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METHOD OF PRODUCING LUBRICATING OILS

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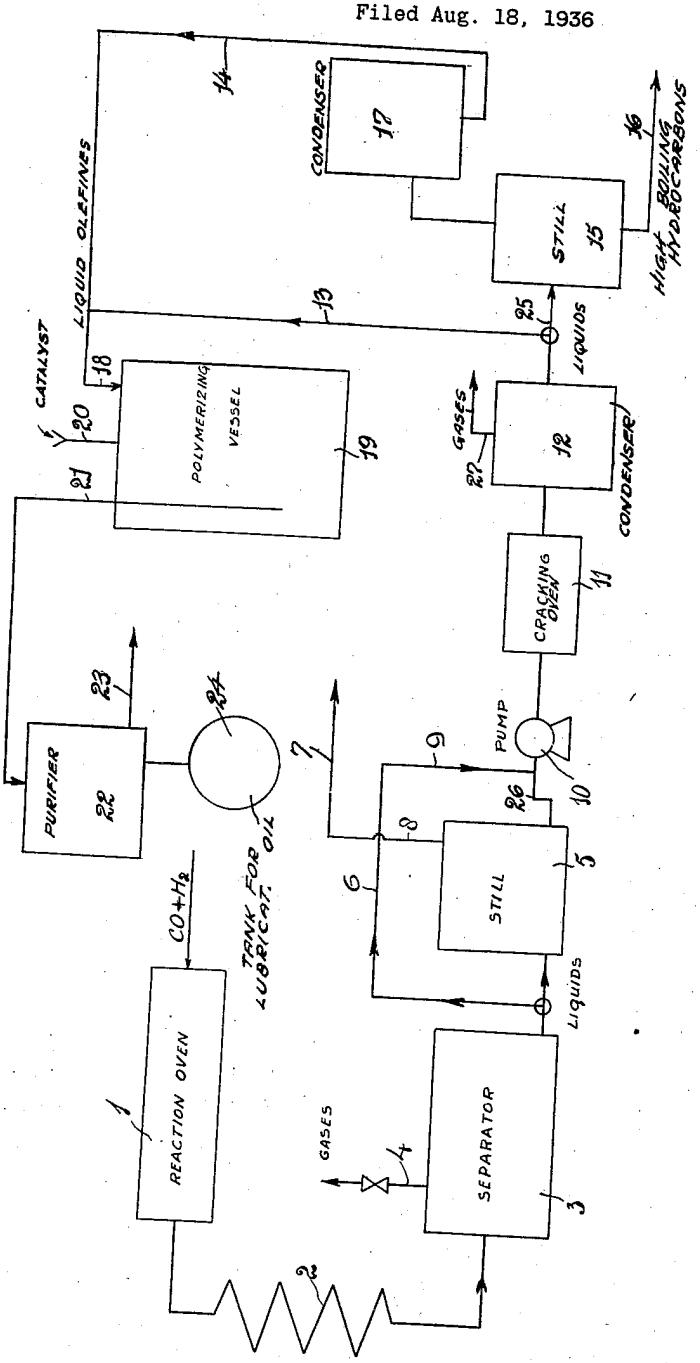

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METHOD OF PRODUCING LUBRICATING OILS

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Our invention relates to lubricating oils, and more particularly to an improved method of artificially producing the same.

It is an object of our invention to produce lubricating oils having a low solidifying point.

It is another object of our invention to produce lubricating oils of substantially constant viscosity at different temperatures.

It is still a further object of our invention to provide, in the production of lubricating oils, for a repeated use of a catalyst and more especially aluminium chloride in the conversion of successive charges of the starting products.

It is a particular object of our invention to improve the general economy of the artificial production of lubricating oils.

In the production of lubricating oils it has already been suggested to condense petroleum distillates having a high content of unsaturated hydrocarbons at normal or elevated temperatures in the presence of a catalyst such as aluminium chloride. After separation of those constituents which have not been converted, and after the usual finishing treatment, lubricating oils having a low solidifying point were obtained.

It has further been suggested to employ cracking products as starting material. Thus for example the hydrocarbons obtained by cracking petroleum oils and other hydrocarbon mixtures have been suggested for this purpose.

In order to obtain a satisfactory yield of lubricating oils, which satisfy all technical requirements and which, in particular possess a low solidifying point and display but a slight variation of viscosity at varying temperatures, the prior art has taught to start from a mixture of hydrocarbons, which consists, entirely or preponderantly, of aliphatic hydrocarbons, which are solid at normal temperature.

