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PATENT SPECIFICATION

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2956

COMPLETE SPECIFICATION

Process for the Production of Lubricating Oils

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a Company 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:—

According to the process of the main Patent Application No. 21393/36 (Serial No. 470,534) the raw material for the production of synthetic lubricating oils is mixtures of liquid hydrocarbons produced at ordinary pressure and at moderately high temperatures as a result of the catalytic conversion of mixtures of carbon monoxide and hydrogen in the use of suitable catalysts. These mixtures of hydrocarbons, which consist principally of liquid paraffin hydrocarbons, and liquid olefines, are previously subjected to cracking, the conditions being such that there is produced a mixture of hydrocarbons having a high content of unsaturated hydrocarbons. The products obtained by cracking, which contain a high percentage of unsaturated hydrocarbons but little or no aromatic hydrocarbons, are then wholly or partly—that is to say, after the distilling off of particular fractions in known manner—treated with anhydrous aluminium chloride or other condensing agents, viscous oils being produced by condensation and polymerization. The condensation agent can be repeatedly used for a similar condensation reaction if during the succeeding condensation reactions the condensation temperature is each time correspondingly raised. The much repeated use of the condensation agent already used for fresh condensation reactions reduces in very large measure the consumption of condensation agents. After many repeated conversions with the same catalyst, the effectiveness of the catalyst is finally reduced in such measure that it must be replaced by fresh catalyst, as by further raising the condensation temperature the course of the reaction would be disturbed and the catalyst affected.

[*Price* 1/-]

It has been found that when the catalyst has passed through a number of such temperature stages it can, by the addition of small quantities of fresh catalyst, be put into a condition in which it is again suitable for carrying out a series of condensation reactions commencing with the initial low reaction temperatures. This effect is obtained for example by an addition of 20% of the original quantity of aluminium chloride. The original spent catalyst is thus completely revivified so that it can be used again for repeated condensation conversions, the condensation being carried out again at first at ordinary temperature and the catalyst separated off from the reaction products being again used for further condensations while each time raising the condensation temperature.

It has further been found that if the catalyst greatly deteriorates, a revivifying action can be secured when the catalyst which has been exhausted in repeated condensation reactions is then used with cracked products of a different composition. In this connection the catalyst, which is otherwise already spent, again shows a great condensation capacity, so that with the same charge of catalyst and changing to the low conversion temperatures originally employed a new series of condensation reactions at which the condensation temperature is raised from stage to stage can be carried out.

As cracked products of a different composition it is possible with great advantage to use cracked products of increasing olefine content. By, for example, distillation or mixing, fractions of increasing olefine content are produced from the synthesized benzines which serve as raw material, and, to convert them into lubricating oils the fractions with the lowest olefine content are converted with the condensation agent, for example aluminium chloride, first of all at low or ordinary temperatures. If the efficiency of the catalyst employed is exhausted after several condensations, use is made of the catalyst which is separated each time from the reaction products for converting the fraction with the next highest olefine content. It is in this connection advisable to employ for the new condensation stage correspondingly higher temperatures. If the catalyst has exhausted its activity after a number of similar conversions of the benzine fraction of higher olefine content, it is employed as condensation agent for the conversion of a different benzine fraction having a still higher olefine content. It is at the same time preferable to employ again a suitably raised conversion temperature. It has thus been found that in contradistinction to former experience in connection with the production of synthetic lubricating oils, a certain quantity of catalyst can be used repeatedly as catalyst for the condensation of mixtures of hydrocarbons to produce lubricating oils if with the same catalyst there be converted at rising conversion temperatures successive mixtures of hydrocarbons which have an increasing content of unsaturated hydrocarbons.

The process is explained by means of the following examples:

EXAMPLE 1.

