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COMPLETE SPECIFICATION

Process for the Continuous Production of Synthetic Lubricating Oil

We, RUHRCHEMIE AKTIENGESELLSCAFT, 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 synthesis of lubricating oil.

It is known to produce synthetic lubricating oils by the polymerisation of normally liquid olefins or aliphatic hydrocarbon mixtures containing such olefins in the presence of aluminium chloride. It has also been proposed to effect the polymerisation not only with aluminium chloride alone but with the simultaneous use of the addition compound or compounds of aluminium chloride and hydrocarbon, the so-called "contact oil", formed from aluminium chloride and olefinic hydrocarbons in previous polymerisation batches.

Lubricating oil syntheses of this kind have been carried out hitherto on a commercial scale in batchwise operation in vessels provided with stirrers or agitators. The reaction times have in general been between 10 and 20 hours so that relatively large reaction spaces have been required and consequently only a low space-time yield was obtained. Attempts are being made at present to improve the space-time yield by carrying out the process in continuous rather than in batch operation. However, when the lubricating oil synthesis is carried out in continuous operation in a vessel provided with stirring means whereby intimate mixing of the reaction mixture takes place in all directions in the vessel, only poor conversions are obtained and the reaction product obtained still contains relatively large proportions of unconverted olefins. While the yield could be improved by connecting several of the vessels in series, this would entail a considerable outlay for plant and heavy power or running costs without bringing about a substantially increased space-time yield.

It has now been found, according to the invention, that the polymerisation of normally liquid aliphatic olefinic hydrocarbons for the purpose of producing synthetic lubricating oils may be carried out in continuous operation and with surprisingly good space-time yields by passing the olefinic hydrocarbons together with a contact oil upwardly through a substantially vertical reaction zone, the contact oil comprising or consisting of addition compounds of aluminium chloride with a hydrocarbon or hydrocarbons, and intimately admixing the contact oil with the olefinic hydrocarbons in a horizontal direction in the reaction zone in such manner as substantially to avoid an intermixing in the vertical direction, whereby the olefinic hydrocarbons at any level of the reaction zone are substantially at the same stage of polymerisation. Thereafter, the contact oil is separated from the reaction products and it may be recycled to the reaction zone.

The reaction zone is advantageously provided as a cylindrical vessel or tube of a length which is great relatively to its internal diameter, for example, the length of the vessel or tube may be about 100 times that of its internal diameter. Two or more of the vertical reaction zones may be used if necessary or desired, the several reaction zones being connected in series.

The reaction product is removed from the upper part of the reaction vessel and passed into one or more settling vessels where it is allowed to separate into an upper layer and a lower, contact oil layer. When two or more reaction vessels or zones are used in series, the reaction product from each reaction vessel or zone is preferably so separated by settling.

The stirring means used to admix the contact oil with the olefinic hydrocarbons in a horizontal direction whilst substantially avoiding intermixing in the vertical direction, may be constructed in various ways. For example, it may consist of a stirrer which extends over the total length of the reaction vessel and on the axis of which horizontal plates are secured at short distances apart. For the further intermixing of the liquid in the horizontal direction, small blade stirrers may be provided between the individual plates. However, any other type

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Price 25p

of stirrer may be used which maintains the direction of motion required. The use of a stirring mean which consists of a rotating cylindrical body of a length not substantially less than that of the reaction zone and provided axially of the reaction zone, has been found to be of particular advantage. The distance between the surface of the stirrer and the tube wall is dependent on the diameter of the reaction tube. For example, for reaction tubes of about 20 mm diameter it is preferably less than 5 mm. The number of revolutions may be varied. However, it is in general of the order of 100 r.p.m. If necessary or desired, the rotating cylinder may also be utilised for the control of temperature. This kind of stirring effects an extremely fine distribution of the contact oil and the olefinic starting material, in a substantially horizontal direction while almost completely avoiding an intermixing in the vertical direction. Therefore, the motion of the reactants in the vertical direction occurs substantially only to the extent occasioned by the rate of feed. As a result, the reaction mixture which flows off from the top of the vessel or zone, is not commingled with unreacted starting material. Therefore, the space-time yield obtained with the method in accordance with the invention can be said to be a particularly good one as compared with the conventional batch operation. The residence time of the olefinic hydrocarbons and contact oil in the reaction zone or zones may be from 3 to 15 hours. However, a residence time of not more than 6 hours has generally been found to be sufficient for the complete conversion of the olefinic starting material, whereas periods of 10—20 hours have hitherto been required for the same conversion.

