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PATENT SPECIFICATION

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504,350

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COMPLETE SPECIFICATION

Process for the Synthetic Production of Lubricating Oils

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a Body Corporate organised and existing according to the laws of the German State, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

It is known to condense or polymerise hydrocarbon mixtures containing unsaturated hydrocarbons under the action of ordinary condensation agents such as aluminium chloride to produce high-molecular viscous hydrocarbons. It has further been proposed to increase the content of unsaturated hydrocarbons by subjecting to cracking or dehydrogenation the hydrocarbon mixtures used as raw materials for the synthetic production of lubricating oils.

Our investigations have shown that it does not suffice for the production of valuable lubricating oils to employ a benzine containing a very large proportion of olefines as raw material for the synthesis of lubricating oils; that is to say, it has in fact been found that benzines with a high olefine content may produce on polymerisation lubricating oils of an unsatisfactory viscosity pole height so that the very high olefine content is in no way a criterion of the special suitability of the benzine for the production on polymerisation of lubricating oils. We have found that it is before all else essential that the crude benzine must correspond to a very definite density curve with variations of at most plus or minus 1%, that is to say, if a suitable benzine is divided into fractions each having a boiling range of 10° C. and the density of the individual benzine fractions covering a boiling range of 10° C. is determined, the density values obtained must correspond within 1% to a curve that is determined by the following values, the mean boiling temperatures of the fractions being indicated as abscissæ and the corresponding densities as ordinates:—

Fraction	Mean boiling temperature	Density	+ 1%	− 1%
45— 55° C	50° C	0.6510	0.6575	0.6445
55— 65° C	60° C	0.6635	0.6701	0.6569
65— 75° C	70° C	0.6755	0.6823	0.6687
75— 85° C	80° C	0.6860	0.6929	0.6791
85— 95° C	90° C	0.6960	0.7030	0.6890
95—105° C	100° C	0.7055	0.7126	0.6984
105—115° C	110° C	0.7120	0.7191	0.7049
115—125° C	120° C	0.7180	0.7252	0.7108
125—135° C	130° C	0.7225	0.7297	0.7153
135—145° C	140° C	0.7275	0.7348	0.7202
145—155° C	150° C	0.7315	0.7388	0.7242
155—165° C	160° C	0.7360	0.7434	0.7286
165—175° C	170° C	0.7400	0.7474	0.7326
175—185° C	180° C	0.7430	0.7504	0.7356
185—195° C	190° C	0.7465	0.7540	0.7390
195—205° C	200° C	0.7500	0.7575	0.7425
205—215° C	210° C	0.7530	0.7605	0.7455
215—225° C	220° C	0.7555	0.7631	0.7479

Hydrocarbon mixtures that contain olefines, and that do not conform to the conditions referred to are less suitable for the synthesis of lubricating oils. Such benzines provide on the one hand only a small yield of lubricating oils, and on the other hand the lubricating oils obtained show an unsatisfactory viscosity pole height, that is to say, lubricating oils were obtained whose viscosity was in very large measure dependent upon the temperature. Benzines of a corresponding density curve produced lubricating oils to the extent of from 42 to 62% (calculated on the weight of benzines employed), the lubricating oils having a viscosity pole height of from 1.82 to 1.95, whereas when using benzines of density curves that do not conform, lubricating oils were obtained to the extent only of 3 to 28%, with a viscosity pole height of 2.12 up to 4.

According to the invention the crude benzines that are used for the production of lubricating oils by polymerisation have densities that conform to the density curve determined by the values hereinbefore specified and are obtained by the cracking at temperatures that lie between 450 and 550° C., preferably between 460 and 510° C. and under pressures lying between about 4 and 12 atmospheres of hydrocarbons obtained by the Fischer-Tropsch synthesis, and that boil at over 150° C. The cracking conditions differ according to the nature of the crude hydrocarbon mixture employed, that is to say, depending upon the end boiling point of the hydrocarbons employed for cracking.

