PATENT SPECIFICATION

754,165

Date of Application and filing Complete Specification: May 18, 1954.
No. 14624/54.
Application made in Germany on May 23, 1953.
Application made in Germany on March 29, 1954.
Complete Specification Published: Aug. 1, 1956.

Index at acceptance:—**Classes 2(3), B1(E : H); and 96, B14D.**

COMPLETE SPECIFICATION

Process for the Production of Flexible Waxes

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a German Company, 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 production of flexible waxes having retention-improving properties.

It is possible by means of the catalytic hydrogenation of carbon monoxide to produce paraffin waxes of very high molecular weight which, in contrast to normal slab paraffin wax derived from petroleum, have considerably higher melting points and a substantially greater hardness. These properties are very desirable for wax-impregnated paper. Unfortunately, these so-called hard paraffin waxes obtained by means of the catalytic hydrogenation of carbon monoxide exhibit an extremely high brittleness which renders them suitable only to a very limited extent for the impregnation or coating of paper.

The flexibility of waxes may be determined in the following manner: A black paper strip is coated on both sides with a film 0·01 mm. in thickness of the paraffin wax to be tested. This corresponds to a quantity of about 15–20 grams of paraffin wax per square metre of paper, as is most commonly applied in practice. The application of the coating to the paper is effected in the laboratory by a process similar to that which is used in commercial manufacture. The coated paper strip is stretched from both sides over a rotating mandrel of about 4 mm. in diameter with the two ends moving several times vertically up and down. Depending on the brittleness of the paraffin wax used, the wax film on the paper will be ruptured to a more or less high degree. The measurement is effected photometrically by determining the brightening developing upon rupture of the film. With normal slab paraffin, the measurement gives, for example, a whiteness of 4. This value is best determined by means of a leucometer and signifies that only 4% of incident light is reflected while 96% is absorbed. Using hard paraffin waxes obtained by the catalytic hydrogenation of carbon monoxide results in values for the whiteness of about 20 because the film produced from hard paraffin wax is almost completely ruptured by the treatment described above.

When, in paper impregnation, coatings are to be obtained which are harder and more temperature-resistant than those obtainable with pure normal slab paraffin wax, the so-called "microcrystalline" waxes must generally be used. Waxes of this kind may be recovered from certain petroleum fractions by relatively costly processing methods. They have pour points of from 70°C. to 90°C. and penetration numbers at 20°C. which generally lie between 3 and 20. It is known that the corresponding values for normal slab paraffin wax lie between 50°C. and 55°C. and 10–20, respectively. When determining the flexibility by the method hereinbefore described, values of the whiteness of between 4 and 10 are obtained depending upon the type of wax tested.

Owing to their higher melting points, these microcrystalline waxes are more temperature-resistant than normal slab paraffin wax. This temperature-resistance may be determined by a simple method. For this purpose, a paper strip is used which is coated with the particular wax. In order to simulate actual service conditions, it is expedient to use the wax film which has previously been subjected to the flexibility test. If water of rising temperature is allowed to act from one side upon the paper strip which has been coated on both sides with wax, it can be observed that water drops will commence to pass through the paper at a certain temperature. This point will hereinafter be referred to as the "temperature-resistance point." The temperature-resistance point of microcrystalline waxes ranges between about 60°C. and 85°C. depending on the type of wax, while with normal slab paraffin wax water will pass through at a temperature of as low as 50°C.

Microcrystalline waxes are used in many cases in the production of floor and boot polishes to improve the retention properties of the pastes. They are extensively used at the present time as a substitute for the naturally occurring ozokerite. Hard paraffin wax from the catalytic hydrogenation of carbon monoxide does not exhibit these retention-improving properties to a sufficient degree.

It has now been found, according to the invention, that flexible and temperature-resistant waxes having retention-improving properties and corresponding to or comparable with the different types of microcrystalline waxes which are on the market, may be produced from hard paraffin wax derived from the catalytic hydrogenation of carbon monoxide, if more than 1 gram atom of chlorine and less than 5 gram atoms of chlorine, preferably between 2 and 4 gram atoms of chlorine, are added to one mole of hard paraffin wax and the reaction product is subsequently subjected to a dehydrochlorination.