Upon settling, the reaction product separates into two layers. The upper layer contains the polymerisation products formed and is worked up by distillation in known manner after the removal of residual aluminium chloride compounds contained therein and after neutralisation. The lower layer consists of the contact oil which is recycled to the reaction vessel. A portion of the contact oil circulating in this manner is continuously or intermittently withdrawn and replaced by freshly prepared contact oil. Thus in contrast to the conventional processes, no aluminium chloride is charged to the reaction vessel in the new method of carrying out the synthesis. Nevertheless, the circulating contact oil used as the catalyst possesses a practically unlimited lifetime. To maintain its activity, only a very small portion of the circulating contact oil is withdrawn and replaced by freshly prepared contact oil.

Fresh contact oil may be produced by reacting a small portion of the olefinic starting material with aluminium chloride outside the reaction zone. This may be effected, for example, by passing the olefinic material over a sufficiently deep and stationary bed of aluminium chloride at temperatures of 40°—100° C., or by stirring or admixing the olefinic material with aluminium chloride. The addition of a small amount of active contact oil is frequently of advantage in that it tends to accelerate the contact oil forming reaction.

It has further been found that it is possible, for the production of active contact oil, to avoid the use of aluminium chloride and to use instead the cheaper, metallic aluminium. In this case, the production of the contact oil is effected by reacting a small portion of the olefinic starting material with hydrogen chloride and aluminium chips or granulated aluminium at temperatures of 40°—100° C. and preferably of 50°—70° C. It is of advantage to charge, at the beginning, a small amount of finished contact oil in order to initiate the reaction. In a preferred manner of carrying out this reaction, use is made of vertical reaction towers or tubes which are filled with metallic aluminium in the form, for example, of chips, and which are provided with a suitable device for feeding the aluminium. The olefinic starting material is trickled downwardly over the aluminium chips whilst the hydrogen chloride is passed upwardly into the tubes. It may also be advantageous to provide the reaction tube with a siphon outlet so that it is completely filled with hydrocarbon or contact oil. In this case, longer times of action and increasing rates of conversion into contact oil are obtained with a single pass. The reaction mixture obtained at the lower outlet of the reaction tube separates, upon settling, into a lower layer of the contact oil which has been produced and an upper layer. This upper layer contains saturated starting hydrocarbons, polymerisation products and cracked products. In addition, gaseous cracked products, chiefly C_1 hydrocarbons, are formed. A part of the olefinic starting material is thereby lost for the lubricating oil synthesis with this method of producing the contact oil.

It was a great step forward, therefore, when it was found that one is not dependent on the use of the olefinic starting material for the production of active contact oil but that the less valuable by-products of the lubricating oil synthesis may be used for this purpose. By-products of this kind are present, on the one hand, in the saturated hydrocarbon portion obtained when the olefinic feedstock is a mixture of olefins and saturated hydrocarbons, and, moreover, in the so-called lubricating oil first runnings which distil over prior to the lubricating oil proper, which first runnings consist of polymers which boil between the upper boiling point of the hydrocarbons and approximately 340° C. and is not yet of a pronounced lubricating oil character. These two hydrocarbon fractions give, when passed over aluminium, for example, aluminium chips, together with hydrogen chloride at temperatures of 40°—100° C. and preferably of 50°—70° C., surprisingly good yields of contact oil of still higher activity than that obtained from olefinic starting material, aluminium and hydrogen chloride. It is of advantage for starting the reaction simultaneously to pass in a small amount of finished contact oil. Although a part of the hydrocarbons charged is in this case also split up or decomposed, the yield of lubricating oil is not lower since no valuable olefins are consumed.

The contact oil produced from aluminium, hydrogen chloride and the by-products of the lubricating oil synthesis which consist substantially of saturated hydrocarbons, is the preferred contact oil for use in the process of the invention. Moreover, its production is effected in an extremely simple manner.

It is possible, if desired, to use aluminium chloride instead of aluminium and hydrogen chloride for the production of contact oil from saturated hydrocarbons of the lubricating oil synthesis or lubricating oil first-runnings. However, it is also necessary in this case to pass in a small amount of hydrogen chloride. The addition of small amounts of finished contact oil may also be of advantage. In other respects, this method producing the contact oil is carried out in substantially the same manner as that used in the production of contact oil from olefinic starting material and aluminium chloride.

The fresh contact oil produced from aluminium chloride and hydrogen chloride contains some dissolved hydrogen chloride. It is not necessary to remove this hydrogen chloride since it even acts as an accelerator of the reaction in the lubricating oil synthesis.

