PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in the manufacture and production of Lubricating Oils

We, I. G. FARBENINDUSTRIE AKTIENGESELLSCHAFT, of Frankfort-on-Main, Germany, a Joint Stock Company, organised under the Laws of Germany, 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 that lubricating oils can be obtained from liquid and solid initial materials by polymerisation or condensation with the aid of anhydrous aluminium chloride. Suitable initial materials are for example liquid and solid unsaturated hydrocarbons and these can be polymerised or condensed either alone or together with other reactive substances. Similar lubricating oils are obtained by halogenating saturated or unsaturated solid or liquid hydrocarbons or their oxygen-containing derivatives, as for example alcohols, acids, esters or ketones, and subjecting the resulting halogenation products to the polymerisation or condensation either directly or after the splitting off of hydrogen halide and, if desired, with an addition of other reactive substances, as for example aromatic or heterocyclic compounds, for example naphthalene, anthracene, carbazole, phenol, diphenylene oxide or mixtures thereof.

As suitable liquid and solid unsaturated hydrocarbons we may mention by way of example cracking products, more particularly those from hydrocarbons of the paraffin series, as for example paraffin waxes, hydrocarbon mixtures resulting from the said cracking products by partial polymerisation or condensation, also hydrocarbons or hydrocarbon mixtures obtained by the interaction of oxides of carbon with hydrogen either directly or by conversion of the oxygen-containing compounds first formed, or the cracking products of the said hydrocarbons and, lastly, also olefines or olefine mixtures obtained by the splitting or catalytic reduction of high molecular organic compounds containing oxygen, for example by the dehydratisation of alcohols having a high molecular weight.

As initial materials to be used for the halogenation we may mention for example liquid and solid hydrocarbons, especially such as are substantially of paraffinic nature, as for example hard and soft paraffin waxes, and also high molecular weight fatty acids or their esters (in the case of fatty acids the halogenation may take place in the hydrocarbon radicle as well as in the carboxyl group) or also high molecular weight alcohols, such as can be obtained by the catalytic reduction of fatty acids or their esters.

If, in the condensation of the initial materials above referred to, other reactive materials are added, these may be taken from any desired series. Use may be made, for example, of mineral oils or refined tar oils or their fractions or cracking products, or also of aromatic hydrocarbons or their derivatives or heterocyclic compounds. It is advantageous to select such substances of the said kind as are practically free from impurities containing oxygen or sulphur. If the materials are not in themselves as pure as is desirable, they may be refined in any suitable manner, for example by subjecting them to a destructive hydrogenation under moderate conditions or by a treatment with bleaching earths or with selective solvents or also to a preliminary treatment with agents having a polymerising action, especially aluminium chloride.

We have now found that in these processes the output and the nature of the lubricating oils obtained are considerably influenced by the constructional materials employed for the reaction vessels in which the polymerisation or condensation is carried through, and that, in particular ordinary iron, as for example pig iron or wrought iron, or ordinary non-alloyed steels, have a detrimental effect on the course of the reaction. Consequently, we have found it advisable to construct the reaction vessels of such materials as do not exert an unfavourable catalytic influence on the polymerisation or condensation. Suitable constructional materials which also have the necessary mechanical strength and sufficient stability towards corrosion, are for example chromium-coated iron, chromium, and chromium- or

[Price 1/-]

chromium-nickel-alloyed steels. It is not necessary that the reaction vessel should be completely made of any of the said materials, it being sufficient that the inner parts which come into contact with the reaction materials be made thereof. In any of the said parts, however, the use of ordinary iron or ordinary steels, even in small amounts, must be avoided. The polymerisation or condensation may also be carried through in vessels lined for example with lead, tin or zinc, but these constructional materials have the drawback that their resistance to corrosion is lower than with the materials above referred to.