The most suitable temperature and pressure conditions must always be determined by a few preliminary experiments. Pressures of from 6 to 8 atmospheres and temperatures around 500° C., may be used with advantage. If higher pressures up to, say, 10 atmospheres are employed, it is possible to produce quantities of oil that are greater proportionately to the rising pressure. Similarly, with a higher temperature, for example 520° C., it is possible to produce larger quantities of oil, or with lower temperatures correspondingly smaller quantities of oil. Further, the steps of varying the pressure and the temperature can be combined; generally it is advisable not to increase the pressure above 10 atmospheres, as when higher pressures are used the resulting density values are too high as the result of the occurrence of polymerisation. The period during which the hydrocarbons remain in the cracking zone is dependent upon the boiling range of the crude hydrocarbons and upon the cracking temperature employed, and it lies between about 3 to 15 minutes. Starting out from hydrocarbon mixtures of the same boiling range the duration of cracking is shorter as the cracking temperature is raised. The quantities of oil that can be passed through in a unit of time are greater according as the pressure and the cracking temperature are raised.

The cracked benzines used according to the invention are employed without the removal of any intermediate fractions although the lower or upper boiling limit or both limits may vary.

The invention is hereinafter described by reference to the accompanying drawings and the examples hereinafter appearing, Examples 1 and 2 showing the behaviour of a benzine corresponding to the density curve and Examples 3 to 6 showing the behaviour of benzines that do not correspond to the density curve, in the synthesis of lubricating oils. In the graph (Figure 1) the curve A represents the density curve in accordance with the requirements of the present invention, and the curves B and C represent the limiting values of the permissible upper and lower variations from the density values. The further curves I to VI correspond to the density values of the benzines employed as raw material in Examples 1 to 6.

In Figure 2 are shown the mean yields of lubricating oils obtained in Examples 1 to 6 and these clearly show the superiority of the oils produced according to the invention. Figure 3 illustrates the viscosity pole heights of the lubricating oils obtained in the examples and at the same time the drawing illustrates the upper limit of the viscosity pole height that is involved in a good lubricating oil. The columns according to Examples 3 to 6 reach above this upper limit of the viscosity pole height, by reason of the lower quality of the lubricating oils obtained in these examples. When cracking, under a pressure of 10 atmospheres and at a temperature of 500° C., for example, a mixture of hydrocarbons that boils at over 200° C. and that has been obtained by the catalytic reduction of carbon monoxide, there are obtained in about 75% yield benzines that correspond to the density curve according to the invention and that have a content of 80% of mono-olefines.

EXAMPLE 1.

A fraction, boiling within the limits 170 and 260° C., of the hydrocarbons resulting from the catalytic conversion of carbon monoxide with hydrogen is fed at a pressure of 11 atmospheres through cracking tubes heated to from 500 to 510° C. The length of time that the hydrocarbons are in the cracking zone amounts to from 9.5 to 10.5 minutes. The ratio of the fresh hydrocarbon oils introduced to the returned uncracked hydrocarbon fractions amounts to 1:3.7. In a yield of 75% a cracked benzine is obtained that contains about 80% of mono-olefines and has the following density curve:—

Mean boiling temperature.	Density.
60° C.	0.659
70° C.	0.671
80° C.	0.681
90° C.	0.692
100° C.	0.700
110° C.	0.708
120° C.	0.715
130° C.	0.720
140° C.	0.724
150° C.	0.728
160° C.	0.730
170° C.	0.734
180° C.	0.738
190° C.	0.741
200° C.	0.744
210° C.	0.746

In a pressure vessel 50 gm. of anhydrous aluminium chloride and 1000 gm. of dry benzine of the quality hereinbefore mentioned are stirred at 20° C. for 24 hours. The reaction mixture is in two layers, namely the so-called " upper layer ", which contains the lubricating oil dissolved, and a lower layer, the so-called " contact layer ", which consists of double compounds of aluminium chloride containing the benzine before referred to. The upper layer, which amounted to 766 gm. was successively washed with caustic soda, sulphuric acid and water to remove the remaining contact substances and then neutralised. After drying, the unconverted benzine up to a boiling point of 200° C. was distilled off. The residue from the distillation was thereupon distilled *in vacuo* at an absolute pressure of 5 mm. Hg. up to 200° C. the lubricating oil remaining as a residue from the distillation. 417 gm. of lubricating oil having a specific gravity of 0.859 at 20° C. and a viscosity of 17.3° Engler at 50° C. were obtained. The viscosity pole height amounted to 1.9: the solidification point was −23° C.

The " contact layer ", which amounted to 283 gm., was in the same manner converted in the vessel at 55° C. with 1000 gm. of fresh benzine of the same properties as hereinbefore given, while being stirred. The upper layer amounted to 803 gm. and contained 450 gm. of lubricating oil. The " contact layer " which had grown to 480 gm., was caused to react in the pressure vessel with 1000 gm. of fresh benzine at 95° C.