The use of freshly prepared contact oil for maintaining the activity of the contact oil circulating in the synthesis has several advantages over the method of maintaining the activity of the contact oil by the addition of solid aluminium chloride formerly practised in batch operation. When adding solid aluminium chloride, an exact dosing is not very simple. Moreover, special measures with respect to the apparatus must be taken in order to feed the aluminium chloride in comminuted form, and to protect it against moisture while being fed. These difficulties are removed by the present process. The addition of the fresh contact oil into the contact oil cycle of the synthesis can be controlled very accurately and without trouble or difficulty.

By virtue of the good space-time yield, one single reaction vessel will generally be sufficient for the complete conversion. However, it may be useful or advantageous in some instances to provide several of such reaction vessels in series as, for example, when the conversion is to be effected at different temperature levels as hereinafter described. In this case, it is possible to operate in such manner that the reaction product, without passing through an intermediate settling vessel, is transferred from one reactor directly into the next reactor, whilst each reactor is maintained at a different temperature level. It is also possible, however, to provide each of these reactors with a separate contact oil cycle and to maintain the activity of the contact oil in each individual cycle by passing the fresh contact oil into the last stage, whilst the corresponding amount of contact oil withdrawn from the last stage is used for freshening or maintaining the activity of the contact oil in the preceding stage, and so on. In this manner, an increase in contact oil activity in the direction of the flow of the olefinic material is obtained in addition to the increase in temperature.

This manner of carrying out the process of the invention is illustrated by way of example in the accompanying drawing. The olefin-containing starting material is passed from a storage vessel 1 through line 2 to the bottom of the first reactor 3. The reactor 3 is provided with a cylindrical stirred 4 and a water jacket 5 5 for temperature control. Contact oil is introduced into the reactor 3 through line 6. The reaction product passes through line 7 to a settling vessel 8. The contact oil which settles as the lower layer in vessel 8, is recycled through line 6 to the reactor 3. For the freshening or maintaining the activity of the circular-contact oil, a small amount of contact oil is drawn from the contact oil cycle of the second reactor 12 through line 9 and an equal volume of contact oil is removed from the entire system through line 10.

The upper layer from the settling vessel 8 is then passed through line 11 to the bottom of the reactor 12. This reactor, in a similar manner to the first reactor 3, is provided with a cylindrical stirrer 13, a water jacket 14, and a settling vessel 15 downstream of the reactor. The contact oil is recycled via line 16. For the freshening of the contact oil, a small amount of contact oil is drawn from the contact oil cycle of the third reactor through line 17, an equal volume being withdrawn and passed through line 9 into the contact oil cycle of the first reactor 3.

The upper layer from settling vessel 15 passes through line 18 into the third reactor 19 which is likewise provided with a cylindrical stirrer 20, a water jacket 21 and a settling vessel 22. The contact oil is recycled through line 23. The upper layer from the settling vessel 22 is withdrawn through line 24 as the final product of the synthesis for further processing. A part of the circulating contact oil is withdrawn through line 17 and passed into the contact oil cycle of the second reactor 12 and is replaced by freshly prepared contact oil from the storage vessel 25 through line 26.

A certain increase in the quantity of the contact oil occurs in the oil synthesis. In order to maintain the contact oil cycles at a constant volume, these excess quantities of contact oil are withdrawn through lines 10, 27 and 28.

Aliphatic olefinic hydrocarbons or hydrocarbon mixtures containing aliphatic olefinic hydrocarbons which are liquid at normal temperature are used as the starting material for the lubricating oil synthesis. It is not necessary to set an upper limit on the olefin content since difficulties caused by undesirable increases of temperature need not be feared owing to the extremely good heat removal when carrying out the oil synthesis in accordance with the invention, in contrast to the former batch synthesis. The olefin-containing hydrocarbon mixtures may, for example, be obtained from the products of the thermal cracking of well refined petroleum paraffin hydrocarbons or waxes or from the products of the hydrogenation of carbon monoxide. It is also possible, however, to process directly with the same success olefin-containing primary products of suitable boiling range obtained by the hydrogenation of carbon monoxide, those obtained by the recycle synthesis over an iron catalyst being particularly suitable. As with the cracked olefins, these primary olefins have a high content (approximately 60—70%) of terminal or alpha olefins which, as is known, yield oils having particularly good viscosity characteristics. However, for the removal of the oxygenated compounds contained therein, the primary olefins must be given a pre-treatment which may be effected in known manner by passing them over aluminium oxide at temperatures of approximately 350° C. Moreover, the quality of the synthetic lubricating oils obtained is dependent on the boiling range of the olefin mixture used. The viscosity and temperature behaviour or characteristics of the oils as well as the resistance to heat and oxidation become better with increase in the number of carbon atoms in the olefin molecules. However the pour point of the oils generally restricts the use of olefinic hydrocarbons to those containing less than 18 carbon atoms in the molecule.