We have now found, that when the products of the hydrogenation of carbon monoxide are used as starting materials in the production of lubricating oils, one is not restricted to hydrocarbon mixtures, which consist entirely or preponderantly of aliphatic hydrocarbons which are solid at normal temperature. On the contrary, lower boiling hydrocarbon mixtures can be used, including all constituents boiling above 150° C.

According to the present invention the fractions boiling above 150° C. of the hydrocarbon mixtures obtained in the catalytic conversion of mixtures of carbon monoxide and hydrogen are used as starting materials in the production of lubricating oils by cracking and subsequent polymerization of the mixtures obtained in the cracking process. Besides a polymerization of similar hydrocarbon molecules to larger ones also condensation of different hydrocarbon molecules takes place, and the terms "polymerization" and "condensation" as used in the present specification are not intended to exclude each other. The polymerization or condensation of the hydrocarbon mixtures obtained in the cracking process, which are rich in unsaturated compounds, is carried through in the usual manner with the aid of a polymerizing agent or catalyst which contains a metal halide such as aluminium chloride. A considerably increased yield of valuable lubricating oils as compared with the amount of cracking products used is thus obtained. Moreover the lubricating oil products thus produced display, apart from a low solidifying point, only slight variations of their viscosity under varying conditions of temperature. Furthermore the method according to the present invention also permits of a repeated and more frequent use of the aluminium chloride for the conversion of successive charges of cracking products in a manner such that hereby also a considerable saving of condensing agents is obtained. In this manner a considerably better economy of the method of recovering lubricating oils is obtained.

According to the present invention we may for example convert, in a manner disclosed for instance in the specification of United States Patent 1,746,464 to Franz Fischer and Hans Tropsch, a mixture of carbon monoxide and hydrogen at normal pressure and but moderately elevated temperatures into liquid hydrocarbons in the presence of suitable catalysts. The fractions boiling above 150° C. of the conversion products which, as shown in an article by Fischer, Koch and Wiedeking in "Brennstoff-Chemie" 1934, pp. 229–233, comprise a substantial portion boiling directly above 150° C., i. e., between about 150° and about 200° C., are subsequently exposed to a cracking process, the cracking conditions being so chosen, that a hydrocarbon mixture rich in unsaturated hydrocarbons results. The process of cracking the above identified fractions of the liquid hydrocarbons recovered from carbon monoxide and hydrogen is preferably carried through at moderate pressure, e. g., at 12 to 15 atm. and at temperatures ranging substantially between 450° C. and 550° C. without using a catalyst. The cracking products obtained in the cracking process, which have a high content of unsaturated hydrocarbons, are treated in a known manner, either totally or partly, e. g., after distillation of of certain fractions, with anhydrous aluminium

chloride or some other condensing agent. By such condensation and polymerization we obtain viscous oils, which display extraordinarily favorable lubricating properties. The products thus obtained are distinguished by a quite extraordinarily low dependency of their viscosity from the temperature, i. e., an extraordinarily favorable value of the viscosity apex, and on the other hand by so low a solidifying point, that the synthetic lubricating oils thus produced will act as lubricants even at low outside or operating temperatures. We found that when starting from the constituents of the cracking products boiling up to 200° C., particularly useful lubricating oils were obtained, which are distinguished primarily by their remarkably low solidifying point. Thus, for example, lubricating oils were obtained, which display a value of the viscosity apex, calculated according to Ubbelohde (cf. "Zur Viskosimetrie", published in 1936 by S. Hirzel, Leipzig, Germany), of from 1.75 to 1.9, an absolute viscosity of from 12 to 22° Engler at 50° C., corresponding to 419–750 Saybolt seconds at 122° F. and a solidifying point of from −32° C. to −20° C. Particularly remarkable is also the extraordinarily high tensile strength of the oil film heavily leaded in bearings.

This property together with their low solidifying point renders the new lubricating oil obtained according to the present invention particularly suitable for many purposes. Also their tendency of resinification and carbon formation during the coking of the lubricating oils obtained according to the invention, are not in any respect less favorable than those of the very best lubricating oils now on the market.

