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PATENT SPECIFICATION

503,206

Convention Dates
(Germany)

Oct. 1, 1936:
Nov. 28, 1936:

Corresponding Applications
in United Kingdom

No. 26644/37.
No. 26645/37. } *Dated Oct. 1, 1937.*

(One Complete Specification Left under Section 91 (2) of the Patents and Designs Acts, 1907 to 1938).

Specification Accepted: April 3, 1939.

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COMPLETE SPECIFICATION

Process for Producing Lubricating Oil

ERRATUM

SPECIFICATION No. 503,206.

Page 6, line 16, at the top of the fifth column, *for* " 4 " *read* " 5 "

THE PATENT OFFICE,
August 28*th*, 1939.

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example for producing lubricating oils with very low solidification points a mixture of hydrocarbons consisting of hard and soft paraffins has been proposed as the raw material for the production of the cracked benzine. It was not known however in what manner the viscosity of the lubricating oils produced during condensation could be influenced. In this connection it is of considerable practical importance to be able to influence the viscosity of the lubricating oils, as only in this way can the special oils required for industrial use be produced having the desired qualities and in the desired quantities.

It has been found that the viscosity of the end products can be affected as desired by correctly selecting the quantity of condensation agent, and by correctly selecting the condensation temperature and period. An increase in the quantity of condensation agent, a lowering of condensation temperature, and a lengthening of condensation period increase viscosity, whereas conversely a reduction in the

general working rule.

It has now been found that the condensation of the cracked products to produce lubricating oils can be carried out within much shorter periods if during the first conversion of the cracked benzine a quantity of condensation agents such principally as aluminium chloride to about three to six times as great as hitherto is employed. If the first charge of the cracked benzine to be converted is mixed with about 5% of aluminium chloride instead of with 1%, the condensation of the cracked products to produce lubricating oils is already finished after the expiry of about 12 hours, if within the whole condensation period the condensation temperature is gradually increased from about 20° C. to about 60—80° C. The contact layer left behind after the separation of the upper layer containing the condensation products serves, after re-activation for the conversion of a new charge of cracked benzines by the addition of a small quantity of fresh condensation agent, amounting to about 0.5 to 2%, calculated on the quantity of the added cracked benzine. By maintaining a

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COMPLETE SPECIFICATION

Process for Producing Lubricating Oils

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a Body Corporate organised and existing under 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 produce lubricating oils by condensing liquid products of cracking by means of known condensation agents such as aluminium chloride. Oils are obtained which are viscous in higher or lower degree according to the nature of the material from which they are derived and the reaction conditions. The selection of the initial materials for producing the cracked benzines employed for condensing lubricating oils has also been found to have an influence on the physical properties of the lubricating oil obtained. Thus for example for producing lubricating oils with very low solidification points a mixture of hydrocarbons consisting of hard and soft paraffins has been proposed as the raw material for the production of the cracked benzine. It was not known however in what manner the viscosity of the lubricating oils produced during condensation could be influenced. In this connection it is of considerable practical importance to be able to influence the viscosity of the lubricating oils, as only in this way can the special oils required for industrial use be produced having the desired qualities and in the desired quantities.

It has been found that the viscosity of the end products can be affected as desired by correctly selecting the quantity of condensation agent, and by correctly selecting the condensation temperature and period. An increase in the quantity of condensation agent, a lowering of condensation temperature, and a lengthening of condensation period increase viscosity, whereas conversely a reduction in the quantity of condensation agent, an increase in condensation temperature, and a shortening of condensation period result in the formation of thinner oils, that is to say oils of lower viscosity. The best effect is secured by the combined use of all the factors that influence viscosity, but each individual factor acts in the manner indicated. Thus it is possible to produce from one and the same benzine, oils having either a high or a low viscosity as desired. It is a remarkable fact in this connection that the yield of oil calculated upon the quantity of benzine employed does not vary much, as the Examples hereinafter appearing show, but merely an influence on the viscosity of the lubricating oils obtained is realised. For various cracked benzines it is necessary to determine variously the absolute values, but these always lie within the above-mentioned general working rule.