The lubricating oil synthesis is preferably effected at a temperature within the range 15°—110° C., and, advantageously from 1% to 8% of the contact oil in the synthesis is replaced per hour by unused or freshly prepared contact oil.

The reaction conditions in the lubricating oil synthesis may be varied within wide limits. The method of operation according to the invention, allows such variations to be carried out more easily than is the case in batch synthesis, particularly owing to the better control the heat or convection currents. Furthermore, the process of the invention offers a number of further possibilities of variations such, for example, as the maintenance of the countercurrent principle with respect to the flow of the fresh contact oil, wherein the fresh contact oil is fed to the last of a series of reaction zones and an equivalent amount of contact oil is passed from the last reaction zone to the preceding reaction zone, and so on. It is possible, therefore, by the process of the invention, to produce oils of various viscosities.

In most cases the synthesis will be carried out in such a manner that, after having distilled off the saturated hydrocarbons, the lubricating oil first runnings and, if necessary or desired, small quantities of a spindle oil, a residual oil is obtained which, at an absolute pressure of 5 mm Hg, boils above 200° C. and has a viscosity at 50° C. of 8—12° Engler. For this purpose, one single reactor is generally sufficient for carrying out the synthesis. The temperature is approximately 60°—90° C. and the residence time is 3—6 hours. About one volume of contact oil per volume of olefinic starting material is likewise added to the cycle. It is also possible, however, to charge substantially larger quantities of contact oil. 1—2% contact oil are withdrawn per hour from the contact oil cycle and replaced by fresh contact oil.

For the production of oils of higher viscosity, lower polymerisation temperatures are used. Moreover, the activity of the contact oil used must be particularly high. This is achieved by adding larger quantities of fresh contact oil and by withdrawing the corresponding quantity of contact oil from the cycle. In practice, two or more reaction tubes or zones connected in series are preferably used through which the mixture of contact oil and olefinic starting material passes in concurrent flow relation. The reaction temperature in the final reaction zone is advantageously increased for a short period up to about 50° C., but is maintained throughout at a level which is not above 50° C., whilst the residence time of the reaction mixture in the final reaction zone is from 1 to 3 hours. The temperature in the other reaction zone or zones is in the range 15°—25° C. with a residence time for the reaction mixture of from 8 to 12 hours, the longer residence time being necessitated by the lower reaction temperature. From 3% to 5% of the circulating contact oil is advantageously replaced every hour by unused or fresh contact oil.

If oils of particularly low viscosity are to be produced, relatively high temperatures should be used. However, the temperatures should not be substantially in excess of 90°—110° C. To avoid too extensive a polymerisation which results in oils of too high a viscosity, it is preferred first to contact the olefinic starting material with a contact oil of lowest activity and to increase the activity of the contact oil towards the end of the reaction. This may be achieved in a simple manner by connecting two or more reactors in series and providing each reactor with a separate contact oil cycle.

This manner of connecting the reactors together is illustrated in the accompanying drawing. In this case, the reaction temperatures are substantially the same in all reactors and are preferably maintained within the range 90°—110° C. with a residence time of from 3 to 6 hours. About 1% of the contact oil used in each of the reaction zones is preferably withdrawn every hour, the contact oil so withdrawn from each zone except the first being fed into the immediately preceding zone whilst an equal amount of unused or fresh contact oil is fed into the final zone.

The reaction conditions mentioned above for the production of lubricating oils of various viscosities apply to a circulating contact oil which has an age of, or has been in use for, several weeks. When starting a new synthesis with wholly fresh contact oil, it is preferred, owing to the very high activity of the contact oil, to adjust the quantity of circulating contact oil, at first to about 0.1 volumes of contact oil per volume of hydrocarbon feed rather than to one volume of contact oil per volume of hydrocarbon feed, and to increase the quantity to the latter value gradually.

For example, the contact oil freshly formed in the synthesis will not be withdrawn during this starting period.