It is known to chlorinate saturated hydrocarbons and subsequently to split off hydrogen chloride from the chlorination products in order to obtain hydrocarbons of the same general structure but having olefinic double bonds. This method of operation, however, involves in most cases the addition of far less than 1 gram atom of chlorine, for example, 0·5 gram atoms of chlorine, per mole of hydrocarbon in order to obtain as high as possible a proportion of mono-olefinic products. Hard paraffin wax, when subjected to this treatment, yields an olefinic product the flexibility of which is practically the same as that of the starting material. Also, the molecular weight of the product is only changed to a very small extent; it increases, for example, from 650 (starting material) to 680. If, in accordance with the invention, more than 1 gram atom and less than 5 gram atoms of chlorine and preferably from 2 to 4 gram atoms of chlorine are added to each mole of hydrocarbon, flexible waxes are obtained which correspond completely or very closely to the microcrystalline petroleum waxes and which are largely or completely free of the brittle properties of the hard paraffin wax. The molecular weights of products of this type range between 800 and 1000.

It is advantageous to hydrogenerate the reaction products after the dehydrochlorination. In this manner a substantial brightening or lightening of the colour is obtained. Moreover, the waxes lose much or all of their tackiness which is far too great, without detracting overmuch, if at all, from their flexibility.

The chlorination is effected in known manner by introducing chlorine into the molten, hard paraffin wax at temperatures little in excess of the melting point of the paraffin wax. The dehydrochlorination is effected by heating the chlorinated product for several hours at temperatures of between 280°C. and 320°C. and preferably at about 300°C. In so doing, it is of advantage to add small amounts of activated carbon. The hydrogenation is effected with the use of hydrogenation catalysts which are known *per se*, as, for example, nickel or cobalt catalysts. The hydrogenation may be carried out batchwise by the slurry process or continuously with fixed bed catalysts.

It is of advantage in some cases if relatively small amounts of constituents of low pour point, which generally amount to 5–15% of the total product, are separated by extraction from the reaction product after the dehydrochlorination and/or the hydrogenation. This extraction may be effected by treating the reaction product with two to five times its quantity of solvent at temperatures of 20°–40°C. The preferred solvents are hydrocarbons such, for example, as hexane or heptane, chlorinated hydrocarbons such, for example, as dichloroethane, oxygenated hydrocarbons such, for example, as methanol and acetone, or mixtures of different solvents. It is of advantage previously to disperse or atomize the paraffin wax to be extracted by spraying.

A hard paraffin wax obtained by the catalytic hydrogenation of carbon monoxide, that is, a hydrocarbon boiling above approximately 400°C. or 450°C., is advantageously used as the starting material for the process of the invention. Certain fractions of hard paraffin wax which may be recovered therefrom by distillation, crystallization or extraction processes are also suitable as starting material for the process of the invention. It is possible in this manner to prepare high melting point, flexible waxes having specific properties.

The microcrystalline petroleum waxes include products with setting points of 65°–70°C. which have a whiteness of 4. The flexibility of these waxes, however, is actually better than that, for example, of the normal slab paraffin wax or that of the microcrystalline waxes with pour points of about 75°C. It is also better than the flexibility of the waxes prepared in the manner described above although the whiteness in all these cases is about 4.

For the determination of the higher flexibility, strips of about 0·5 mm. in thickness, 50 mm. in length and 15 mm. in width are cut out from the wax to be tested. These strips are stretched over a round stick or mandrel of about 1 mm. diameter so that the ends of the strip show or extend vertically downward. A wax strip from petroleum waxes with setting points of 65°–70°C. will not break upon being subjected to this severe test, whereas strips of other waxes, when subjected to this treatment, will break or crack to a more or less large extent although they have also a whiteness of 4.

It is also possible by the process of the invention to obtain waxes which meet the severe flexibility test mentioned above in spite of having a much higher setting point than commercial microcrystalline waxes, if the reaction period of the dehydrochlorination is extended to more than 10 hours and preferably to 20 to 40 hours. With the dehydrochlorination effected within 3 to 5 hours, the olefinic product contains a residual content of chlorine of from about 0.1% to 0.3% which is somewhat further reduced in the subsequent hydrogenation. It is not possible by an extended dehydrochlorination period to achieve a substantial decrease in the residual content of chlorine. The extension of the dehydrochlorination period has, however, the surprising advantage that the quality of the reaction product undergoes a substantial improvement.