Further conversions of a like kind were carried out at temperatures of 110° C., 130° C. and 150° C. The data of the experiments are given in the following table:—

Conversion	1	2	3	4	5	6
Temperature	20° C	55°C	95°C	110°C	130°C	150°C
Quantity of benzine	1000 gm	1000 gm	1000 gm	1000 gm	1000 gm	1000 gm
Contact layer before conversion	50 gm. ($AlCl_3$)	283 gm	480 gm	510 gm	470 gm	520 gm
Contact layer after conversion	283 gm	480 gm	510 gm	470 gm	520 gm	550 gm
Upper layer	766 gm	803 gm	968 gm	1040 gm	945 gm	969 gm
Quantity of lubricating oil in gm.	417 gm	450 gm	550 gm	610 gm	480 gm	520 gm
Quantity of lubricating oil in % calculated on the quantity of benzine used	41.7%	45%	55%	61%	48%	52%
Density at 20° C	0.859	0.856	0.865	0.868	0.866	0.865
Viscosity in deg. Engler at 50° C	17.3°	16°	19.1°	18°	19.6°	18.6°
Viscosity pole height	1.9	1.82	1.88	1.95	1.88	1.92

EXAMPLE 2.

A mixture of hydrocarbons that has been obtained by the catalytic hydrogenation of carbon monoxide and that boils within the limits 150 and 240° C. is fed under a pressure of 10 atmospheres through cracking apparatus whose cracking tubes have been heated to 490° C. The length of time the mixture remains in the cracking zone amounts to from 6 to 7 minutes. The return flow ratio—that is to say the ratio of the fresh hydrocarbon oils introduced to the uncracked hydrocarbon fractions returned—amounts to 1:4.5. From the cracked benzines obtained by this cracking a fraction that boils at between 50 and 160° C. and that showed the following density curve is separated off:—

Mean Boiling Temperature.	Density.
50° C.	0.652
60° C.	0.668
70° C.	0.679
80° C.	0.690
90° C.	0.701
100° C.	0.710
110° C.	0.716
120° C.	0.721
130° C.	0.726
140° C.	0.731
150° C.	0.735
160° C.	0.739

15 kg. of the benzine previously described were stirred for 4 hours at 20° C. and then for 8 hours at 50° C. in a 50 litre pressure vessel with 200 gm. of fresh aluminium chloride and 11150 gm. of a contact layer produced during the 30 preceding condensation reactions, the contact layer containing double compounds of aluminium chloride. The upper layer which forms after the liquid has been allowed to stand amounted to 14800 gm. The upper layer was removed and neutralised. Distillation at ordinary pressure, followed by distillation *in vacuo*, produced 9060 gm. of lubricating oils as residue from distillation which corresponds to a yield of 60.4% calculated on the quantity of the benzine used. The contact layer amounting to 11550 gm. after the reaction was again converted with 15 kg. of fresh benzine of the same quality under the same temperature and time conditions—after the addition of 200 gm. of aluminium chloride. Any number of conversions may follow with the repeated use of the contact layer with fresh quantities of benzine.

In the following table the data of five such conversions are recorded:—

Conversion	1	2	3	4	5
Reaction Conditions	Each time 4 hrs. at 20 C, 8 hrs at 50 C.				
Quantity of benzine	15,000 gm	15,000 gm	15,000 gm	15,000 gm	15,000 gm
Addition of fresh $AlCl_3$	200 gm	200 gm	200 gm	200 gm	200 gm
Contact layer before conversion	11,150 gm	11,750 gm	12,450 gm	12,800 gm	12,600 gm
Contact layer after conversion	11,550 gm	12,250 gm	12,600 gm	12,400 gm	13,050 gm
Upper layer	14,800 gm	14,500 gm	14,850 gm	15,400 gm	14,550 gm
Quantity of lubricating oils in gm.	9,060 gm	8,760 gm	8,700 gm	9,240 gm	8,720 gm
Quantity of lubricating oils in % calculated on quantity of benzine used	60.4%	58.4%	58%	61.6%	58.1%
Density at 20° C	0.860	0.859	0.860	0.858	0.860
Viscosity in deg. Engler at 50° C	13.38°	14.79°	17.42°	13.88°	12.2°
Viscosity pole height	1.9	1.88	1.92	1.9	1.88

EXAMPLE 3.