The contact oil withdrawn from the contact oil cycle of the synthesis may be worked up in known manner, for example, by extraction with hydrocarbons for the removal of the lubricating oil constituents contained in the contact oil, or by decomposition with water. It may also be advantageous first to use the contact oil withdrawn from the synthesis for a pretreatment of the olefinic starting material. This pre-treatment is effected in a reactor of the same construction as that of the synthesis reactors, but the contact oil used in such pretreatment will not be passed in a cycle through the pre-treating zone. The starting material is introduced, together with the contact oil withdrawn from the synthesis, into the base of the vessel and is withdrawn at the top and passed into a settling vessel. The upper layer obtained therein is passed to the synthesis apparatus proper while the contact oil obtained as the lower layer is passed to the contact oil processing unit. During the passage of the starting material through this pre-treatment stage, certain components which are detrimental to the synthesis are removed such, for example, as when using cracked olefins, the diolefins which are present in small amounts in the cracked olefins and, when using primary olefins obtained by the hydrogenation of carbon monoxide, the last residues of oxygenated compounds. In this way, deactivation of the contact oil circulating in the synthesis is reduced, thus making it possible to lessen the quantity added for the freshening or maintaining the activity of the contact oil. Moreover, a better utilisation of the aluminium chloride charged is achieved, and that not only because the aluminium chloride is used for the removal of the impurities but also because polymerisation is initiated in the pre-treating stage.

The invention is illustrated by the following examples:—

EXAMPLE 1

A C_{10}—C_{16} hydrocarbon fraction obtained from the products of the hydrogenation of carbon monoxide carried out by means of an iron catalyst and boiling between about 160° C. and 290° C. was used as the starting material for the lubricating oil synthesis. The fraction was first passed over an aluminium oxide catalyst at a temperature of 350° C. at a rate of one volume of hydrocarbon fraction per volume of catalyst per hour. The fraction had an olefin content of 64% and was free from oxygenated compounds (hydroxyl number below 1).

The apparatus used consisted of two series-connected glass tubes each of a length of 1.5 metres and of 20 mm inner diameter, in each of which a co-axial cylindrical stirrer of the same length and 15 mm outside diameter was rotated at about 150 r.p.m. The two tubes were externally heated to 80°—85° C. by a thermo-siphon.

60 cc. of the C_{10}—C_{16} fraction were introduced per hour into the base of the first glass tube together with 60 cc. of a circulating contact oil. The circulating contact oil had an age of about 2 weeks. The reaction mixture was passed from the top of the first tube to the bottom of the second tube and was withdrawn from the top of the second tube into a settling vessel where it separated into a lower contact oil layer and an upper layer. The upper layer was clarified with "Tonsil" (Registered Trade Mark) and soda and separated by vacuum distillation into first runnings consisting of saturated hydrocarbons, and a lubricating oil fraction which at 5 mm vacuum boiled above 185° C. The quantity of contact oil which had newly formed was withdrawn from the lower contact oil layer. In this run, it averaged about 3 cc./hr. 0.9 cc. of the remaining 60 cc. of contact oil was withdrawn each hour, and replaced by freshly prepared contact oil. These 60 cc. of contact oil were then returned together with fresh C_{10}—C_{16} fraction to the first reaction tube.

The fresh contact oil used for freshening or maintaining the activity of circulating contact oil may be prepared in different ways:—

Contact oil a) was prepared in the following manner:—

1000 grams of the olefinic C_{10}—C_{16} fraction were stirred for 6 hours at 40° C. with 60 grams of aluminium chloride in a 2 litre stirring flask. The mixture was then allowed to settle and the lower layer of contact oil was separated from the upper layer. The yield of contact oil was 170 grams. It contained 110 grams of hydrocarbon material, so that about 11% of the hydrocarbon fraction charged had been converted into contact oil.

The production of contact oil b) was effected in a glass tube of 2 metres length and 20 mm inside diameter filled with aluminium chips, provided with a siphon-like outlet and externally heated to 60° C. The olefinic C_{10}—C_{16} fraction was charged from above at a rate of 90 grams per hour. At the same time, about 15 litres per hour of hydrogen chloride were passed into the lower end of the tube. The tube was completely filled with liquid. 38 grams per hour of contact oil were separated from the reaction product withdrawn from the base of the tube. Since the aluminium chloride content of this contact oil was about 50%, about 20% of the C_{10}—C_{16} fraction charged had thus been converted into contact oil.

The production of contact oil c) was effected as follows: 1000 grams of a saturated hydrocarbon fraction obtained from the lubricating oil synthesis of an olefinic C_{10}—C_{16} fraction and boiling between 160° C. and about 340° C. and 330 grams of aluminium chloride were stirred together for about 5 hours at 55° C. in a 2000 cc. glass flask. About 1—2 litres per hour of hydrogen chloride were simultaneously introduced. Upon the termination of the reaction, the lower contact oil layer was separated. The yield of contact oil was 668 grams. It contained 322 grams of hydrocarbon material, that is to say, about 32% of the saturated hydrocarbon fraction charged had been converted into contact oil. 350 grams of the upper layer of the settled reaction product could be returned to the process. With complete working up, 49.5%, that is practically 50% of the hydrocarbon charged was converted into contact oil in this manner.