This mode of operation results in waxes which meet the aforesaid severe flexibility test just as well as microcrystalline petroleum waxes having a setting point of 65° to 70°C. In contrast to petroleum waxes, however, these waxes have setting points of 80°C. to 85°C. Thus, it is not only possible in accordance with the invention to attain the extremely good flexibility of some microcrystalline petroleum waxes but also to achieve, in addition, a substantial increase in the setting point. In this manner, products are obtained which are far superior to all flexible waxes hitherto on the market.

The improvement of the quality of these waxes becomes particularly apparent if the waxes are separated into individual fractions by extraction with solvents as, for example, with heptane or dichloroethane. For this purpose, the extraction is carried out at increasing temperatures in such a manner as first to extract 20% by weight of the material, then again 20% by weight thereof from the remaining extraction residue and so on, until the last fraction remains which, in the following Table, is designated "V. 80 to 100% by weight."

The extraction was applied in the same manner to a wax obtained in accordance with the invention with the use of both a short and a long dehydrochlorination period. As is to be noted from the whiteness values given in the Table, all of the individual fractions of the wax according to the invention exhibit low whiteness values, which corresponds to or indicates correspondingly good flexibilities. However, the last extract fractions of the wax prepared with a short dehydrochlorination period show considerably poorer whiteness values and consequently poorer flexibilities. The presence of fractions of poor flexibility in the waxes prepared with a short dehydrochlorination period cannot be ascertained in determining the flexibility of the total wax. The poor flexibility, however, of the last extract fractions is probably the reason why the wax prepared with a short dehydrochlorination period does not meet the severe flexibility test while the wax prepared with a long dehydrochlorination period entirely meets these conditions.

	Exact fraction	*Whiteness*	
		Rapid dehydrochlorination	Slow dehydrochlorination
I	0–20% by weight	4.0	4.0
II	20–40% „ „	4.3	4.1
III	40–60% „ „	4.8	4.3
IV	60–80% „ „	6.1	4.4
V	80–100% „ „	8.6	4.6

The waxes prepared in accordance with the invention have properties which correspond in every respect to those of the microcrystalline waxes on the market. The waxes may be used with particular advantage for paper impregnation. They may also be used, however, as a substitute for ozokerite because they have an extremely good retention effect, that is to say, even small portions effect a very considerable reduction of the solvent loss of pastes.

The process of the invention has the advantage that waxes which are equivalent in every respect to the so-called microcrystalline waxes obtained from petroleum may now be prepared from synthetic hydrocarbons. Moreover, the properties of these waxes may be varied within wide limits depending upon the reaction conditions chosen. Starting with the hard paraffin waxes derived from the catalytic hydrogenation of carbon monoxide which are readily available in large amounts, the process of the invention permits the production of substantially any desired type of wax in any quantity and in a relatively simple and cheap manner.

The invention is illustrated in the following examples.

Example 1

Hard paraffin wax derived from the catalytic hydrogenation of carbon monoxide and containing only hydrocarbons boiling above 460°C., have a setting point of 100°C. and a penetration number at 20°C. of 0.5, was chlorinated at 110°–120°C. with irradiation with actinic light and stirring until 1.5 gram atoms of chlorine had been absorbed per mole of hydrocarbon. The chlorinated product was mixed with 1% activated carbon and heated for 3 hours at 300°C. with stirring whilst small amounts of nitrogen were passed through the mixture. After removal of the active carbon by filtration, a pale yellow reaction product was obtained which had a setting point of 89°C. and a penetration number of 7·5. The determination of the flexibility effected in the same manner hereinbefore described in relation to the invention, resulted in a whiteness of 5. The temperature-resistance point was 75°C. The hard paraffin wax used as the starting material had a whiteness of 20 when subjected to the flexibility test.

Example 2

The finished product of Example 1 was stirred for 30 minutes at about 20°C. with twice its quantity of ethylene chloride and subsequently filtered. In addition to 10% of extract there was obtained a pale yellow extraction residue or raffinate which had a setting point of 91°C., a penetration number of 3, a whiteness of 6 as determined by the flexibility test, and a temperature-resistance point of 80°C.

Example 3

Hard paraffin wax of the type used in Example 1 was chlorinated until 2 gram atoms of chlorine per mole of hydrocarbon had been absorbed. After the dehydrochlorination which in this case was effected for 4 hours at about 300°C., a pale yellow product was obtained which has a setting point of 85°C., a penetration number of 17, a whiteness of 4 as determined by the flexibility test, and a temperature resistance point of 70°C.

