340 and 460° C.

In the third distillation:

80.0 wt.-percent of a fraction boiling between 460 and 550° C.

The two fractions 340–460° C. and 460–550° C. were separately hydrogenated and de-oiled, as described in Example 1.

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

71.8 wt.-percent of paraffin having a pour point of 73.0° C.

5.7 wt.-percent of slab paraffin having a pour point of 56.0° C.

2.5 wt.-percent of soft paraffin having a pour point of 43.0° C.

12.2 wt.-percent of extraction oil having a pour point of 27.0° C.

5.1 wt.-percent of a fraction boiling between 160–340° C.

0.5 wt.-percent of gas.

We claim:

1. Process for the treatment of hard paraffins obtained by the catalytic hydrogenation of carbon monoxide, which comprises passing the hard paraffin through a heating zone with a residence time therein of about 3 to 20 minutes, while heating the paraffin in said zone to a temperature of about 390 to 450° C. at about normal pressure, thereafter distilling off the fraction boiling up to about 340° C. at about normal pressure in a first distillation zone, distilling off from the residue of the first distillation zone the fraction boiling between about 340 and 550° C. in a second distillation zone, at a reduced pressure of about 1 to 3 mm. Hg absolute while utilizing the heat content of said residue, admixing the second distillation zone residue boiling above about 500° C. with fresh hard paraffin, recycling said mixture to said first heating zone and recovering paraffins having a melting point between 40 and 80° C. from said last mentioned fraction.

2. Process according to claim 1, in which said heating zone is a substantially tubular-shaped zone.

3. Process according to claim 2, in which said heating in said heating zone is effected at a temperature of about 420 to 450° C.

4. Process according to claim 3, in which said hard paraffin is passed through said heating zone with a residence time therein of about 6 to 15 minutes.

5. Process according to claim 1, in which said distillation in said second zone is effected in at least two distillation stages with decreasing pressure in each subsequent stage and in which said paraffin is separately recovered from the distillation fraction from each stage.

6. Process according to claim 1, in which said distillation in said second distillation zone is effected, so that the distillation residue has an initial boiling point of not less than about 480° C.

7. Process according to claim 1, in which said fraction from said second distillation zone boiling between about 340 and 550° C. is hydrogenated prior to said recovery.

8. Process according to claim 7, in which said recovery is effected with distillation.

9. Process according to claim 7, in which said recovery is effected with selective solvent extraction.

10. Process according to claim 7, in which said recovery includes removing the oil from said fraction.

11. Process for the treatment of hard paraffins obtained by the catalytic hydrogenation of carbon monoxide, which comprises passing the hard paraffin through a heating zone with a residence time therein of about 3 to 20 minutes, while heating the paraffin in said zone to a temperature of about 370 to 410° C. at about normal pressure, thereafter distilling off the fraction boiling up to about 340° C. at about normal pressure in a first distillation zone, distilling off from the residue of the first

distillation zone the fraction boiling between about 340 to 550° C. in a second distillation zone, at a reduced pressure of about 1 to 3 mm. Hg absolute while utilizing the heat content of said residue, thereafter passing the distillation residue from said second distillation zone to a second separate heating zone and heating the same therein to a temperature between about 410 and 450° C., thereafter admixing the second distillation zone residue with the residue from said first mentioned heating zone, recycling said mixture to said first distillation zone and recovering paraffins having a melting point between 40 and 80° C. from said last mentioned fraction.

12. Process according to claim 11, in which the distillation residue from said second distillation zone is passed through said separate heating zone with the residence time of about 6 to 15 minutes and heated therein to a temperature of about 420 to 430° C.

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