A fraction, boiling at between 150 and 260° C., of the hydrocarbons produced on the catalytic hydrogenation of carbon monoxide with hydrogen, is cracked at a temperature of 570° C. by the so-called true-vapour-phase process as described, for example, in " Refiner and Natural Gasolines Manufacturer ", Volume 15, pages 430 to 431, October 1936. In the true-vapour-phase process such quantities of superheated heat carrier gases are fed into the oil vapours which are themselves heated that the desired cracking temperature is produced by the mixing of the hot gases with the heated oil vapours. As heat carrier gases there may be used, for example, the gases that arise during the cracking process. The hydrocarbon oils to be cracked are vaporized and heated by themselves to from 540 to 550° C. Into the hot oil vapours gases heated to about 620° C. and that arise during the cracking are then introduced in such quantity that the temperature in the cracking chamber is 570° C. The cracked benzines obtained in accordance with this cracking process have the following density curve:—

Mean Boiling Temperature.	Density.
50° C.	0.663
60° C.	0.678
70° C.	0.690
80° C.	0.706
90° C.	0.718
100° C.	0.728
110° C.	0.736
120° C.	0.740
130° C.	0.743
140° C.	0.747
150° C.	0.752
160° C.	0.759

In the same manner as in Example 1 three conversions were effected in succession at 20° C., 40° C., and 70° C. with this benzine. The reaction period was 24 hours in each case. Only small quantities of lubricating oils were obtained, and lubricating oils of too high a viscosity pole height were produced. The data of the experiments are given in the following table:—

Conversion	1	2	3
Quantity of benzine	1000 gm	1000 gm	1000 gm
Contact layer before conversion	(50 g. $AlCl_3$)	220 gm	249 gm
Contact layer after conversion	220 gm	249 gm	295 gm
Upper layer	825 gm	970 gm	950 gm
Quantity of lubricating oils in gm.	223 gm	171 gm	232 gm
Quantity of lubricating oils in % calculated on the quantity of benzine used	22.3%	17.1%	23.2%
Density at 20° C	0.882	0.895	0.892
Viscosity in deg. Engler at 50° C	49°	56°	22°
Viscosity pole height	3.03	3.25	3.12

Example 4.

The crude substance employed was a uniform hydrocarbon mixture as secured during the catalytic hydrogenation of carbon monoxide, as in Example 3. The hydrocarbon oils were vaporized and the oil vapours were heated to from 540 to 550° C. The gas arising during cracking, which was to serve as heat carrier, was heated to about 620° C. and was added at intervals to the oil vapours that have been heated alone in such quantities that an equally high cracking temperature of 580° C. was always again obtained. The cracked benzines obtained had the following density curve:—

Mean Boiling Temperature.	Density.
50° C.	0.656
60° C.	0.672
70° C.	0.684
80° C.	0.697
90° C.	0.711
100° C.	0.720
110° C.	0.730
120° C.	0.736
130° C.	0.741
140° C.	0.745
150° C.	0.749
160° C.	0.755
170° C.	0.760
180° C.	0.765
190° C.	0.770

In the same manner as in Example 1 conversions were carried out with this benzine at 20° C., 40° C., and 70° C.; and again lubricating oils were obtained having too great a viscosity pole height in an unsatisfactory quantity. The following table gives the details of the experiments:—

Conversion	1	2	3
Quantity of benzine	1000 gm	1000 gm	1000 gm
Contact layer before conversion	(50 g. $AlCl_3$)	179 gm	198 gm
Contact layer after conversion	179 gm	198 gm	245 gm
Upper layer	875 gm	980 gm	951 gm
Quantity of lubricating oils in gm.	280 gm	186 gm	229 gm
Quantity of lubricating oils in % calculated on the quantity of benzine used	28%	18.6%	22.9%
Density at 20° C	0.864	0.906	0.907
Viscosity in deg. Engler at 50° C	34	172°	51°
Viscosity pole height	2.12	3.7	3.25

EXAMPLE 5.

