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PROCESS OF IMPROVING LUBRICATING OILS

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Our invention relates to lubricating oils and more particularly to means for increasing the stability of lubricating oils when exposed to high temperatures.

It is an object of our invention to provide means for the production, from unsaturated hydrocarbons, such as olefines, or from hydrocarbon mixtures containing such unsaturated hydrocarbons, of lubricating oils of high value, the viscosity qualities of which are not affected at all at high temperatures or not to the extent as in the case of the hitherto known synthetically produced lubricating oils.

Other objects of our invention will appear as the specification proceeds.

It is known that lubricating oils of high value can be produced by polymerizing, in the presence of metal halides, olefines and more particularly mono-olefines, or mixtures containing such compounds, which may for instance be obtained by the cracking, under well defined conditions, of liquid or solid hydrocarbons prepared by catalytically hydrogenizing carbon monoxide according to the well known method of Fischer and Tropsch.

We have now found that these highly qualified lubricating oils can be further improved, more particularly with regard to the stability which these oils possess at high temperatures. Generally the stability of lubricating oils can be influenced only with great difficulty. We succeed however in considerably improving this stability by acting, under vigorous stirring, at a high temperature with small quantities of aluminium chloride or aluminium chloride double compounds on such lubricating oils, either in the course of their formation, or on the finished lubricating oils. Other polymerizing agents such as zinc chloride or boron fluoride may also be employed, instead of aluminium chloride, in quantities which are adjusted to the lower or higher polymerizing capacity of the individual agent.

In our new process we treat the lubricating oil at a temperature substantially not below 140° C., since at lower temperatures only a small effect can be attained. Moreover the aluminium chloride layer formed in a treatment carried out at a lower temperature can only be separated with difficulty from the layer which contains the lubricating oil, while at the same time the period of time required for a treatment at such a low temperature is extremely long even for the production of a small effect. Temperatures sub-

stantially above 140° C. must therefore be employed when practicing our invention.

Example I

A lubricating oil having a viscosity of 20° E. (Engler) at 50° C. and obtained by the polymerization of a benzine rich in olefines was heated 10 hours to 160° C. in the presence of 2.5% aluminium chloride. After the reaction had come to an end, the layer which contained the lubricating oil was separated from the contact layer; from the raw lubricating oil there were distilled in an oil bath under an absolute pressure of 5 mms. mercury column those splitting or cracking products which were formed in the treatment of the starting lubricating oil with aluminium chloride and which distilled over up to 250° C. (measured in the oil bath). There remained as distillation residue, with a yield of 75%, a lubricating oil having a viscosity of 20° E. at 50° C. and a flash point of 268° C.

Temperatures in the neighborhood of 180° C. proved to be especially satisfactory in this process.

Example II

The starting lubricating oil mentioned in Example I may for instance be treated four hours at approximately 180° C. in the presence of about 1% aluminium chloride. The viscosity qualities of the oil thus treated are not materially affected even by high temperatures.

When treating a lubricating oil in accordance with our invention, smaller or larger quantities of cracking or splitting products are formed which must be separated from the lubricating oil. Under the conditions mentioned in Example II approximately 80% of the starting lubricating oil were for instance converted into a thermally stable oil, while approximately 20% of the starting lubricating oil were converted into splitting or cracking products of petroleum-like character.

Generally spoken, by employing larger quantities of aluminium chloride for increasing the stability of the oil similar effects can be obtained already by operating at somewhat lower temperatures and with shorter times of reaction. It is then possible to compensate to a certain extent a variation of one of the operating conditions by correspondingly varying another condition.

If temperatures higher than 180° C. are employed, thermally stable oils can also be obtained, but in that case the period of time during which the lubricating oils are acted on with the poly-

merizing agents must be materially shortened.

The following tests show more in detail, how the time of reaction may be selected in dependency on the operating temperature in the process of our invention. The starting lubricating oil was the synthetically produced oil mentioned in Example I and having a viscosity of 20° E. at 50° C. This oil, with an addition of 2.5% aluminium chloride to each sample, was subjected to an aftertreatment which at 160°, 180°, 200°, 220° and 240° C. lasted 10 hours, 4 hours, one hour, 10 minutes and 2 minutes, respectively. The aluminium chloride added to the individual samples of the lubricating oil formed reaction products with some parts of the lubricating oil, which settled in the reaction vessel and formed a lower layer. The upper layer containing the lubricating oil was separated from the lower layer and distilled in a vacuum of 5 mms. mercury column up to a temperature (of the oil bath) of 250° C., when the low boiling cracking products formed during the treatment with aluminium chloride distilled over. The remainder of lubricating oil was determined in per cents by weight, calculated on the quantity of the starting lubricating oil employed. The results obtained are compiled in the following table:

Quantity of AlCl ₃ employed	Operating temperature	Time of treatment	Yield of lubricating oil in per cent by weight	Viscosity of the improved lubricating oil obtained
	°C.			
2.5%-----	160	10 hours	75	20° E. at 50° C.
2.5%-----	180	4 hours	75	20° E. at 50° C.
2.5%-----	200	1 hour	75	20° E. at 50° C.
2.5%-----	220	10 min.	75	20° E. at 50° C.
2.5%-----	240	2 min.	73	13° E. at 50° C.

(20° E. and 13° E. correspond to 699 and 454 Saybolt seconds, respectively).