We have also found that the properties of the aluminium chloride which is employed as the polymerising or condensing agent, more particularly its degree of purity, have also a large influence on the yield and properties of the resulting lubricating oils. Commercial aluminium chloride contains considerable amounts of non-volatile impurities, whether from its preparation or due to a decomposition resulting from exposure to the influence of atmospheric moisture. We have found it advantageous to use as anhydrous aluminium chloride which contains less than 5 per cent., preferably less than 2.5 per cent., of unsublimable residue. In the production and storage of such an aluminium chloride special precautions should be taken to keep the content of non-volatile impurities as low as possible. The use of an aluminium chloride which is particularly pure has a highly favourable effect on the polymerisation or condensation. The improvement thus achieved may result for example in an increase in the output of lubricating oil, or in an improvement in the properties of the oil, or in a reduction of the time of reaction or in a decrease in the amount of aluminium chloride required. In some cases, the separation of the sludge formed during the reaction, which contains aluminium chloride, is also facilitated.

The following Examples will further illustrate how the said invention may be carried out in practice, but the invention is not restricted to these Examples. The parts are by weight.

EXAMPLE 1.

100 parts of a liquid mixture of olefines resulting from the cracking of soft paraffin wax (melting point at 42° Centigrade) in the gas phase at 530° Centigrade are placed in a vessel made of a steel which contains 6 per cent. of chromium, and 8 parts of anhydrous aluminium chloride which contains 0.8 per cent. of non-volatile constituents are added at 80° Centigrade within 30 minutes, while vigorously stirring. 200 parts of a fraction of German crude mineral oil with a boiling point above 350° Centigrade which has been pretreated with a little aluminium chloride are then added and the mixture is vigorously stirred at 45° Centigrade for another 2 hours. The contents of the reaction vessel are then poured into an aqueous common salt solution to destroy the double compounds of aluminium chloride with hydrocarbons and, after removing the salt solution and sludge, the oil is thoroughly washed with water which has preferably been given a small addition of common salt to avoid the formation of emulsions. The oil is then dried and subjected to a fractional distillation *in vacuo* under a pressure of 1 millimetre (mercury gauge). There are obtained, in addition to 15 parts of first runnings, 255 parts of a lubricating oil which on account of its good temperature-viscosity curve is excellently adapted for use as a motor oil. By removing from the oil the constituents boiling up to 285° Centigrade by distillation, a residual oil is obtained which, on account of its high flash point, may be used as hot steam cylinder oil.

EXAMPLE 2.

Chlorine is led into hard paraffin wax (melting point 52° Centigrade) at between 100° and 150° Centigrade, while stirring, until the increase in weight amounts to about 12 per cent. of the weight of the paraffin wax used. The absorption of chlorine may be promoted by the action of light or by the presence of a catalyst, for example iodine. 100 parts of the chlorinated paraffin wax thus obtained are placed in a stirring vessel lined with V2A steel (of the firm of Krupp) and condensed with 10 parts of naphthalene at between 30° and 50° Centigrade in the presence of 10 parts of an anhydrous aluminium chloride containing 1.5 parts of an unsublimable residue and of illuminating oil as a diluent. After cooling, two layers are obtained, the upper of which contains illuminating oil, unchanged paraffin wax and the condensation product. By distilling off the illuminating oil, removing the paraffin wax and eliminating the constituents boiling up to 200° Centigrade at a pressure of 15 millimetres (mercury gauge) from the upper layer, a high grade motor oil is obtained in a yield of about 50 parts.

EXAMPLE 3.

Chlorine is led into paraffin wax obtained from brown coal tar at from 60° to 70° Centigrade until the increase in weight amounts to about 25 to 30 per cent. of the weight of the paraffin wax used. From the chlorinated paraffin wax thus

obtained hydrogen chloride is split off by steam distillation *in vacuo* at a temperature up to 360° Centigrade. 100 parts of the resulting unsaturated product, which is practically free from chlorine, are filled into a stirring vessel made of a steel containing 6 per cent. of chromium and condensed at between 40° and 60° Centigrade by means of 7 per cent. of aluminium chloride containing 1.2 per cent. of an unsublimable residue which is added in small portions. After working up in the usual manner, a high grade cylinder oil is obtained in addition to a solid, high-molecular, non-fusible, insoluble substance which consists of carbon and hydrogen.

EXAMPLE 4.