It has now been found that the condensation of the cracked products to produce lubricating oils can be carried out within much shorter periods if during the first conversion of the cracked benzine a quantity of condensation agents such principally as aluminium chloride to about three to six times as great as hitherto is employed. If the first charge of the cracked benzine to be converted is mixed with about 5% of aluminium chloride instead of with 1%, the condensation of the cracked products to produce lubricating oils is already finished after the expiry of about 12 hours, if within the whole condensation period the condensation temperature is gradually increased from about 20° C. to about 60—80° C. The contact layer left behind after the separation of the upper layer containing the condensation products serves, after re-activation for the conversion of a new charge of cracked benzines by the addition of a small quantity of fresh condensation agent, amounting to about 0.5 to 2%, calculated on the quantity of the added cracked benzine. By maintaining a

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uniform rise of temperature from 20° C. to about 60—80° C. the condensation of the cracked benzines to produce lubricating oils is completed in the course of 12 hours. The contact layer obtained in the conversion of the first charge can be again used frequently after corresponding reactivation. Particularly favourable conditions arise in the use of a cracked benzine that was produced from the products of the benzine synthesis, without pressure, obtained from carbon monoxide and hydrogen according to Fischer-Tropsch.

The invention may be carried out under the conditions indicated in the following Examples in which the raw material consists of cracked benzines which have been produced from the benzines obtained by the hydrogenation of carbon monoxide according to the Fischer-Tropsch process. The working rules referred to are however also applicable in the case of other hydrocarbons containing olefines, for example, in the use of benzines rich in olefines obtained by catalytic de-hydrogenation.

A few examples are first given showing the dependence of the viscosity of the oils obtained on the quantity of condensation agent and on condensation temperature.

In Examples 1 to 5 there are combined five separate experiments, which were carried out one after the other under like conditions. In every case the condensation period was 12 hours. The temperatures employed were different as was also the quantity of condensation agents which were added before the commencement of each conversion. The condensation operation was always carried out in the following manner, that is to say:

15,000 gm. of dried cracked benzine and a determined quantity of fresh aluminium chloride were added in an autoclave to the quantity of the double compound of aluminium chloride produced from the reactions previously carried out by the conversion of cracked benzine with aluminium chloride. The autoclave had a capacity of 50 litres, and was equipped with a stirrer. During the whole condensation period, amounting to 12 hours, the contents of the autoclave were thoroughly stirred and the temperature during this period was raised as indicated in the Examples. The periodic rise of temperature differed in the various Examples. After the expiry of the 12-hour condensation period the autoclave was allowed to cool to room temperature and the contact substance settled to the bottom as an oily layer. The upper layer containing the lubricating oil produced and the benzine not converted to lubricating oil was separated from the contact substance. The upper layer referred to was treated with acid and alkali, then washed with water, and finally dried. The unconverted benzine up to 180° C. was distilled off from the dried reaction product. This distillate is indicated in the following tables as residual benzine. The residue left after distillation under ordinary pressure was thereupon subjected under 5 mm. of mercury to vacuum distillation up to 200° C., the lubricating oil remaining as residue of distillation. The distillate that passes over during the distillation under vacuum is referred to in the following tables as middle oil. The content in the upper layer that contains the reaction products, of residual benzine, middle oil, and lubricating oil, is given in the tables in percentages by weight calculated on the quantity of cracked benzine added. As characteristic of the physical properties of the lubricating oils obtained the viscosities are given at 50° C. and the densities are given at 20° C.

Example 1. Five experiments were carried out in which before commencement of condensation, 0.5% by weight of aluminium chloride calculated on the quantity of benzine used was added to the layer of contact oil. The condensation temperature was raised in stages during the course of each conversion, condensation being carried out for two hours at 20° C., four hours at 50° C. and six hours at 70° C.

The results of the experiments are given in the following tables:

Charge		1 gm.	2 gm.	3 gm.	4 gm.	5 gm.
Quantity of contact oil before conversion		7330	8055	9080	8455	8980
Quantity of contact oil after conversion		8055	9080	8455	8980	15150
Addition of benzine		15000	15000	15000	15000	15000
$AlCl_3$ addition		75	75	75	75	75
Reaction product obtained (upper layer)		14350	14050	15700	14550	15150
Content of residual benzine	of the upper layer	22.6%	22.5%	33.9%	32%	32%
Content of middle oil		21.4%	13.2%	16.0%	14%	20%
Content of lubricating oil		51%	56.6%	54%	48%	48%
Density of lubricating oil at 20° C.		0.858	0.853	0.852	0.852	0.858
Viscosity at 50° C.		8.55° E	8.04° E	8.08° E	7.95° E	8.16° E

EXAMPLE 2. In the next five experiments 1% by weight of aluminium chloride calculated on the quantity of cracked benzine introduced was added to the conversion mixture before condensation commenced, and condensation was carried out for two hours at 20° C., for four hours at 50° C., and for six hours at 70° C. In comparison with Example 1 lubricating oils having a greater viscosity were obtained under like condensation temperatures and periods, by the use of a large quantity of aluminium chloride.

