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COMPLETE SPECIFICATION

Process for improving 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:—

It has already been proposed to improve lubricating oils by the use of hydrocarbons which are colloidally soluble in the oils. Examples of such hydrocarbons that have been suggested are polystyrol, hydrogenated polystyrol, polyindene, and like substances. Commercially it is very difficult to secure these substances, and complicated chemical processes are necessary to produce them.

It has now been found possible to improve lubricating oils and raise the viscosity of benzines, gas oils and lignite tarry oils, as well as of liquid hydrocarbons obtained by hydrogenation and hydrocarbons resembling benzine obtained by converting carbon monoxide with hydrogen at normal pressure, by the use of products which are obtained in a simple manner by treating gases containing propylene and ethylene with such polymerisation and condensation catalysts as aluminium chloride, iron chloride, zinc chloride and boron fluoride, to which, if required, reaction-accelerating substances such as mercuric chloride, or reaction-retarding substances such as aluminium oxide, water, and zinc oxide, have been added. The polymerisation is carried out at temperatures lying below 0° C. The reaction on the ethylene and propylene may take place in the presence of diluting gases or on the olefines mentioned in a practically pure state. The gases which are treated may be of any suitable kind, and more particularly industrial gases resulting from cracking or coking, or similar gases, and the mixtures of propylene and ethylene may be obtained by treatment with active carbon or by low temperature condensation. It has been found that a particularly suitable commencing substance for obtaining the additional substances is coke oven gas, or a mixture of the olefines present in the coke oven gas. During the reaction of, for example, aluminium chloride on the ethylene and propylene of coke oven gas polymerisation products in a highly viscous state are obtained, which at 100° C. have, for example, a viscosity of 20° Engler. By adding these substances to paraffin oil it is possible to produce a usable lubricating oil from the paraffin oil. For example, very small quantities of the added substances suffice to remove from benzine the property of eating into moving machine elements, such as shafts or pistons, with which the benzine comes into contact. It has furthermore been found that the olefinic raw materials referred to can be converted in a very effective manner and valuable lubricating oils be obtained at the same time by carrying out the polymerisation at temperatures below 0° C. in the presence of the hydrocarbon oils to be improved, with or without the use of super-pressure.

It thus becomes a simple matter to render of use for a very valuable purpose just those two very low olefines which occur in commerce on a large scale as a by-product which hitherto has been practically useless. The action of the catalysts referred to may be carried out at normal pressure or at a higher pressure. It has been recognised as being of importance that in all these cases of the treatment of gases the content of water in the gases reacting on the catalysts be kept as low as possible, as otherwise the catalysts are consumed too quickly. The gases may be dried, for example, by washing with anhydrous glycerine in counter-current, by washing

[*Price* **Price 4s 6d**

with a mixture of glycol and glycerine, or in any other suitable manner. The presence of small quantities of other higher olefinic hydrocarbons does not affect the process.

The improvements obtained by adding the polymerisation product of a mixture of olefines obtained from ethylene and propylene to commercial refrigerator oil are set out in the accompanying Table. These improvements consist in the raising of viscosity and the lowering of the viscosity pole height. The term "viscosity pole height" has the meaning that is attached to it by Prof. Dr. L. Ubbelohde in his work "Zur Viskosimetrie", published by Mineralölforschung, of Berlin, W.8. The greater the pole height of a series of oils the greater is the dependence of the viscosity on temperature and the less valuable is the oil. The best American oils have a pole height of 1.9, Russian oils, for example, 2.6 to 2.7 and very poor oils 3.7. The improvements also include a substantial increase in the resistance to oxidation, which is demonstrated by a corresponding lowering of the coking and tarification coefficients. The solidification point is satisfactory even when a 50% addition of an ethylene-propylene polymerisation product is added to a commerical refrigerator oil, since it lies at – 29° C.

TABLE.

Experiments conducted on a refrigerator oil and its mixtures with a propylene-ethylene polymerisation product.