A hydrocarbon fraction that was produced by the catalytic reduction of carbon monoxide with hydrogen and that boiled at between 150 and 220° C. was cracked at 40 atmospheres pressure and at a temperature of 455° C. The cracked benzines had the following density curve:

Mean Boiling Temperature.	Density.
60° C.	0.668
70° C.	0.677
80° C.	0.694
90° C.	0.706
100° C.	0.717
110° C.	0.727
120° C.	0.737
130° C.	0.747
140° C.	0.756
150° C.	0.764
160° C.	0.773
170° C.	0.780

This benzine was converted at 20° C., 55° C., and 95° C., in the same manner as in Example 1, and a very small yield of lubricating oils of a viscosity pole height of from 2.45 to over 4 was produced. The data of the experiments are given in the following table:—

Conversion	1	2	3
Quantity of benzine	1000 gm	1000 gm	1000 gm
Contact layer before conversion	(50 gm.$AlCl_3$)	160 gm	90 gm
Contact layer after conversion	160 gm	90 gm	90 gm
Upper layer	888 gm	1069 gm	1000 gm
Quantity of lubricating oils in gm.	77 gm	53 gm	37 gm
Quantity of lubricating oils in % calculated on the quantity of benzine used	7.7%	5.3%	3.7%
Density at 20° C	0.889	0.931	0.9486
Viscosity in deg. Engler at 50° C	17.5°	77.6°	39°
Viscosity pole height	3.6	2.45	Over 4

EXAMPLE 6.

Conversions were carried out, as in Example 1, at 20° C., 50° C., and 80° C., in succession with a benzine fraction of boiling limits of from 150 to 180° C. occurring primarily on the catalytic conversion of carbon monoxide with hydrogen; the benzine fraction had the following density curve:—

Mean Boiling Temperature.	Density.
50° C.	0.647
60° C.	0.657
70° C.	0.667
80° C.	0.675
90° C.	0.684
100° C.	0.690
110° C.	0.697
120° C.	0.704
130° C.	0.711
140° C.	0.717
150° C.	0.721
160° C.	0.726
170° C.	0.730
180° C.	0.733

The yield of lubricating oils was small and they had a viscosity pole height of approximately 2.5. The data of the experiments are given in the following table:—

Conversion	1	2	3
Quantity of benzine	1000 gm	1000 gm	1000 gm
Contact layer before conversion	(50 gm.$AlCl_3$)	140 gm	210 gm
Contact layer after conversion	140 gm	210 gm	230 gm
Upper layer	910 gm	930 gm	980 gm
Quantity of lubricating oils in gm.	100 gm	75 gm	130 gm
Quantity of lubricating oils in % calculated on the quantity of benzine used	10%	7.5%	13%
Density at 20° C	0.846	0.844	0.846
Viscosity in deg. Engler at 50° C	12.7°	12.8°	5.4°
Viscosity pole height	2.32	2.5	2.44

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the synthetic production of lubricating oils by the condensation of mixtures of hydrocarbons containing olefines, using known condensation agents such as aluminium chloride, wherein the hydrocarbon mixtures employed consist of benzines obtained by cracking at temperatures of 450° to 550° C., and preferably 460° C. to 510° C., and under pressures of about 4 to 12 atmospheres, mixtures of hydrocarbons obtained synthetically from carbon monoxide and hydrogen by the Fischer-Tropsch process and boiling at over 150° C. which benzines have a range of fractions boiling over a considerable portion of the following boiling temperature range, the said fractions having at the specified boiling temperatures the following specified densities with a variation plus or minus of 1%:—

Mean Boiling Temperature.	Density.
50° C.	0.6510
60° C.	0.6635
70° C.	0.6755
80° C.	0.6860
90° C.	0.6960
100° C.	0.7055
110° C.	0.7120
120° C.	0.7180
130° C.	0.7225
140° C.	0.7275
150° C.	0.7315
160° C.	0.7360
170° C.	0.7400
180° C.	0.7430
190° C.	0.7465
200° C.	0.7500
210° C.	0.7530
220° C.	0.7555

2. A process for the synthetic production of lubricating oils according to claim 1, wherein the hydrocarbons, obtained by the catalytic hydrogenation of carbon monoxide and that boil at over 150° C. are cracked at pressures of not substantially more than 10 atmospheres and temperatures of about 500° C.