The production of contact oil d) was effected in the same apparatus as that used for the production of contact oil b). The reaction temperature was 60° C. 190 grams per hour of the same hydrocarbon fraction as used in Example c) were charged and 15 litres per hour of hydrogen chloride were introduced into the lower end of the tube. 53 grams per hour of contact oil were separated from the reaction product withdrawn from the base of the tube. The aluminium chloride content was 51%, that is, 26 grams of hydrocarbon material or about 14% of the hydrocarbon fraction charged had been converted into contact oil in a single pass. 110 grams of hydrocarbons from the upper layer of the settled, reaction product could be returned to the process. Upon complete working up, 33% of the hydrocarbons charged had thus been converted into contact oil.

With the use of the contact oils a) to d), the following percentages by weight of the olefins of the C_{10}—C_{16} fraction were converted into lubricating oil.

Contact oil	a 83	b 80	c 85	d 85 by wt.
Characteristics of the lubricating oils:—				
Viscosity at 50° C. °Engler	12.0	11.5	12.5	12.0
Viscosity index	123	123	124	124
Flash point °C.	260	260	260	255
Pour point	−36	−40	−38	−42
Conradson carbon test	0.05%	0.06%	0.05%	0.04%

These yields were obtained in the third week of the runs. Thereafter, they remained constant for months.

EXAMPLE 2

The apparatus consisted of four glass tubes of 20 mm inside diameter which were connected in series and in which cylindrical stirrers of the same length as that of the tubes and of 15 mm outside diameter were rotated at about 150 r.p.m. The first three tubes were of a length of 2 metres whilst the length of the fourth tube was 75 cm. The temperature in tubes 1 to 3 was 20° C. and in tube 4 it was 50° C.

The starting material was a C_{10}—C_{16} hydrocarbon fraction of the same olefin content and obtained from the same source as the fraction used in Example 1. 45 cc. per hour of this fraction were charged to the base of tube 1 together with 45 cc. of contact oil. The circulating contact oil had been prepared in the same manner as that used in the preparation of contact oil d) in Example 1 and had been in use for 3 weeks. A quantity of contact oil corresponding to that newly formed during the synthesis and amounting to about 2 cc. per hour was withdrawn from the contact oil cycle. From the remaining 45 cc. of contact oil, 2 cc. were withdrawn per hour and replaced by freshly prepared contact oil.

From the top of the last tube, the reaction product was passed into a settling vessel. The upper layer obtained therein was clarified with "Tonsil" (Registered Trade Mark) and soda in known manner and fractionated by vacuum distillation. 18 grams of lubricating oil were obtained per hour. This was equal to a yield of lubricating oil of 83% by weight based on the C_{10}—C_{16} olefins charged.

The lubricating oil had the following characteristics:—

Viscosity at 50° C.	24.5 °Engler
Viscosity index	125
Flash point	275° C.
Pour point	−30° C.
Conradson carbon test	0.08%

EXAMPLE 3

The apparatus consisted of two glass tubes, each of 2 metres length and of 20 mm inside diameter, which were connected together in series and in each of which a cylindrical stirrer of the same length as the tube and of 15 mm outside diameter was rotated at 150 r.p.m. The two reaction vessels were maintained at a temperature of 100° C. by means of an oil jacket. The starting material was a C_{10}—C_{16} hydrocarbon fraction having the same olefin content and derived from the same source as the fraction used in Example 1, whilst the contact oil had been prepared in accordance with the method used for the preparation of contact oil d) of Example 1 and had been in use for 3 weeks.

60 cc. per hour of the C_{10}—C_{16} fraction and an equal volume per hour of the contact oil were passed from two feed vessels to the base of the first reaction tube. The reaction mixture was withdrawn from the top of the first tube into one of two alternately operated settling receivers. After every 12 hours of reaction time, the settling receivers were changed over. The reaction mixture was then allowed to settle for 8 hours. Thereafter, the upper layer was drawn off into the feed vessel of the second reaction tutbe while the lower contact oil layer was passed into the feed vessel of the first tube after having separated the contact oil newly formed in the synthesis (12 cc. of contact oil in 12 hours) and after having withdrawn 8.5 cc. contact oil and replaced it by 8.5 cc. of contact oil drawn from the cycle of the second reaction stage. The second reaction tube was in a similar way provided with a feed vessel for the upper layer of the reaction product from the first reaction stage and with a feed vessel for contact oil, and with two alternatively operated receivers which were likewise changed after every 12 hours. After a settling time of 8 hours, the newly formed contact oil (6 cc. in 12 hours) was drawn off and, moreover, 8.5 cc. of contact oil were withdrawn and passed to the first stage and replaced by 8.5 cc. of fresh contact oil. The upper layer of the second stage was clarified in known manner by a treatment with soda and "Tonsil" (Registered Trade Mark) and fractionated by vacuum distillation. The yield of lubricating oil was 25.3 grams per hour, being a yield of 87% by weight based on the C_{10}—C_{16} olefins charged.