	Refrigerator oil	Refrigerator oil + 30% polymerisation product.	Refrigerator oil + 50% polymerisation product.	Refrigerator oil + 80% polymerisation product.
Specific gravity				
at 20° C.	0.8924	0.8855	0.8821	0.8771
at 50° C.	0.8699	0.8665	0.8638	0.8602
Viscosity in Centipoises				
at 20° C.	28.5	97	169.6	2340
at 50° C.	7.9	18.86	28.9	188.6
Viscosity in degrees Engler				
at 20° C.	4.34	14.25	25.45	351
at 50° C.	1.73	3.07	4.55	28.9
Viscosity pole height	3.3	3.2	2.9	3.18
Coking coefficient	102	56	32	28
Tarification coefficient	0.43	0.29	0.19	0.04
Solidification point	–55° C.	–37° C.	–29° C.	+1° C.

EXAMPLE 1.

A dry gas mixture containing 37% (by volume) propylene and 15% (by volume) ethylene, obtained from coke oven gas either by low temperature condensation or by adsorption by active carbon with subsequent driving off, is fed into 10 parts of anhydrous aluminium chloride, while stirring is carried on for two to three hours, in a pressure vessel at a pressure of 15 atmospheres super pressure. During this period the pressure vessel is maintained by external agency at a temperature of –30° C. During this time, of 500 parts by weight of gas mixture containing 300 parts by weight of olefines, 150 parts by weight of olefines are polymerised. The precipitated dark brown sticky reaction product is freed in the usual manner from its aluminium chloride by the addition of water. The liquid, which is washed in petroleum ether and dried has, after the solvent has been distilled off, a specific weight of 0.9012 and a viscosity of 21° Engler at 100° .

If one part of this oil be mixed with the same quantity of paraffin oil (specific gravity 0.8670, viscosity 3.68° Engler at 25° C. and 1.9 Engler at 50° C.), the product after the removal of the solvents and after distillation under reduced pressure is a lubricating oil of a specific gravity of 0.8865 at 22° C. with a viscosity of 59.3° Engler at 22° C. a viscosity of 9.8° Engler at 50° C., and a solidification point of -46° C. In the production of lubricating oils by carrying out the polymerisation in the presence of hydrocarbon oils, it has been found that such oils as paraffin oils and petroleum distillates are excellent for the purpose as well as oils secured synthetically from mixtures of carbon monoxide and hydrogen. The mixtures of ethylene and propylene that are obtained by the adsorption of active carbon or by low temperature condensation or by a washing process always contain saturated hydrocarbons. These quickly boiling saturated hydrocarbons during condensation seem to play directly the part of an extracting agent, and cause especially good useful oil to be produced. As catalysts it is possible to employ aluminium chloride, iron chloride, zinc chloride, boron fluoride, and the like. The most suitable polymerisation temperatures have been found to be temperatures of about -30° C. It has been found an advantage to carry away continuously the reaction heat which is generated during the process. It is a very easy matter during the process to separate out the polymerisation products secured from the layers of catalysts so that the catalysts can be used many times, for instance up to ten times, without it being necessary to effect decomposition by the use of water or lye which is otherwise carried out in the usual manner. Active stirring and good distribution have been found to be advantageous. Furthermore, it is in certain circumstances preferable to heat the reaction mixture to room temperature in the presence of catalysts after the most violent reaction at low temperature has died down. It has been found when working under ordinary pressure to be advisable to employ a return-flow cooler cooled to a low temperature, and operating at such low temperatures as to cause the mixtures of ethylene and propylene to condense. The oils secured have a flat viscosity curve resembling Pennsylvanian oils with low tarification and coking co-efficients and suitably placed solidifying points.

EXAMPLE 2.

