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COMPLETE SPECIFICATION

A process for the Synthesis of High Boiling Viscous Hydrocarbon Mixtures

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The invention relates to a process for the synthesis of mixtures of viscous hydrocarbons of high boiling point.

The catalytic hydrogenation of carbon monoxide may be effected with the use of finely-divided moving catalysts, the main or effective constituents of which are metals and/or metal oxides of the eighth group of the periodic system. The synthesis may be operated either by the "fluidized process" with the catalyst maintained in a dense, turbulent, suspended state, or with the use of pulverulent catalysts which are continuously passed through the reaction zone in suspension in the gas stream. The quantity of catalyst used in the fluidized process is, in general, 400—2000 grams of catalyst per litre of the fluidized catalyst layer, the particle size being generally above 0.25 mm. If the hydrogenation of carbon monoxide is carried out with pulverulent catalysts suspended in the synthesis gas, the quantity of catalyst is, in general, 15—300 grams per litre of synthesis gas. In the latter case, the particle size of the catalyst is generally somewhat smaller than in the fluidized process and lies, for example, in the range 0.04—0.25 mm.

The flow rate of the synthesis gas when working with finely-divided moving catalysts is dependent on the particle size of the catalyst and is, for example, 50—13000 centimetres per second or more. The synthesis temperatures lie between 180° C. and 400° C. The carbon monoxide to hydrogen ratio of the gases to be reacted may vary within wide limits and may range, for example, between 1:1 and 1:3. When using moving finely-divided catalysts, the synthesis gases are in general recycled, with the use of up to 10 or more volumes of recycle gas per volume of fresh gas. The conversion of carbon monoxide may be, for example, 70—80%, with gas contractions of approximately 35—40% being reached.

Finely divided catalysts used in the moving state for the hydrogenation of carbon monoxide contain in most cases iron and/or iron oxides as the main effective constituent. However, other metals and metal oxides of the eighth group of the periodic system, particularly cobalt and nickel, are also suitable for this purpose. The catalysts are advantageously activated by substantially non-reducible metal oxides such, for example, as alkali-metal oxides, silicic acid (silica), thorium oxide, manganese oxide, magnesium oxide, aluminium oxide, titanium oxide, and alkaline earth oxides. Moreover, the catalysts may contain suitable carrier materials such, for example, as kieselguhr, bleaching or fuller's earths, aluminium oxide or magnesium oxide.

Catalysts which are suitable for the hydrogenation of carbon monoxide carried out with moving catalyst masses may be prepared, for example, by the combustion of iron powder in a stream of oxygen, by fusing the iron oxides formed thereby, impregnating them with potassium compounds, crushing the mass to a suitable particle size and treating the granular mass with reducing gases. By another method, the catalyst has been prepared by mixing iron oxide with more than 2% of potassium carbonate, sintering the mixture at 1000° C., leaching the mass with water to bring the content of potassium carbonate into the range 1—2%, crushing the mass to a suitable particle size, and reducing the granulated catalyst in the conventional manner. Iron ores having a sufficiently high content of iron may also be used for the preparation of catalysts of this kind by melting the iron ores. In this case, the finished catalyst contains aluminium oxide, titanium oxide and silicic acid (silica) in addition to iron. Moreover, 1.2—1.4% of potassium oxide may be admixed therewith.

If gas mixtures containing carbon monoxide

[*Price 3s. 0d.*]

and hydrogen are reacted with finely divided moving catalysts of the eighth group of the periodic system and preferably with catalysts containing iron and/or iron oxide at superatmospheric pressures and preferably at gas pressures ranging between 10 and 30 kilograms per square centimetre and at temperatures which are sufficiently high to give conversions of more than 60—70%, then a smaller proportion of the synthesis products is obtained as dark brown to black liquid or paste-like masses of higher molecular weight, which may either be separated from the condensed synthesis products as a residue upon distillation or may be recovered in the working up and regeneration of the catalyst as, for example, by extraction with solvents or by means of steam. These products are of very mixed composition which is detrimental to profitable utilization. These products consist in part of aliphatic compounds, more or less having branched chains, in part of mono- or polynuclear cyclic compounds, in part of cyclic compounds having side chains. Moreover these compounds are highly unsaturated and contain oxygen, which is the cause of their dark colour.

It has now been found that mixtures of high boiling, viscous hydrocarbons may be obtained from these higher molecular weight products.