The lubricating oil had the following characteristics:—

Viscosity at 50° C. - -	6.0 °E
Viscosity index - - -	123
Flash point - - -	260° C.
Pour point - - - -	—40° C.
Conradson carbon test -	0.06%

EXAMPLE 4

60 cc. per hour of a C_8—C_{12} hydrocarbon fraction obtained by the hydrogenation of carbon monoxide over an iron catalyst, which had previously been contacted at 350° C. with an aluminium oxide catalyst and had a content of oxygenated compounds of below 1% and an olefin content of 65%, were converted into lubricating oil with the use of 60 cc. per hour of contact oil which had been prepared in accordance with the method employed for the preparation of contact oil d) of Example 1 and had an age of several weeks. The synthesis was effected in the apparatus described in Example 1 using a reaction temperature of 85° C. 1 cc. per hour of contact oil was withdrawn from the contact oil cycle and replaced by fresh contact oil.

Upon working up the upper layer from the settling vessel, a yield of lubricating oil of 85% by weight based on the C_8—C_{12} olefins charged was obtained. The lubricating oil had the following characteristics:—

Viscosity at 50° C. - -	13.5 °Engler
Viscosity index - - -	118
Flash point - - - -	245° C.
Pour point - - - -	—40° C.
Condradson carbon test -	0.04%

EXAMPLE 5

60 cc. per hour of a C_7—C_{15} hydrocarbon fraction, having an olefin content of 70%, which had been obtained from the thermal cracking of paraffins boiling above 320° C. and produced by the hydrogenation of carbon monoxide by means of an iron catalyst, were converted into lubricating oil with the use of 60 cc. of contact oil produced in accordance with the method employed for the preparation of contact oil d) of Example 1 and having an age of several weeks. The synthesis was effected in the apparatus described in Example 1 using a reaction temperature of 80—85° C. 1.2 cc. per hour of contact oil were withdrawn from the contact oil cycle and replaced by fresh contact cycle. Upon working up the upper layer from the settling vessel, a yield of lubricating oil of 81% by weight based on the C_7—C_{15} olefins charged was obtained. The lubricating oil had the following characteristics:—

Viscosity at 50° C. - -	13.2 °Engler
Viscosity index - - -	116
Flash point - - - -	245° C.
Pour point - - - -	—40° C.
Conradson carbon test -	0.08%

EXAMPLE 6

60 cc. of the C_7—C_{15} fraction of Example 5 prior to being charged to the lubricating oil synthesis were introduced into the lower end of a glass tube of 1 metre length and 20 mm inside diameter in which a co-axially provided cylindrical stirrer of the same length and 15 mm outside diameter was rotated at about 150 r.p.m. The glass tube, which was filled with the contact oil withdrawn from the lubricating

oil synthesis, was externally heated to 60° C. In a settling vessel downstream of the glass tube, the C_7—C_{15} fraction was separated from the contact oil and then passed to the lubricating oil synthesis proper. 3.3 cc. per hour of contact oil which had been withdrawn from the contact oil cycle of the lubricating oil synthesis were simultaneously passed in.

The lubricating oil synthesis was effected in the same apparatus as that used in Example 1. The pre-treated C_7—C_{15} fraction was introduced together with 60 cc. of contact oil. 0.7 cc. per hour of contact oil were withdrawn from the contact oil cycle and replaced by fresh contact oil. Upon working up the upper layer from the settling vessel in known manner, a yield of lubricating oil of 83% by weight based on the C_7—C_{15} olefins charged was obtained. The lubricating oil had the following characteristics:—

Viscosity at 50° C. - -	13.8 °Engler
Viscosity index - - -	119
Flash point - - - -	245° C.
Pour point - - - -	−42° C.
Conradson carbon test -	0.04%

What we claim is:—

1. A process for the synthesis of a lubricating oil by the polymerisation of normally liquid aliphatic olefinic hydrocarbons, which comprises passing the olefinic hydrocarbons together with a contact oil upwardly through a substantially vertical reaction zone, the contact oil comprising or consisting of addition compounds of aluminium chloride with a hydrocarbon or hydrocarbons, and intimately admixing the olefinic hydrocarbons with the contact oil in a horizontal direction in the reaction zone in such manner as substantially to avoid an intermixing in the vertical direction, whereby olefinic hydrocarbons at any level of the reaction zone are substantially at the same stage of polymerisation.