The results are given in the following table:

Charge		1 gm.	2 gm.	3 gm.	4 gm.	5 gm.
Quantity of contact oil before conversion		10150	10500	11100	10800	11180
Quantity of contact oil after conversion		10500	11100	10800	11180	11280
Addition of benzine		15000	15000	15000	15000	15000
$AlCl_3$ addition		150	150	150	150	150
Reaction product obtained (upper layer)		14800	14550	15450	14770	15050
Content of residual benzine	of the upper layer	42.5%	47.3%	36.5%	35.5%	32%
Content of middle oil		11.0%	6.4%	20.0%	10.1%	17.2%
Content of lubricating oil		44.6%	40.2%	43.8%	44.8%	50%
Density of lubricating oil at 20° C.		0.851	0.851	0.852	0.853	0.852
Viscosity at 50° C.		12.5° E	12.15° E	14.2° E	12.12° E	12.4° E

EXAMPLE 3. In the Examples 3 and 4 the same duration of condensation was selected, but with lower condensation temperatures, in both cases condensation being carried on for four hours at 20° C., and for eight hours at 50° C. Examples 3 and 4 differ one from the other by the quantity of condensation agent used. When using a medium quantity of condensation agent to the amount of 1% calculated on the amount of cracked benzine used, lubricating oils were obtained whose viscosity amounted at 50° C. to from 15 to 18° Engler:

Charge		1 gm.	2 gm.	3 gm.	4 gm.	5 gm.
Quantity of contact oil before conversion		17820	18350	18950	19150	19380
Quantity of contact oil after conversion		18350	18950	19150	19380	19980
Addition of benzine		15000	15000	15000	15000	15000
$AlCl_3$ addition		150	150	150	150	150
Reaction product obtained (upper layer)		14620	14550	14950	14920	14550
Content of residual benzine		41.4%	42.8%	33.7%	39.9%	33.8%
Content of middle oil	of the upper layer	10.1%	8.9%	14.55%	7.0%	6.8%
Content of lubricating oil		45.0%	45.0%	50.4%	51.6%	55.3%
Density of lubricating oil at 20° C.		0.862	0.858	—	—	—
Viscosity at 50° C.		18.0° E	15.0° E	15.4° E	17.5° E	18° E

EXAMPLE 4. The working conditions were the same as in the experiments of Example 3, but a larger quantity of aluminium chloride was added to the charges, that is to say 1.3% instead of 1%. By increasing the quantity of condensation agent, oils were obtained which were correspondingly more viscous, having a viscosity at 50° C. of from 20 to 22° Engler:

Charge		1 gm.	2 gm.	3 gm.	4 gm.	5 gm.
Quantity of contact oil before conversion		13810	15210	14910	15510	15990
Quantity of contact oil after conversion		15210	14910	15510	15990	16890
Addition of benzine		15000	15000	15000	15000	15000
$AlCl_3$ addition		200	200	200	200	200
Reaction products obtained (upper layer)		13800	15500	14600	14720	14300
Content of residual benzine		35.1%	39.6%	34%	37.3%	41.6%
Content of middle oil	of the upper layer	7.6%	10.6%	11%	7.4%	3.8%
Content of lubricating oil		47.0%	52.1%	51.6%	53.0%	49.5%
Density of lubricating oil at 20° C.		—	—	—	—	—
Viscosity at 50° C.		20° E	22° E	24.5° E	20.3° E	21° E

Example 5. While maintaining the same condensation period of twelve hours, five experiments were carried out in which the condensation temperature was maintained for two hours at 20° C., for four hours at 50° C. and for six hours at 70° C. The quantity of aluminium chloride added to the charges amounted to 1.3%. The experiments demonstrated that by simultaneously raising the temperature and increasing the quantity of condensation agent, the viscosity of the lubricating oils obtained is increased in larger measure, the lubricating oils obtained having a viscosity of from 15 to 20° Engler at 50° C :