A cracked benzine of specific gravity 0.684 at 20° C. having a content of unsaturated hydrocarbons of 53.3% was employed for the condensation reactions. 1000 gm. of the cracked benzine were converted with 50 gm. of fresh anhydrous aluminium chloride while maintained at ordinary temperature (20° C.) for 21 hours. After the conversion had ceased the reaction mixture separated out into two layers the upper of which, the benzine, contained the lubricating oil produced during condensation. This benzine layer was separated from the lower layer containing the aluminium chloride and double compounds of aluminium chloride. The contact layer amounted to 255 gm. after the first conversion, while 473 gm. of lubricating oil were distilled from the benzine layer. The contact layer separated off was again converted with 1000 gm. of the same cracked benzine at 55° C. for a period of about 24 hours. The contact layer which separated off from the reaction mixture after conversion had ceased was converted at 90° C., 120° C., and 140° C., each time with 1000 gm. of the cracked benzine and for periods of 24 hours. The quantities of lubricating oil obtained in the second to the fifth conversions amounted to 533 gm., 436 gm., 620 gm. and 718 gm. respectively.

After the fifth conversion 10 gm. of fresh anhydrous aluminium chloride were added to the separated off contact layer weighing 437 gm., and in the same way 1000 gm. of the same cracked benzine were converted each time, the conversion reactions being allowed to recommence at normal temperature. In this way the succeeding condensations were carried out at 20° C., 55° C., 90° C. and 120° C. After the ninth conversion 10 gm. of fresh anhydrous aluminium chloride were added to the separated off contact layer, and the tenth, eleventh and twelfth conversions were carried out at 20° C., 55° C. and 90° C. respectively and after the twelfth conversion 10 gm. of fresh anhydrous aluminium chloride were added and the thirteenth and fourteenth conversions carried out at 20° C. and 55° C. respectively. Altogether with a consumption of 80 gm. of aluminium chloride 6.66 kg. of lubricating oil were obtained.

The individual data are shown in the following table:

	1st conversion	2nd conversion	3rd conversion	4th conversion	5th conversion
Quantity of contact substance before conversion	50 gm. $AlCl_3$	255 gm.	347 gm.	497 gm.	493 gm.
Contact layer after conversion	255 gm.	347 gm.	497 gm.	493 gm.	437 gm.
Temperature	20° C.	55° C.	90° C.	120° C.	140° C.
Reaction period	21 hrs.	22 hrs.	21 hrs.	23 hrs.	24 hrs.
Quantity of benzine added	1000 gm.	1000 gm.	1000 gm.	1000 gm.	1000 gm.
Quantity of lubricating oil obtained	473 gm.	583 gm.	436 gm.	620 gm.	718 gm.

	6th conversion	7th conversion	8th conversion	9th conversion
Quantity of contact substance before conversion	437 gm. +10 gm. $AlCl_3$	941 gm.	767 gm.	870 gm.
Contact layer after conversion	941 gm.	767 gm.	870 gm.	822 gm.
Temperature	20° C.	55° C.	90° C.	120° C.
Reaction period	24 hrs.	24 hrs.	24 hrs.	20 hrs.
Quantity of benzine added	1000 gm.	1000 gm.	1000 gm.	1000 gm.
Quantity of lubricating oil obtained	292 gm.	587 gm.	475 gm.	475 gm.

	10th conversion	11th conversion	12th conversion	13th conversion	14th conversion
Quantity of contact substance before conversion	822 gm. +10 gm. $AlCl_3$	924 gm.	895 gm.	888 gm. +10 gm. $AlCl_3$	1041 gm.
Contact layer after conversion	924 gm.	895 gm.	888 gm.	1041 gm.	1108 gm.
Temperature	20° C.	55° C.	90° C.	20° C.	55° C.
Reaction period	22 hrs.	24 hrs.	24 hrs.	24 hrs.	24 hrs.
Quantity of benzine added	1000 gm.	1000 gm.	1000 gm.	1000 gm.	1000 gm.
Quantity of lubricating oil obtained	453 gm.	540 gm.	325 gm.	412 gm.	373 gm.

Example 2.