The above shows that the lubricating oil improved by the treatment in accordance with our invention had a viscosity which practically corresponded to the viscosity of the starting lubricating oil. Only by the treatment at 240° C. the viscosity of the improved lubricating oil had dropped from 20° E. to 13° E. at 50° C., which drop resulted from the fact that the synthetic oil was already cracked to a rather great extent at this relatively high temperature.

We therefore do not as a rule employ temperatures above 240° C., since at higher temperatures, even with short times of operation, the oil is cracked to such an extent, that oils of lower viscosity than the starting lubricating oil are obtained. We prefer operating at temperatures between 140 and 240° C. and more particularly between 180 and 240° C.

Instead of aluminium chloride we may also employ, in the treatment or aftertreatment of the lubricating oils according to our invention, double compounds of aluminium chloride, for instance with the mono-olefines which are contained in the cracking benzines formed by cracking the products of the hydrogenation of carbon oxides. However double compounds formed by a combination of gaseous olefines with aluminium chloride may be used also. In consequence of the more gentle action of these double compounds larger quantities must be employed than when using aluminium chloride. In the aftertreatment of a lubricating oil having a viscosity of approximately 20° E. at 50° C. there are for instance required about 10% of an aluminium chloride double compound when operating at 180° C.

Even if aluminium chloride double compounds are used, we are enabled to vary the temperature and time of reaction on principle as described above so as to compensate a lower temperature by a more extended time of reaction.

In any case we prefer to thoroughly stir the lubricating oil under treatment.

Synthetic lubricating oils, when treated in accordance with our invention, possess an improved heat stability. In order to test the thermic stability of lubricating oils, we heat such oil several hours at a high temperature, for instance above 300° C. In this test we prefer to heat the oil through a metal block, while the lubricating oil is enclosed in a glass vessel. In order to exclude the action of oxygen, the lubricating oil is tested in inert surroundings, for instance in a nitrogen atmosphere. After this heating treatment has come to an end, the flash point and the viscosity of the oils are determined. Parallel tests carried out with the oils in engines showed that lubricating oils which in the above described test proved to be thermally stable, show a quite particularly increased stability also when used in the engine, while at the same time behaving favorably with regard to the engine.

When heated the same length of time to temperatures above 300° C., a lubricating oil treated in accordance with our invention showed after several hours a decrease of the flash point of 3 to 10° C. and a decrease in the viscosity amounting to about 5%. The same lubricating oil, when not treated in accordance with our invention with aluminium chloride or an aluminium chloride double compound or another polymerizing agent, when tested with regard to its thermal stability under the same testing conditions showed a decrease of the flash point of about 70° and a drop of the viscosity to about 60% of the starting viscosity, determined at 50° C. This comparison shows clearly the excellent influence of the treatment according to this invention on the thermal stability of the lubricating oils.

Our new process may be applied with particular advantage to the lubricating oils which can be obtained according to the methods disclosed in the copending applications for U. S. Letters Patent Serial No. 96,594, now U. S. Patent 2,172,441, filed August 18, 1936, by Herbert Goethel and Heinrich Tramm, Serial No. 115,950, now U. S. Patent 2,187,704, filed December 15, 1936, by Nikolaus Geiser and Herbert Goethel, Serial No. 115,951, filed December 15, 1936, by Heinrich Tramm, Serial No. 165,566, now U. S. Patent 2,206,391, filed September 24, 1937, by Carl Clar and Herbert Goethel and Serial No. 168,794, now U. S. Patent 2,199,200, filed October 13, 1937, by Herbert Goethel, Paul Schaller, and Heinrich Tramm. The process according to the present invention may also be combined with the processes disclosed in any of these copending applications.

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. In the production of lubricating oils by catalytically hydrogenating carbon monoxide, cracking the non-gaseous hydrocarbons thus obtained and converting the cracking products by means of a polymerizing agent which contains a substantial proportion of aluminium chloride into lubricating oils, the step of heating such a lubri-

cating oil in the presence of a polymerizing agent to a temperature ranging between about 140 and 240° C., while excluding additions of halogenated hydrocarbons.

2. In the production of lubricating oils by catalytically hydrogenating carbon monoxide, cracking the non-gaseous hydrocarbons thus obtained and converting the cracking products by means of a polymerizing agent containing a substantial proportion of aluminium chloride into lubricating oils, the step of heating such lubricating oil in the presence of a polymerizing agent at a temperature ranging between about 140° and 240° C. while excluding additions of halogenated hydrocarbons, said last named polymerizing agent being an aluminium chloride double compound formed in the polymerization of unsaturated hydrocarbons with aluminium chloride and being employed in an amount exceeding about 1% of the oil under treatment.

3. The process of improving lubricating oils obtained by catalytically hydrogenating carbon monoxide, cracking the non-gaseous hydrocarbons thus obtained and converting the cracking products by means of a polymerizing agent containing a substantial proportion of aluminium

chloride into lubricating oils, which comprises separating such lubricating oil from the other products formed in said polymerization and thereafter heating it in the presence of a small amount of a polymerizing agent to a temperature ranging between about 140° and 240° C. while excluding additions of halogenated hydrocarbons.

4. The process of improving lubricating oils obtained by catalytically hydrogenating carbon monoxide, cracking the non-gaseous hydrocarbons thus obtained and converting the cracking products by means of a polymerizing agent containing a substantial proportion of aluminium chloride into lubricating oils, which comprises heating such lubricating oil in the presence of a small quantity, exceeding about 1% of the oil under treatment, of a polymerizing agent to a temperature ranging between about 140° and 240° C. while excluding additions of halogenated hydrocarbons, and separating the low boiling cracking products thus produced from the lubricating oil formed.

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