2. A process according to Claim 1, in which the contact oil is separated from the reaction products and recycled to the reaction zone.

3. A process for the synthesis of a lubricating oil by the polymerisation of normally liquid aliphatic olefinic hydrocarbons, which comprises passing the olefinic hydrocarbons together with a contact oil upwardly through two or more vertical reaction zones connected together in series, the contact oil consisting of or comprising aluminium chloride/hydrocarbon addition compounds, separating the olefinic hydrocarbons from the contact oil after passage through each reaction zone and recycling the separated contact oil to the reaction zone from which it was withdrawn, the olefinic hydrocarbons and the contact oil being intimately admixed in a horizontal direction in each reaction zone in such manner as substantially to avoid an intermixing in the vertical direction.

4. A process according to Claim 2 or Claim 3, in which a part of the contact oil is continuously or intermittently withdrawn and replaced by unused or freshly prepared contact oil.

5. A process according to Claim 4, in which the unused or fresh contact oil is prepared outside the reaction zone from part of the hydrocarbon feed and aluminium chloride.

6. A process according to Claim 4, in which the unused or fresh contact oil is prepared from part of the hydrocarbon feed, aluminium and hydrogen chloride.

7. A process according to Claim 6, in which the part of the hydrocarbon feed used for the preparation of the contact oil is passed downwardly in counter-current to the hydrogen chloride through a bed of aluminium in the form of chips, granules or the like.

8. A process according to Claim 6 or Claim 7, in which the preparation of the unused or fresh contact oil is commenced in the presence of a quantity of previously prepared contact oil.

9. A process according to Claim 4, in which the unused or fresh contact oil is prepared from aluminium chloride and by-products of the synthesis which consist substantially of saturated hydrocarbons.

10. A process according to Claim 4, in which the unused or fresh contact oil is prepared from aluminium, hydrogen chloride, and by-products of the synthesis which consist substantially of saturated hydrocarbons.

11. A process according to any one of the preceding claims, in which each reaction is cylindrical.

12. A process according to any one of the preceding claims, in which the mixing of the hydrocarbons and the contact oil in a reaction zone is effected by means of a rotating cylindrical body of a length not substantially less than that of the reaction zone, the cylindrical body being provided axially of the reaction zone.

13. A process according to any one of the preceding claims, in which the synthesis is effected at a temperature within the range 15°—110° C.

14. A process according to any one of the preceding claims, in which the residence time of the olefinic hydrocarbons and contact oil in the reaction zone or zones is from 3 to 15 hours.

15. A process according to any one of Claims 4 to 14, in which from 1% to 8% of the contact oil in the synthesis is replaced by unused or freshly prepared contact oil per hour.

16. A process according to any one of the preceding claims, in which the olefinic hydrocarbons and contact oil are used in about equal volumes in the synthesis.

17. A process acccording to any one of the preceding claims, in which the synthesis is effected at a temperature in the range 60°—90° C., the residence time of the olefinic hydrocarbons and contact oil in the reaction zone or zones being from 3 to 6 hours whilst from 1%

to 2% of the circulating contact oil is replaced by unused or fresh contact oil per hour.

18. A process according to any one of Claims 1 to 16, in which, for the synthesis of oils of high viscosity, two or more reaction zones in series are employed, the temperature in the final reaction zone being not in excess of 50° C. with a residence time of from 1 to 3 hours whilst the temperature in the other reaction zone or zones is in the ranage 15°—25° C., with a residence time of from 8 to 12 hours, from 3% to 5% of the circulating contact oil being replaced by unused or fresh contact oil per hour.

19. A process according to any one of Claims 3 to 16, in which, for the synthesis of oils of low viscosity, two or more reaction zones each provided with a separate circuit for the contact oil are used whilst the temperature is maintained within the range 90°—110° C. with a residence time of from 3 to 6 hours.

20. A process according to Claim 19, in which about 1% of the contact oil used in each of the reaction zones is withdrawn every hour, the contact oil so withdrawn from each zone except the first being fed into the immediately preceding zone whilst an equal amount of unused or fresh contact oil is fed into the final zone.

21. A process according to any one of the preceding claims, in which the olefinic hydrocarbons are pre-treated with contact oil which has been withdrawn from the synthesis.

22. A continuous process for the synthesis of a lubricating oil, substantially as hereinbefore described.

23. A process for the synthesis of a lubricating oil, substantially as hereinbefore described with reference to any one of the examples.

24. A lubricating oil whenever prepared by the process claimed in any one of the preceding claims.

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776,436 COMPLETE SPECIFICATION

1 SHEET This drawing is a reproduction of the Original on a reduced scale.