A cracked benzine fraction of specific gravity 0.708 at 20° C. and having an olefine content of 33.4% is polymerized in the manner described in Example 1 with 50 gm. fresh anhydrous aluminium chloride in five successive conversions at successively higher temperatures of 20° C., 55° C., 90° C., 120° C. and 140° C. Starting with the third conversion the activity of the catalyst lessens so that the contact layer of 405 gm. which has been separated off after the fifth conversion is converted in three further conversions with a cracked benzine of a different composition. The cracked benzine employed during the succeeding condensation reactions had a specific gravity of 0.692 at 20° C. and an olefine content of 45%. 1000 gm. of this second cracked benzine were caused to react at a temperature of 20° C. for 22 hours with the contact layer separated off from the preceding conversion reaction and the experiment was repeated twice, each time with 1000 gm. of the cracked benzine, the temperatures being 55° C. and 90° C. and the contact periods 23 and 25 hours respectively. Altogether 3787 gm. of lubricating oil were obtained for a consumption of 50 gm. of aluminium chloride. As the data given in the following table show, after the eighth conversion the activity of the contact layer was by no means exhausted.

	1st conversion	2nd conversion	3rd conversion	4th conversion	5th conversion
Nature of benzine employed	Cracked benzine I	I	I	I	I
Quantity of contact substance before conversion	50 gm. $AlCl_3$	212 gm.	296 gm.	309 gm.	376 gm.
Contact layer after conversion	212 gm.	296 gm.	309 gm.	376 gm.	405 gm.
Temperature	20° C.	55° C.	90° C.	120° C.	140° C.
Reaction period	21 hrs.	23 hrs.	24 hrs.	22 hrs.	22 hrs.
Quantity of benzine added	1000 gm.	1000 gm.	1000 gm.	1000 gm.	1000 gm.
Quantity of lubricating oil obtained	468 gm.	542 gm.	548 gm.	528 gm.	502 gm.

	6th conversion	7th conversion	8th conversion
Nature of benzine employed	Cracked benzine II	II	II
Quantity of contact substance before conversion	405 gm.	490 gm.	436 gm.
Contact layer after conversion	490 gm.	436 gm.	455 gm.
Temperature	20° C.	55° C.	90° C.
Reaction period	22 hrs.	23 hrs.	25 hrs.
Quantity of benzine added	1000 gm.	1000 gm.	1000 gm.
Quantity of lubricating oil obtained	160 gm.	517 gm.	522 gm.

EXAMPLE 3.

Five fractions having a rising olefine content and a falling specific gravity are obtained by fractional distillation from benzine produced from carbon monoxide and hydrogen at normal pressure:

	Range of boiling points.	Olefine content.	Specific gravity at 20° C.
1st fraction - -	140—200° C.	17.0%	0.7233
2nd ,, - -	35—200° C.	22.7%	0.6975
3rd ,, - -	35—170° C.	28.6%	0.6717
4th ,, - -	25—120° C.	30.0%	0.6670
5th ,, - -	35— 90° C.	33.2%	0.6525

For the purposes of comparison two condensation experiments were conducted with these five benzines, by which the advantage of the method according to the invention is demonstrated.

First Series.

In the first experiment 50 gm. of anhydrous aluminium chloride were brought into reaction with 1000 gm. of the first benzine fraction for 24 hours at room temperature in a vessel provided with stirrers. The reaction mixture separated into two layers. The upper layer, consisting of 938 gm. of benzine, was separated from the lower contact layer which consisted of aluminium chloride and double compounds of aluminium chloride. After the first conversion the contact layer amounted to 112 gm. This layer of catalyst was brought into reaction with 1000 gm. of the second benzine fraction (the fraction with the next highest olefine content) for 24 hours at 55° C. When the conversion had finished the benzine layer weighed 918 gm. and the contact layer 186 gm. The contact layer was converted with 1000 gm. of the third benzine fraction at 90° C. In the same way the fourth and fifth benzine fractions were converted at 130° and 160° C. respectively each time with the contact layer left over. The contact layer each time grew heavier, amounting after the fifth conversion to 290 gm. Similarly the quantities of lubricating oil recovered from the benzine layer by the repeated use of the same contact layer increased from 96 gm. in the first conversion to 192 gm. in the fifth conversion, so that starting with 50 gm. of aluminium chloride a total of 750 gm. of lubricating oil was obtained. The ratio of lubricating oil to aluminium chloride was thus 15 : 1.