Charge	1 gm.	2 gm.	3 gm.	4 gm.	4 gm.
Quantity of contact oil before conversion	7000	7750	8550	7250	7650
Quantity of contact oil after conversion	7750	8550	7250	7650	8950
Addition of benzine	15000	15000	15000	15000	15000
$AlCl_3$ addition	200	200	200	200	200
Reaction products obtained (upper layer)	14450	14400	16500	14800	13900
Content of residual benzine } of the upper layer	32.0%	31.1%	35.0%	24.6%	24.0%
Content of middle oil } of the upper layer	11.2%	11.0%	12.3%	13.4%	14.6%
Content of lubricating oil } of the upper layer	52.8%	53.6%	62.0%	59.8%	54.1%
Density of lubricating oil at 20° C.	0.858	0.857	0.857	0.856	0.856
Viscosity at 50° C.	20.85° E	18° E	15.8° E	15.5° E	17.8° E

Example 6. The influence of the duration of condensation on the viscosity of the lubricating oils obtained will be clear from the following experiments :

150 gm. of aluminium chloride and 15000 gm. of cracked benzine were added under agitation in an autoclave to 6650 gm. of a layer of contact oil originating from previous experiments. The temperature in the autoclave was first maintained at 20° C. for four hours, then at 50° C. for eight hours. Thereupon the reaction products were allowed to settle and a sample taken from the upper layer. After distilling off the residual benzine and the insufficiently condensed middle oils by an immediate distillation under vacuum, there remained in a yield of 49%, a lubricating oil that at 50° C. had a viscosity of 16.8° Engler. Thereupon at the same temperature of 50° C. the condensation was continued for a further four hours, and a sample taken from the product after the expiry of four hours. This product of the reaction contained 49.4% of lubricating oil which had at 50° C. a viscosity of 19.7° Engler. A further extension of the condensation period by four hours increased the content of lubricating oil in the reaction product to 50.4%, and the lubricating oil obtained had a viscosity of 20.8° Engler. The treatment of the samples taken from the upper layer was carried out in the manner hereinbefore described, by washing with acid, alkali and water and finally drying.

In further experiments employing a like condensation temperature the influence of the condensation period and the quantity of condensation agent on the viscosity of the lubricating oils obtained is demonstrated, that is to say it has been found that by increasing the condensation period and raising the quantity of aluminium chloride, oils that are more viscous are obtained, while by using higher temperatures and shorter condensation periods thin oils of low viscosity are obtained.

EXAMPLE 7. 200 gm. of fresh aluminium chloride and 15000 gm. of cracked benzine are added under agitation to 9520 gm. of a contact oil in an autoclave. For sixty hours the temperature in the autoclave was maintained at 20° C. and the reaction mixture was vigorously stirred. After the reaction had ceased an upper layer containing the reaction products was obtained to the extent of 14650 gm., while 10050 gm. of contact oil used for further conversions remained in the autoclave. When treating the upper layer in the manner described in the preceding examples, 7280 gm. of lubricating oil were obtained whose viscosity was 27.2° Engler at 50° C.

EXAMPLE 8. 8650 gm. of contact oil were mixed with 150 gm. of fresh aluminium chloride and 15000 gm. of cracked benzine in an agitated autoclave. After stirring for 48 hours at 20° C., 14200 gm. of the upper layer were removed from the autoclave. The lubricating oil obtained to the extent of 7290 gm. had a viscosity of 20.5° Engler at 50° C.

EXAMPLE 9. In a similar autoclave 15000 gm. of cracked benzine were caused to react under agitation with 1% by weight of fresh aluminium chloride (100% $AlCl_3$) and 11250 gm. of contact oil, at 50° C., and condensation was stopped after four hours. An upper layer of 15290 gm. was obtained, which gave after treatment 7040 gm. of lubricating oils with a viscosity of 15.5° Engler at 50° C.

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 influencing the viscosity of lubricating oils produced synthetically by the polymerisation of hydrocarbons of the benzine type, by varying the quantity of the condensation agent, the condensation temperature, and the condensation periods, temperatures that lie between 20 and 120° C., and periods of from 12 to 20 hours being employed, wherein a double compound of metal halogenide produced in an initial charge of benzine by the addition of from 3 to 6% of metal halogenide is repeatedly used for further charges while raising the temperature and adding fresh metal halogenide for each charge; for producing oils of low viscosity about 0.5 to 0.7% of metal halogenide being added, for obtaining medium viscosities, from 0.7 to 1% metal halogenide being added, and for obtaining high viscosities over 1% of metal halogenide being added, the metal halogenide being calculated on the quantity of the benzine added.

2. Lubricating oils when prepared by the process according to claim 1, in the manner substantially as hereinbefore described.

Dated this 1st day of October, 1937.

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