3. Lubricating oils when produced according to the process of claim 1 or claim 2.

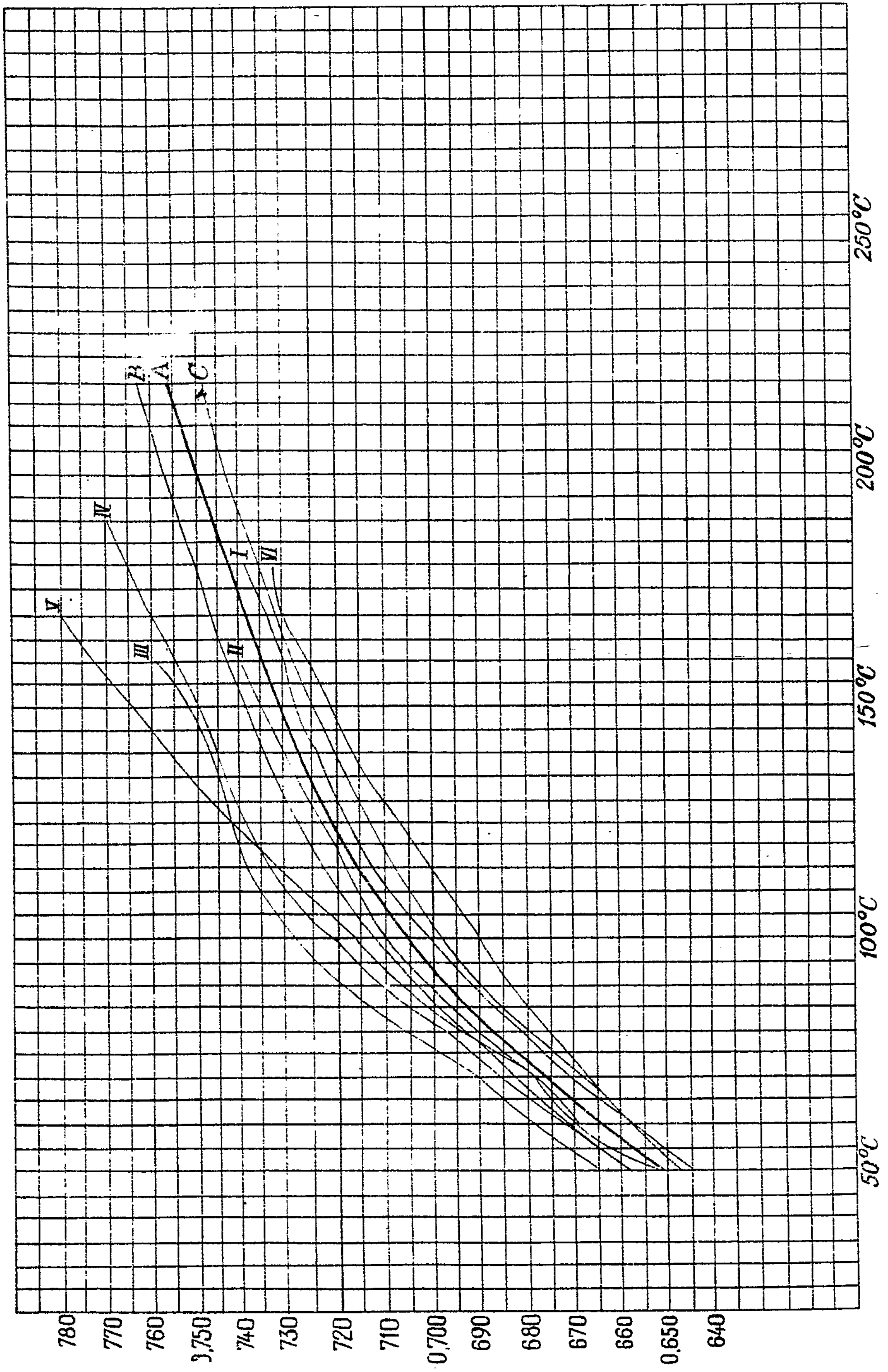
4. A process for the synthetic produc-

tion of lubricating oils substantially as hereinbefore described.

Dated this 19th day of October, 1937.
EDWARD EVANS & CO.
40—43, Chancery Lane, London, W.C.2.
Agents for the Applicants.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1939.

Fig.1.



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SHEET 1

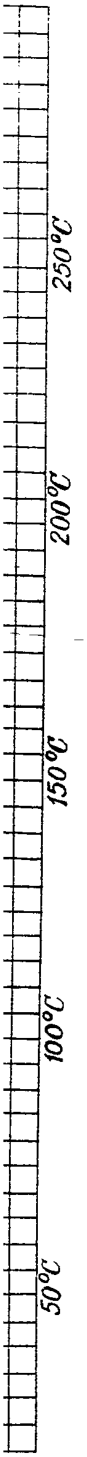


Fig. 2.