Stearic acid is converted into stearic acid chloride by treatment with thionyl chloride at 80° Centigrade. 100 parts of the resulting product are dissolved in 100 parts of illuminating oil and filled into a stirring vessel made of steel NCT6 (62.3 per cent. of nickel, 1.75 per cent. of manganese, 12.5 per cent. of chromium and 22.8 per cent. of iron). After adding 20 parts of naphthalene and 7 parts of aluminium chloride containing 1.9 per cent. of non-volatile residue, the mixture is kept at about 30° Centigrade for 24 hours and then heated to 90° Centigrade for another 1 to 2 hours. The resulting condensation product is separated from aluminium chloride by centrifuging and distilled *in vacuo*. The distillation residue consists of 85 parts of a waxy product which is a high quality agent for depressing the pour point of oils.

EXAMPLE 5.

100 parts of soft paraffin wax (melting point 42° Centigrade) are passed at 500° Centigrade in the vapour form over lumps of calcium silicide at such a low speed that a cracking product with an iodine value of 280 is obtained. The said product is introduced into a vessel made of steel which contains 6 per cent. of chromium, whereupon 100 parts of decahydronaphthalene, 10 parts of naphthalene and 8 parts of aluminium chloride with 1.1 per cent. of unsublimable residue are added. After stirring for three hours at 120° Centigrade the contents of the stirring vessel are mixed with water. The solution of aluminium chloride is then separated, any cyclic hydrocarbons present are distilled off and the lower boiling and low-viscosity oils are removed by distillation *in vacuo*. 60 parts of a highly viscous lubricating oil are thus obtained which has a flat temperature-viscosity curve.

EXAMPLE 6.

A petroleum obtained by subjecting brown coal tar to destructive hydrogenation at moderate temperature, having about 85 per cent. of waxy and 15 per cent. of oily constituents is evaporated and the vapours are cracked at between 480° and 525° Centigrade under atmospheric pressure in a column made of V2A steel and filled with turnings of the same steel. The resulting product is fractionally condensed, so that a distillate is obtained which has a final boiling point of about 260° Centigrade. The condensate having a higher boiling point is recycled and cracked together with fresh initial material. The operation is most preferably so conducted that about 10 to 25 per cent. of distillate are obtained with each throughput. The said cracking operation yields 30 per cent. by weight of gas and 70 per cent. by weight of distillate boiling up to 260° Centigrade.

The distillate is introduced into an autoclave made of a steel containing 6 per cent. of chromium and fitted with a stirring mechanism, whereupon about 3 to 4 per cent. of anhydrous aluminium chloride with 0.8 per cent. of a non-volatile residue are added, and the mixture is kept at about 100° Centigrade for 6 hours while stirring carefully. Stirring is then discontinued and the sludge of double compounds of aluminium chloride with hydrocarbons, which amounts to about 7 to 10 per cent. of the starting material, is separated by centrifuging. The oil left is distilled by means of steam. The yield amounts to about 10 per cent. of light distillates and about 90 per cent. of lubricating oil which is after-treated with a small amount of bleaching earth.

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 manufacture and production of lubricating oils which consists in polymerising or condensing, with the aid of anhydrous aluminium chloride, liquid or solid unsaturated hydrocarbons or halogenation products of saturated or unsaturated liquid or solid hydrocarbons or their oxygen-containing derivatives, while employing reaction vessels constructed of materials which do not exert an unfavourable catalytic influence on the polymerisation or condensation.

2. In the process as claimed in claim 1, excluding ordinary iron and ordinary non-alloyed steels from the reaction vessel.

3. In the process as claimed in claim 1 or 2, constructing the reaction vessel of chromium-coated iron, chromium, chromium-alloyed steels or chromium-

nickel-alloyed steels.

4. In the process as claimed in claim 1, 2 or 3, employing an anhydrous aluminium chloride which contains less than 5 per cent. of unsublimable residue.

5. In the process as claimed in claim 1, 2, 3 or 4, employing an anhydrous aluminium chloride which contains less than 2.5 per cent. of unsublimable residue.

6. The process for the manufacture and production of lubricating oils, substantially as described in each of the foregoing Examples.

7. Lubricating oils when prepared by the process particularly described and ascertained or its obvious chemical equivalents.

Dated this 25th day of April, 1938.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

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