According to the invention, a process for the production of a mixture of viscous hydrocarbons of high boiling point from constituents boiling above 340° C. of the products containing aliphatic hydrocarbons, mononuclear and polynuclear compounds and obtained by contacting a gas containing carbon monoxide and hydrogen in synthesis proportions at superatmospheric pressure and at a temperature within the range 180°—400° C. with a finely-divided, moving catalyst the main constituent of which is a metal, and/or an oxide thereof, of the eighth group of the periodic system is characterised in that a fraction boiling above 340° C. is separated from the product and is hydrogenated with hydrogen in the presence of a hydrogenation catalyst.

According to the invention furthermore, a process for the synthesis of a mixture of viscous hydrocarbons of high boiling point comprises contacting a gas containing carbon monoxide and hydrogen in synthesis proportions at superatmospheric pressure and at a temperature within the range 180°—400° C. with a finely-divided, moving catalyst the main constituent of which is a metal, and/or an oxide thereof, of the eighth group of the periodic system to yield a synthesis product containing aliphatic hydrocarbons, mononuclear and polynuclear compounds, separating from the synthesis product a fraction boiling above 340° C. and hydrogenating the separated fraction with hydrogen in the presence of a hydrogenation catalyst at a pressure in the range 5—100 kilograms per square centimetre and at a temperature within the range 100°—300° C. in the presence of a hydrogenation catalyst, whereby the cyclic compounds in the fraction are partially decyclised and the oxygen-containing radicals and the unsaturated linkages are partially or completely eliminated.

The gas containing carbon monoxide and hydrogen is preferably contacted with the catalyst at a pressure within the range 10—30 kilograms per square centimetre and at a temperature within the range 250°—350° C.

The conversion of the gas mixtures containing carbon monoxide and hydrogen may be effected with the catalyst in a dense, turbulent, suspended bed by the fluidized process. However, pulverulent catalysts suspended in the synthesis gas may also be used by suspending 15—300 grams of a catalyst, of a particle size below 0.25 mm., per litre of synthesis gas.

The fraction boiling above 340° C. is preferably subjected to hydrogenation, with hydrogen or a gas mixture containing free hydrogen, at a partial pressure of hydrogen within the range 20—50 kg./sq.cm. and at a temperature which is advantageously within the range 230°—270° C.; hydrogenation at a partial pressure of hydrogen of about 30 kg./sq.cm. and at a temperature of about 250° C. has been found to be particularly effective.

The catalyst employed in the hydrogenation of the fraction boiling above 340° C., may contain a metal of the eighth group of the periodic system, and may advantageously be the catalyst used for the hydrogenation of the carbon monoxide. However, other known hydrogenation catalysts may also be used, a catalyst consisting largely or wholly of a mixture of nickel, magnesia and kieselguhr being particularly suitable. Other suitable hydrogenation catalysts include Raney nickel, molybdenum sulphide and tungsten sulphide.

The hydrogenation proceeds smoothly and results in products of light colour which may be easily separated into individual fractions by distillation or extraction processes.

It is of particular advantage if the synthesis products boiling above 340° C. are diluted, before the hydrogenation, with hydrocarbons containing from 4 to 15 carbon atoms in the molecule. The diluent preferably contains one or more C_4—C_8 hydrocarbons. In the hydrogenation, the partial pressure of hydrogen is preferably approximately 30 kilograms per square centimetre. Pure hydrogen or gas mixtures consisting of hydrogen and inert constituents such, for example, as nitrogen, are used as the hydrogenating gases. The hydrogenation conditions are advantageously adjusted in such a manner that the bi- and polycyclic compounds contained in the products boiling above 340° C. are split up into alkylated mono- and/or polycyclic hydrocarbons.

The hydrogenated products are freed by distillation from the constituents boiling up to 340° C. Before the distillation, the products

may be subjected to a low temperature cooling to separate the ceresin-like hydrocarbons. If the separation of the hydrogenated products is effected with solvents, the conventionally known extracting agents such, for example, as aliphatic or aromatic hydrocarbons or chlorination products thereof and/or mixtures thereof or liquefied gases, for example, liquid sulphur dioxide, may be used.