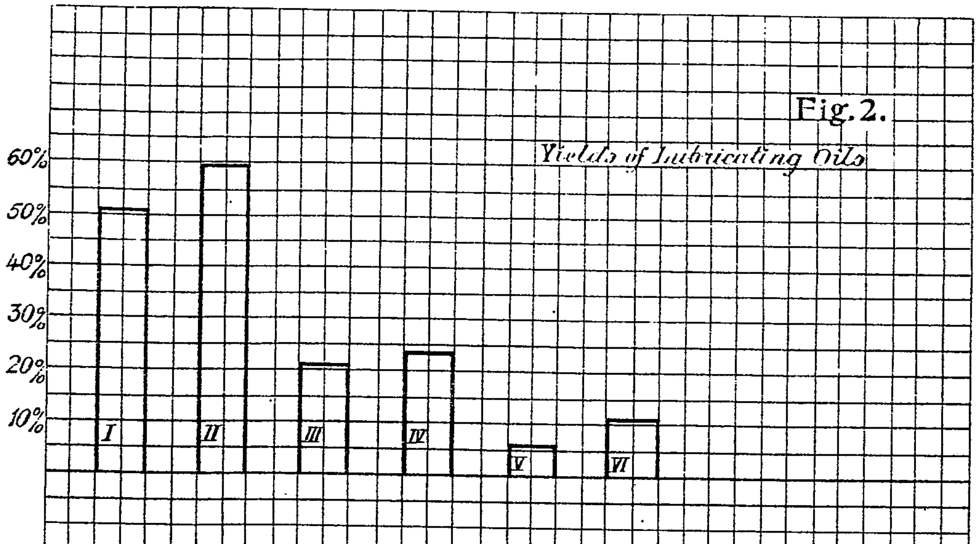
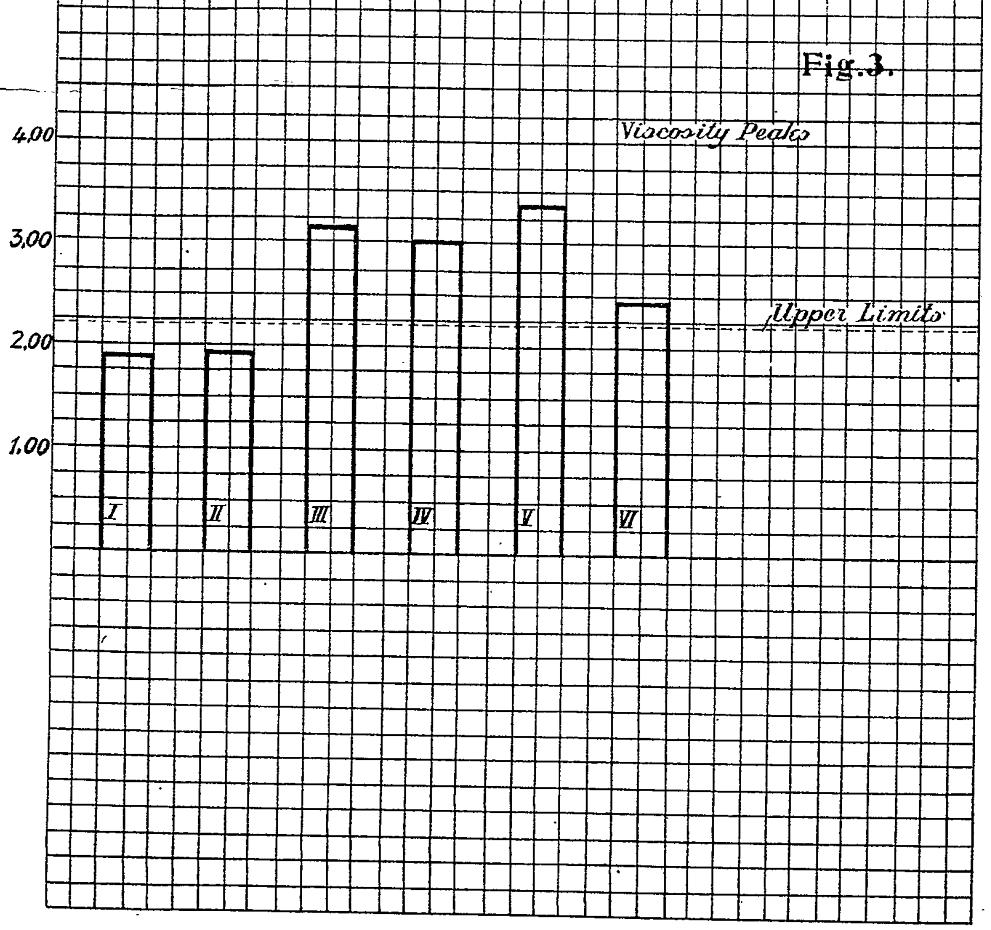