	1st conversion	2nd conversion	3rd conversion	4th conversion	5th conversion
Nature of benzine employed	1st fraction	2nd fraction	3rd fraction	4th fraction	5th fraction
Quantity of contact substance before conversion	50 gm. $AlCl_3$	112 gm.	186 gm.	232 gm.	280 gm.
Contact layer after conversion	112 gm.	186 gm.	232 gm.	280 gm.	290 gm.
Temperature	20° C.	55° C.	90° C.	130° C.	160° C.
Reaction period	24 hrs.	24 hrs.	24 hrs.	24 hrs.	24 hrs.
Quantity of benzine added	1000 gm.	1000 gm.	1000 gm.	1000 gm.	1000 gm.
Benzine layer containing lubricating oil after conversion	938 gm.	918 gm.	943 gm.	922 gm.	972 gm.
Quantity of lubricating oil obtained	96 gm.	128 gm.	168 gm.	166 gm.	192 gm.

Second Series.

Again starting with 50 gm. of aluminium chloride, five condensation reactions were carried out at increasing temperatures, with benzine fractions of uncontrolled olefine content. In the first conversion 50 gm. of aluminium chloride were brought into reaction with 1000 gm. of the first benzine fraction for 24 hours at 20° C. After completion of conversion the reaction mixture separated into two layers; the upper layer, the benzine, amounting to 925 gm., and the lower layer, the contact layer, amounting to 127 gm. This contact layer was used for converting 1000 gm. of the fifth benzine fraction during 24 hours at 55° C.; after the reaction had finished the benzine layer amounted to 923 gm. and the contact layer amounted to 201 gm. The contact layer was employed to convert 1000 gm. of the second benzine fraction for the same length of time at 90° C. The weight of the benzine layer increased to 1135 gm. but the contact layer amounted only to 76 gm. In like manner 1000 gm. of each of the fourth and third benzine fractions were brought into reaction in a fourth and a fifth conversion with the contact layer from a preceding operation. The quantities of lubricating oil secured from the benzine layers furnished by the several conversion reactions were very dissimilar, amounting to 86 gm., 143 gm., 116 gm., 47 gm., and 35 gm. respectively. In all, 427 gm. of lubricating oil were obtained in the five condensation reactions, so that, in this case the ratio of lubricating oil to aluminium chloride was only 8.5:1. Comparison with the first series of experiments clearly reveals the advantage of using benzine fractions of progressively increasing olefine content.

The figures are given in the following table:—

	1st conversion	2nd conversion	3rd conversion	4th conversion	5th conversion
Nature of benzine employed	1st fraction	5th fraction	2nd fraction	4th fraction	3rd fraction
Quantity of contact substance before conversion	50 gm. $AlCl_3$	127 gm.	201 gm.	76 gm.	41 gm.
Contact layer after conversion	127 gm.	201 gm.	76 gm.	41 gm.	37 gm.
Temperature	20° C.	55° C.	90° C.	120° C.	160° C.
Reaction period	24 hrs.	24 hrs.	24 hrs.	24 hrs.	24 hrs.
Quantity of benzine added	1000 gm.	1000 gm.	1000 gm.	1000 gm.	1000 gm.
Benzine layer containing lubricating oil after conversion	925 gm.	923 gm.	1135 gm.	1020 gm.	1002 gm.
Quantity of lubricating oil obtained	86 gm.	143 gm.	116 gm.	47 gm.	35 gm.

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. An improvement in or modification of the process claimed in the Specification of Application No. 21393 of 1936 (Serial No. 470,534), characterised in that the spent catalyst is regenerated by the addition of small quantities of fresh catalyst and while commencing with the low conversion temperatures originally employed is again used for carrying out a series of similar condensations in which the reaction temperatures are raised from condensation to condensation.

2. An improvement in or modification of the process claimed in the specification of Application No. 21393/36 (Serial No. 470,534), in which the spent catalyst is used for the condensation of products obtained by the process described but of a different composition.

3. A process as set forth in claim 2, in which the successive products to be condensed comprise fractions of rising olefine contents.

Dated this 19th day of December, 1936.

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Agents for the Applicants.

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