The invention is illustrated by the following examples:—

EXAMPLE 1

A product boiling above 340° C. of dark brown colour and prepared by the hydrogenation of carbon monoxide carried out at a gas pressure of approximately 17 kilograms per square centimetre and at a synthesis temperature of 325° C. with the use of a pulverulent iron catalyst suspended in the synthesis gas and with gas recycling, had the following characteristics:—

Iodine number - -	39.0
Neutralization number	1.3
Saponification number	10.9
Hydroxyl number -	2
Carbonyl number -	0
Molecular weight - -	371
Ash - - - - -	0.108%

1000 grams of this synthesis product were mixed with 50 grams of a catalyst which consisted of 61 parts of nickel, approximately 8 parts of magnesium oxide and 31 parts of kieselguhr. The mixture was treated in an autoclave provided with a stirrer for 4 hours at a temperature of 250° C. and at a pressure of 50 kilograms per square centimetre with a gas mixture which contained 75 parts by volume of hydrogen and 25 parts by volume of nitrogen. After the hydrogenation was finished, the catalyst was separated from the hydrocarbon mixture by filtration.

The liquid filtrate was light yellow in colour. By fractionation, 11.8% of hydrocarbons boiling up to 340° C. were separated therefrom. The residue boiling above 340° C. amounted to 88.2%. This residue was mixed at 60° C. with dichloroethane in a proportion of 1:4 and was then cooled to −25° C. By filtering the mixture at the low temperature, 23.5% of ceresin-like paraffinic hydrocarbons of low viscosity and an average pour point of approximately 50° C., and 76.5% of a lubricating oil of approximately 6° E, were obtained.

EXAMPLE 2

A product boiling above 343° C. of very dark brown colour and prepared by the hydrogenation of carbon monoxide at a pressure of approximately 17 kg./sq.cm. and at a temperature of 360° C. with the use of a pulverulent iron catalyst suspended in the synthesis gas, had the following characteristics:—

Iodine number - -	46.0
Neutralization number	1.0
Saponification number	26.5
Hydroxyl number -	8
Carbonyl number - -	4
Molecular weight - -	467
Ash - - - - -	0.144%

1000 grams of this synthesis product were mixed with 4000 cc. of a saturated C_7 fraction from the carbon monoxide hydrogenation. 100 grams of a pulverulent catalyst consisting of 63 parts of nickel, 7 parts of magnesium oxide and 30 parts of kieselguhr were added to the mixture. The mixture was then treated for 4 hours at a total pressure of 60 kilograms per square centimetre equal to a hydrogen pressure of approximately 30 kilograms per square centimetre and at a temperature of 250° C. with a gas mixture which contained 25 volumes of nitrogen and 75 volumes of hydrogen. After the treatment with the gas mixture, the reaction mixture was cooled and separated from the catalyst by filtration. The catalyst was rewashed with the C_7 fraction used as the diluent.

The liquid filtrate was almost colourless and showed a blue-green fluorescence. It was cooled to −10° C. and the solid hydrocarbon mixture which separated upon cooling was removed at the same temperature from the liquid constituents by filtration. The filtrate so obtained was subjected to distillation at atmospheric pressure to remove the C_7 hydrocarbons added before the hydrogenation and then subjected to a vacuum distillation to separate the constituents boiling between 100° C. and 340° C.

After the separation of the C_7 hydrocarbon, approximately 100 grams of a ceresin-like wax were obtained having a pour point of 73° C. and a penetration number of 12. The distillate boiling between 100° C. and 340° C. had a density of 0.776 (20° C.), a refractive index of 1.4325 (n^{20}_D) and a molecular weight of 177. It consisted of approximately 40% naphthenic and 60% paraffinic hydrocarbons. It could be separated by distillation into 50 grams of gasoline and 150 grams of diesel oil.

The residue boiling above 340° C. comprised 700 grams of a very light yellow, viscous oil having the following characteristics:—

Iodine number - -	0.
Neutralization number	0
Saponification number	0
Hydroxyl number -	0
Carbonyl number -	0
Density at 20° C. -	0.873
Refractive index n^{20}_D	1.4800
Viscosity at 50° C. -	6.10° E=213 SSU.
Viscosity index - -	104
Flash point - - -	212°C
Conradson carbon test	0.27%
Molecular weight -	470.

The lubricating properties of this oil were good.