Example 4

Hard paraffin wax of the type used in Example 1 was chlorinated until 2·5 gram atoms of chlorine per mole of hydrocarbon had been absorbed. After dehydrochlorination which was effected in the manner set forth in Example 3, a yellowish product was obtained which had a setting point of 82°C., a penetration number of 34, a whiteness of 4 as determined by the flexibility test, and a temperature resistance point of 65°C.

Example 5

Hard paraffin wax of the type used in Example 1 was chlorinated until 3 gram atoms of chlorine per mole of hydrocarbon had been absorbed. After dehydrochlorination which was effected for 5 hours at about 300°C., the reaction product was hydrogenated with hydrogen using a nickel catalyst. After removing the catalyst by filtration, a white reaction product was obtained which was subsequently stirred for 30 minutes at about 20°C. with twice its quantity of ethylene chloride. In addition to 14% extract there was obtained a product which has a setting point of 91°C., a penetration number of 3.5, a whiteness of 7 as determined by the flexibility test, and a temperature resistance point of 82°C.

Example 6

Hard paraffin wax of the type used in Example 1 was chlorinated until 4 gram atoms of chlorine per mole of hydrocarbon had been absorbed. After dehydrochlorination and subsequent hydrogenation effected in the manner set forth in Example 5, there was obtained a white reaction product which had a setting point of 85°C., a penetration number of 22, a whiteness of 4 as determined by the flexibility test, and a temperature resistance point of 65°C.

Example 7

A paste was prepared from 6 parts by weight of the hard paraffin wax used in Example 1, 24 parts by weight of slab paraffin wax having a setting point of 50°–52°C., and 70 parts by weight of a mixture of solvent naptha and turpentine. This paste was placed in an air conditioning box for free evaporation at 20°C. The retention number measured after 10 days was 30.

The retention number of a paste consisting of 4.8 parts by weight of the hard paraffin wax used in Example 1, 1.2 parts by weight of commercial ozokerite having a setting point of 70°C., 24 parts by weight of slab paraffin wax and 70 parts by weight of a mixture of solvent naphtha and turpentine amounted to 20 after 10 days.

When the commercial ozokerite in the paste was replaced by the finished product of Example 1, then this paste had a retention number of 12 after 10 days.

Example 8

Hard paraffin wax derived from the catalytic hydrogenation of carbon monoxide, containing only hydrocarbons boiling above about 450°C., having a setting point of 96°C., and a penetration number of 1·0 was chlorinated at 110°–120°C. with irradiation with actinic light and stirring until 3.5 gram atoms of chlorine had been absorbed per mole of hydrocarbon. The chlorinated product was mixed with 1% active carbon and heated for 40 hours at 300°C. with stirring whilst small amounts of nitrogen were passed through the mixture. After separating the solid constituents by filtration, a yellowish reaction product which contained 0.1% chlorine was obtained.

In a pressure-resistant vessel provided with a stirrer, the olefinic hydrocarbon mixture was hydrogenated with hydrogen for 3 hours at 200°–250°C. and at a pressure of 120–150 kg./square centimetre using a nickel catalyst. After having filtered off the catalyst, a pale yellow product which had a setting point of 83°C. was obtained.

A strip of 0.5 mm. in thickness, 50 mm. length and 15 mm. in width was cut out from the wax thus prepared. This strip of wax was bent over a round stick of 1 mm. diameter so that the two ends of the strip showed or extended vertically downward. No rupture of the wax strip could be observed.

What we claim is:

1. A process for the production of flexible waxes having retention-improving properties, which comprises chlorinating a hard paraffin wax derived from the catalytic hydrogenation of carbon monoxide in such manner as to introduce more than 1 gram-atom and less than 5 gram-atoms of chlorine per mole of hydrocarbon, and subjecting the chlorinated product to a dehydrochlorination.

2. A process according to claim 1, in which the product of dehydrochlorination is subjected to catalytic hydrogenation.

3. A process according to claim 1 or claim 2, in which from 2 to 4 gram-atoms of chlorine are introduced per mole.

4. A process according to any one of the preceding claims, in which the final product is subjected to solvent extraction for the removal of constituents of low pour point.

5. A process according to claim 4, in which the solvent used is a hydrocarbon, a chlorohydrocarbon, an oxygen-containing organic compound or a mixture thereof.

6. A process according to any one of the preceding claims, in which the reaction period for the dehydrochlorination is more than 10 hours.