The amount of condensation agents, which are required in each individual operation, for the polymerization and condensation of the cracking products obtained in the manner above referred to, lies within the usual limits. It has, however, been found, that the starting material employed according to the present invention is particularly suited for a repeated use of the condensing agent in the condensation of new charges of hydrocarbons. Therefore the layer containing the condensing agent which remains over when separating the products of conversion is used repeatedly for like reactions of condensation. Preferably, whenever the already used condensing agent is put to renewed use, the temperature of condensation is increased correspondingly. This step results in a considerable saving of the condensing agent required in the execution of the method according to the invention; no detrimental effect of a repeated use of the condensing agent on the quality of the lubricating oils has been observed. Thus, for example, the catalyst used in the first charge was re-used in the condensation reaction eight times, each time with a new charge, without being exhausted after such repeated use. While, according to the methods hitherto known of producing synthetic lubricating oils, one part aluminium chloride was required per 6 to 10 parts of the lubricating oil recovered, with the present method of producing lubricating oils the amount of catalyst required is reduced to at least one tenth.

This saving of condensing agent could by no means be expected. On the contrary, one was rather inclined to fear that just the hydrocarbon mixtures obtained in the cracking process, owing to their content of constituents tending toward resinification, would render the catalyst inoperative within a very short time. In the practice of the present invention the contrary has been established.

After the separation of the lubricating oils, the hydrocarbons not converted in the condensation of the liquid cracking products can be exposed to a renewed cracking process and to further treatment.

In carrying out the present invention we may for instance proceed as follows:

Example 1

A gas mixture containing one part by volume of carbon monoxide and two parts hydrogen, which had been freed from sulfur compounds, is passed at about 180° C. and under normal pressure in contact with a cobalt catalyst. After cooling, liquid hydrocarbons separate out from the reaction gas obtained, which is now passed over active carbon in order to extract therefrom the lower boiling benzines, which have remained in the gaseous phase. The constituents boiling above 150° C. of the liquid hydrocarbons thus obtained are cracked at a pressure of 8 atm. and at a temperature of 493° C. From the cracking products thus obtained a fraction distilling up to 200° C. is separated, which at 20° C. has a density of 0.702. This distillate is reacted with 5% aluminium chloride in an agitator, while cooling it at −20° C. during 48 hours. The reaction product freed from the contact mass by washing with water is distilled in vacuo, after having been dried and treated with fuller's earth. There are obtained per 100 parts of the cracking products used 53 parts of oil, from which, after the separation of refrigerator oil, 43 parts of an extraordinarily valuable lubricating oil possessing the above-mentioned properties are obtained.

The cobalt catalyst mentioned above may for instance consist of cobalt-thorium-oxide deposited on kieselguhr and obtained by adding kieselguhr to a solution of a cobalt-thorium-salt and precipitating this solution with an aqueous solution of carbonate of soda. The precipitate obtained is filtered from the solution and dried and, before the operation, reduced with hydrogen at 300–350° C. The catalyst thus prepared may for instance consist of 37.3 percent cobalt, 6.7 per cent thorium oxide and 56.0 per cent kieselguhr. Instead of a cobalt catalyst a nickel catalyst may be used which may for instance be obtained by suspending purified kieselguhr in water, adding to the suspension a mixture of nickel nitrate and thorium nitrate, which contains 12 per cent thorium, calculated as metal, in relation to the nickel, precipitating with a soda solution, and sucking off the precipitate thus obtained, washing and drying it and subsequently reducing this catalyst at 350° C. in a current of hydrogen. Any other catalyst known to promote the reduction of a mixture of carbon monoxide and hydrogen under the formation of hydrocarbons may be used instead of the catalysts specified above.

Example 2

A cracking benzine produced in the manner described in Example 1 is distilled off up to 230° C. It has a density of 0.715 at 20° C. and a content of unsaturated hydrocarbons amounting to 39.2 per cent by volume, determined according to Kattwinkel's method as described in "Brennstoff-Chemie", vol. 8 (1927), page 353. This fraction serves as starting product for the condensation process. 100 parts of this starting product are polymerized during 24 hours in the presence of 5 parts of fresh aluminium chloride at 20° C. in an agitator. The product of reaction is separated

from the liquid layer containing the catalyst, which layer is again used in the conversion of a similar amount of freshly charged cracking products. The materials are allowed to react for 24 hours at a temperature of 55°. The oils recovered are separated in a similar manner from the liquid layer containing the catalyst. This catalyst layer is then caused again to react with new cracking products for 24 hours at 90° C. In a similar manner the process is repeated at 120° C., at 145° C., and at 170° C., always one and the same quantity of catalyst or condensing agent being used. The total process results in a yield of lubricating oils amounting to 52% of the 600 parts of cracking product used, the following amounts being recovered from the individual charges:

From the first charge 42 parts;
From the second charge 52 parts;
From the third charge 55 parts;
From the fourth charge 58 parts;
From the fifth charge 57 parts, and
From the sixth charge 50 parts.