Fig. 3.



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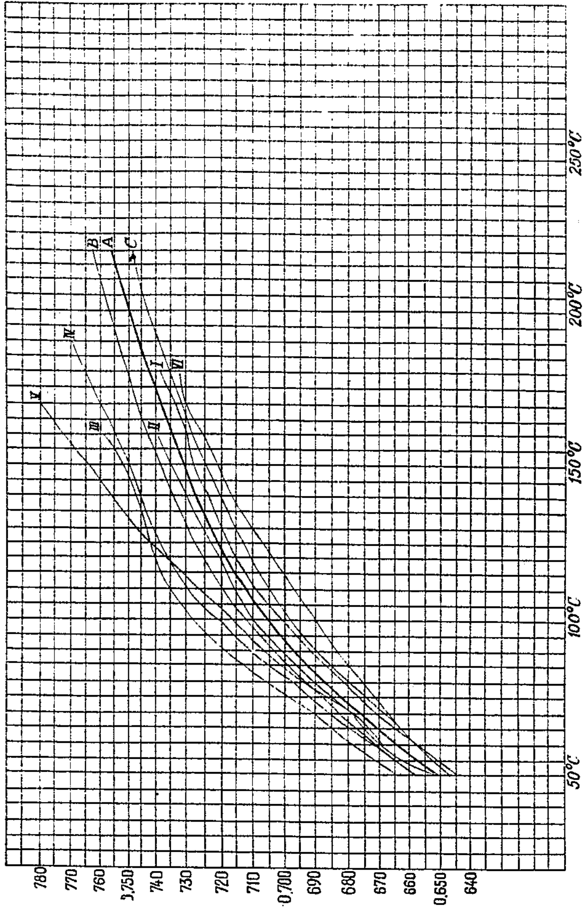
2 SHEETS
SHEET 1

Fig.1.



SHEET 2

Fig.2.

Yields of Lubricating Oils

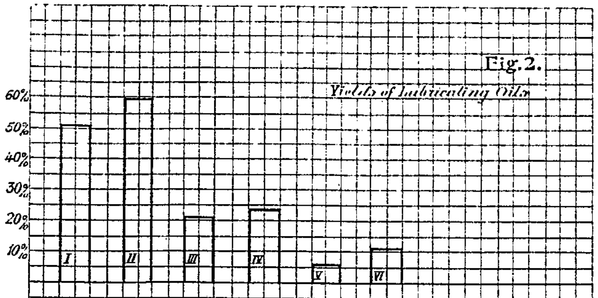
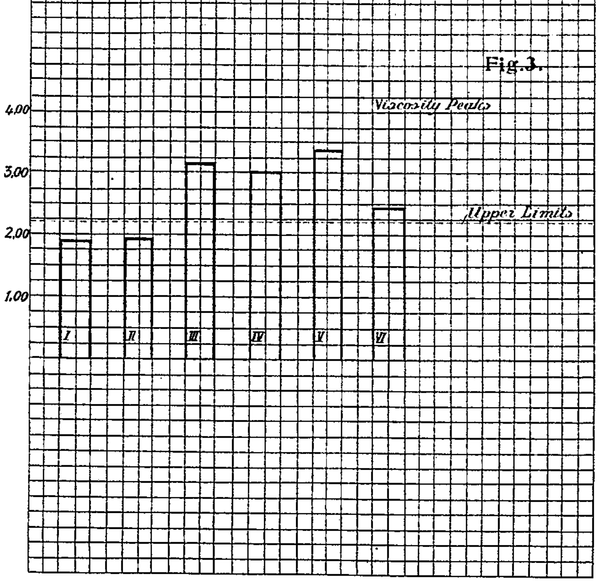


Fig.3.

Viscosity Peaks



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