7. A process according to any one of the preceding claims, in which the reaction period for the dehydrochlorination is from 20 to 40 hours.

8. A process according to any one of the preceding claims, in which the dehydrochlorination is effected by heating the chlorinated hard paraffin wax at a temperature within the range 280°–320°C. in the presence of activated carbon.

9. A process according to any one of the preceding claims, in which the hydrocarbons in the hard paraffin wax used as the initial material, have boiling points above 450°C.

10. A process for the production of a flexible wax from hard paraffin wax obtained as a product of the catalytic hydrogenation of carbon monoxide, comprising chlorination and subsequent dehydrochlorination substantially as hereinbefore described.

11. A process for the production of a flexible wax from hard paraffin wax obtained as a product of the catalytic hydrogenation of carbon monoxide, comprising the successive steps of chlorination, dehydrochlorination and hydrogenation substantially as hereinbefore described.

12. A process for the production of a flexible wax, substantially as hereinbefore described in any one of Examples 1, 2, 3, 4, 5, 6, and 8.

13. A flexible wax whenever obtained by the process claimed in any one of the preceding claims.

14. Paper coated or impregnated with the wax obtained by the process claimed in any one of claims 1 to 12.

15. A paste or polish containing a wax obtained by the process claimed in any one of claims 1 to 12.

EDWARD EVANS & CO.,
14–18 High Holborn, London, W.C.1.
Agents for the Applicants.

Belfast: Printed for Her Majesty's Stationery Office, by The Universities Press.—1956.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

PATENT SPECIFICATION

754,165

Date of Application and filing Complete Specification: May 18, 1954.
No. 14624/54.
Application made in Germany on May 23, 1953.
Application made in Germany on March 29, 1954.
Complete Specification Published: Aug. 1, 1956.

Index at acceptance:—**Classes 2(3), B1(E : H): and 96, B14D.**

COMPLETE SPECIFICATION

Process for the Production of Flexible Waxes

ERRATUM

SPECIFICATION NO. 754,165

Page 3, line 86, *for "Exact fraction" read "Extract fraction".*

THE PATENT OFFICE,
13th December, 1956

DB 40949/1(17)/3636 150 12/56 R

duce paraffin waxes of very high molecular weight which, in contrast to normal slab paraffin wax derived from petroleum, have considerably higher melting points and a substantially greater hardness. These properties are very desirable for wax-impregnated paper. Unfortunately, these so-called hard paraffin waxes obtained by means of the catalytic hydrogenation of carbon monoxide exhibit an extremely high brittleness which renders them suitable only to a very limited extent for the impregnation or coating of paper.

The flexibility of waxes may be determined in the following manner: A black paper strip is coated on both sides with a film 0·01 mm. in thickness of the paraffin wax to be tested. This corresponds to a quantity of about 15–20 grams of paraffin wax per square metre of paper, as is most commonly applied in practice. The application of the coating to the paper is effected in the laboratory by a process similar to that which is used in commercial manufacture. The coated paper strip is stretched from both sides over a rotating mandrel of about 4 mm. in diameter with the two ends moving several times vertically up and down. Depending on the brittleness of the paraffin wax used, the wax film on the paper will be ruptured to a more or less high degree. The measurement is effected photometrically by determining the brightening developing upon rupture of the more temperature-resistant than those obtainable with pure normal slab paraffin wax, the so-called "microcrystalline" waxes must generally be used. Waxes of this kind may be recovered from certain petroleum fractions by relatively costly processing methods. They have pour points of from 70°C. to 90°C. and penetration numbers at 20°C. which generally lie between 3 and 20. It is known that the corresponding values for normal slab paraffin wax lie between 50°C. and 55°C. and 10–20, respectively. When determining the flexibility by the method hereinbefore described, values of the whiteness of between 4 and 10 are obtained depending upon the type of wax tested.

Owing to their higher melting points, these microcrystalline waxes are more temperature-resistant than normal slab paraffin wax. This temperature-resistance may be determined by a simple method. For this purpose, a paper strip is used which is coated with the particular wax. In order to simulate actual service conditions, it is expedient to use the wax film which has previously been subjected to the flexibility test. If water of rising temperature is allowed to act from one side upon the paper strip which has been coated on both sides with wax, it can be observed that water drops will commence to pass through the paper at a certain temperature. This point will hereinafter be

[*Price 3s. 0d.*]