The oils thus produced possess the same extraordinarily favorable characteristics, which were referred to above in detail.

The drawing illustrates the mode of operation as explained with reference to the examples. 1 is a reaction oven containing a suitable catalyst for the conversion of the CO and H_2 introduced into this oven. The products of reaction, after being cooled in the cooler 2, are introduced into the separator 3, from which the gases may escape through pipe and valve 4, while lower boiling benzines may be extracted for instance with activated carbon. The liquid hydrocarbons thus obtained which boil above 150° C., are led through the pipes 6 and 9 to the pump 10, which forces them into the cracking oven 11. The separation of the constituents boiling above 150° C. may also be carried out in the still 5; the undesired products are allowed to escape through pipe 8 at 7, while the constituents boiling above 150° C. flow through pipe 26 to the pump 10. The gaseous cracked products leaving the oven 11 are introduced into the condenser 12, from which those parts which remain gaseous, escape at 27, while the condensed parts are caused to flow either through pipes 13 and 18 to the polymerizing vessel 19 or through pipe 25 to the still 15 in which they are distilled. The hydrocarbon materials boiling above 200 or 230° C. are withdrawn at 16, while the cracking products which boil up to 200 or 230° C., are condensed in the condenser 17 and pass in liquid state through pipes 14 and 18 into the polymerizing vessel 19 which is provided with the feed pipe 20 for the catalyst. The polymerized products are withdrawn through pipe 21 and are led to a purifier 22 from which the undesired products are withdrawn at 23, while the lubricating oil formed enters the tank 24.

Numerous advantages are obtained with the method of producing lubricating oils according to the present invention. The percentage of valuable lubricating oils recovered from a predetermined quantity of cracking products is greatly increased. The lubricating oils obtained possess a remarkably low solidifying point and quite particularly show a great constancy of the viscosity at varying temperatures. The condensing agent such as aluminium chloride can be reused a great number of times in the conversion of subsequent charges of cracking products. Summarizing the above advantages of the new method, the economy of the production of valuable lubricating oils is greatly enhanced.

Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

We claim:

1. The method of producing lubricating oils from conversion products of the hydrogenation of carbon monoxide, comprising the steps of subjecting the fractions, which are liquid at room temperature, boil above 150° C. and comprise a substantial portion boiling directly above 150° C., of hydrocarbon mixtures obtained in the catalytic conversion of mixtures of carbon monoxide and hydrogen, to a cracking treatment such as to yield a mixture of hydrocarbons having a high content of unsaturated hydrocarbons, and subsequently polymerizing said last-named mixture in the presence of a polymerizing agent or catalyst containing a metal halide.

2. The method of producing lubricating oils from conversion products of the hydrogenation of carbon monoxide, comprising the steps of subjecting the fractions which are liquid at room temperature, boil above 150° C. and comprise a substantial portion boiling directly above 150° C., of hydrocarbon mixtures obtained in the catalytic conversion of mixtures of carbon monoxide and hydrogen, to a cracking treatment at temperatures ranging between about 450 and 550° C. and at a pressure ranging between about 8 and 15 atmospheres, and subsequently polymerizing, in the presence of a polymerizing agent or catalyst containing a metal halide, the mixtures obtained in this treatment of hydrocarbons rich in unsaturated compounds.

3. The method of claim 2, wherein aluminium chloride is employed as the polymerizing agent.

4. The method of claim 2, wherein the fractions boiling to about 200° C. of the hydrocarbon mixtures rich in unsaturated compounds obtained in the cracking process are subjected to polymerization.

5. The method of claim 2, wherein the polymerizing agents used in the polymerization of the liquid cracking products are reused repeatedly in a number of successive polymerization operations.

6. The method of claim 2, wherein the polymerizing agents used in the polymerization of the liquid cracking products are reused repeatedly in a number of successive polymerization operations, a higher polymerizing temperature being maintained in each subsequent operation.

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