What we claim is:—

1. A process for the production of a mixture of viscous hydrocarbons of high boiling point from constituents boiling above 340° C. of the products containing aliphatic hydrocarbons, mononuclear and polynuclear compounds and obtained by contacting a gas containing carbon monoxide and hydrogen in synthesis proportions at superatmospheric pressure and at a temperature within the range 180°—400° C. with a finely-divided, moving catalyst the main constituent of which is a metal, and/or an oxide thereof, of the eighth group of the periodic system, characterised in that a fraction boiling above 340° C. is separated from the product and is hydrogenated with hydrogen in the presence of a hydrogenation catalyst.

2. A process for the synthesis of a mixture of viscous hydrocarbons of high boiling point, which comprises contacting a gas containing carbon monoxide and hydrogen in synthesis proportions at superatmospheric pressure and at a temperature within the range 180°—400° C. with a finely-divided, moving catalyst the main constituent of which is a metal, and/or an oxide thereof, of the eighth group of the periodic system, to yield a synthesis product containing aliphatic hydrocarbons, mononuclear and polynuclear compounds, separating from the synthesis product a fraction boiling above 340° C. and hydrogenating the separated fraction with hydrogen at a pressure in the range 5—100 kilograms per square centimetre and at a temperature within the range 100°—300° C., in the presence of a hydrogenation catalyst, whereby the cyclic compounds in the fraction are partially decyclised and the oxyen-containing radicals and the unsaturated linkages are partially or completely eliminated.

3. A process according to claim 2, in which the gas containing carbon monoxide and hydrogen is contacted with the catalyst at a pressure within the range 10—30 kilograms per square centimeter.

4. A process according to claim 2 or claim 3, in which the gas containing carbon monoxide and hydrogen is contacted with the catalyst at a temperature within the range 250°—350° C.

5. A process according to any one of the preceding claims, in which the separated fraction is treated with hydrogen or with gases containing free hydrogen at a temperature within the range 230°—270° C., the partial pressure of the hydrogen being within the range 20—50 kilograms per square centimetre.

6. A process according to claim 5, in which the partial pressure of hydrogen is about 30 kilograms per square centimetre and the temperature is about 250° C.

7. A process according to any one of the preceding claims, in which the separated fraction is hydrogenated in the presence of a catalyst containing a metal of the eighth group of the periodic system.

8. A process according to any one of claims 2 to 4, in which the catalyst with which the gas mixture containing carbon monoxide and hydrogen is contacted, is in a dense, turbulent, fluidised state.

9. A process according to any one of claims 2 to 4, in which the catalyst is in the form of a moving bed or mass.

10. A process according to claim 9, in which the catalyst is in suspension in, and is carried along by, the gas mixture.

11. A process according to claim 10 in which the gas mixture contains from 15 to 300 grams of catalyst per litre, the particle size of the catalyst being less than 0.25 mm.

12. A process according to any one of claims 2 to 4 and 8 to 11, in which the metal of the eighth group in the catalyst contacted with the mixture of carbon monoxide and hydrogen, is iron, cobalt or nickel.

13. A process according to claim 12, in which the metal is iron.

14. A process according to any one of the preceding claims, in which the separated fraction is hydrogenated in the presence of the catalyst contacted with the mixture of carbon monoxide and hydrogen.

15. A process according to any one of claims 1 to 12, in which the separated fraction is hydrogenated in the presence of a nickel-containing catalyst.

16. A process according to claim 15, in which the catalyst consists largely or wholly of a mixture of nickel, magnesium oxide and kieselguhr.

17. A process according to any one of the preceding claims, in which the separated fraction is hydrogenated in the presence of a diluent.

18. A process according to claim 17, in which the diluent consists of a hydrocarbon or hydrocarbons containing from 4 to 15 carbon atoms in the molecule.

19. A process according to claim 18, in which the diluent consists of one or more C_7—C_9 hydrocarbons.

20. A process according to any one of the preceding claims, in which the hydrogenation of the separated fraction is effected to decompose all or part of the di- and polycyclic compounds into alkylated mono- and/or polycyclic hydrocarbons.

21. A process according to any one of the preceding claims, in which the separated fraction is, after the hydrogenation, separated into ceresin-like paraffinic hydrocarbons of low viscosity and a lubricating oil of higher viscosity by a physical process, such as fractional distillation, extraction, fractional concentration by cooling, or the like.

22. A process for the production of mixtures of viscous hydrocarbons of high boiling point

suitable for use as, or in the production of, a lubricating oil, substantially as described with reference to Example 1 or Example 2.

23. Mixtures of viscous hydrocarbons of high boiling point, whenever produced by the process of any preceding claim.

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