100 parts by weight of a mixture of hydrocarbon gases obtained from coke oven gas by low temperature cooling, containing 33% (by volume) of C_3H_6, 10% (by volume) of C_2H_4, and the remainder substantially comprising ethane, propane and methane, are fed during five hours while stirring into a mixture of 20 parts of an industrial paraffin oil and 10 parts of an aluminium chloride that has already been used as contact material for the second time for the same process contained in an autoclave in which are maintained a temperature of -30° C. and a super-pressure of 8.5 atmospheres. For ten hours the autoclave is maintained at an internal temperature of -30° C. and thereupon is allowed to revert to room temperature. The pressure thus rises to 28 atmospheres super-pressure. The unconverted gases are expanded as a gas poor in olefines containing 9% (by volume) of C_3H_6 and 6% of C_2H_4. Of 51 parts by weight of olefines introduced, 41 parts by weight are polymerised. The reaction mixture is dissolved in petroleum ether and poured off from the contact substance. Purification is carried out in the solution of petroleum ether with 30% sulphuric acid and 30% caustic soda and then drying is effected. The oil from which the solvents have been removed and having a density of 0.8645, has a viscosity of 105° Engler at 20° C. 17.6° Engler at 50° C. and 3.2° Engler at 100° C. corresponding to a viscosity pole height of 1.77 and a solidifying point of -24° C. The Sligh Test (A.S.T.M. Oxydisation co-efficient) gives 0.2 while the coking value according to Conradson is 0.16.

EXAMPLE 3.

Five hundred and fifty grammes of a gas mixture containing 44% by volume of C_3H_6 and 13% by volume of C_2H_4 are added to 100 gm. of anhydrous aluminium chloride and 200 gm. of industrial paraffin oil in a vessel circular in cross-section cooled to -30% C., the whole representing a liquid volume of 900 cubic cm. After maintaining the temperature for 7 hours, the mixture being stirred all the time, the mixture is allowed to warm to room temperature. The quickly boiling parts that have not yet entered into the reaction are held back during reaction in a return-flow cooler and supplied again continuously to the reaction mixture. After 24 hours the reaction mixture is poured off from the contact substance. Of the olefines present 260 gm. are polymerised. The oil after being cleansed with sulphuric acid and caustic soda (as indicated in Example 2) has a density of 0.8869, a viscosity of

215° Engler at 20° C. 31° Engler at 50° C. and 4.4° Engler at 100° C., corresponding to a viscosity pole height of 1.78 and a sodifying point of –17° C. The Sligh Test (A.S.T.M. Oxydisation co-efficient) gives 0.1 and the Conradson test, a figure of 0.47.

EXAMPLE 4.

One hundred gm. of a synthetically produced hydrocarbon fraction boiling at over 200° C. are added to 50 gm. of aluminium chloride that has already been used four times as contact substance. At a temperature of –30° C. the mixture has added thereto 600 cubic cm. of liquefied gas mixture containing 39% by volume of C_3H_6 and 24% by volume of C_2H_4. After 7 hours the reaction vessel is permitted to warm to room temperature. Of the olefines present 187 gm. are polymerised. The reaction mixture dissolved in petroleum ether is poured off the contact substance. The reaction mixture is cleansed with sulphuric acid and caustic soda. After the quickly boiling constituents have been distilled off the oil with a density of 0.8670 has a viscosity of 318.5° Engler at 20° C., 45.5° Engler at 50° C. and 6.0° Engler at 100° C. corresponding to a viscosity pole height of 1.68. The solidifying point is at –6° C. while the Conradson coking test gives 0.46.

It has been proposed, in Specification No. 293,487, to carry out a process of polymerisation of propylene, ethylene, and like hydrocarbons either singly or in admixture at any desired temperature such as room temperature or under, by means of boron fluoride and under pressure. In the examples no temperature lower than room temperature is specified.

Again, it has been proposed, in Specification No. 358,068, to effect the polymerisation of unsaturated hydrocarbons such as, for example, ethylene, propylene and isobutylene either singly or in admixture at room temperature or at higher or lower temperatures. Thus, when using iso-butylene the temperature may be between –10° C. and 10° C. while in the case of propylene a higher temperature, usually room temperature, is employed if the same end product is desired. The examples relating to the polymerisation of propylene do not, however, specify the use of temperatures other than room temperature.

It has also been proposed, in Specification No. 432,310, to produce highly viscous polymerisation products having a molecular weight above 800 by effecting polymerisation of a fraction of cracked hydrocarbons with an active halide polymerising agent at a temperature below 32° F. Generally, reaction temperatures below 32° F. are preferred when semi-solid products of relatively high molecular weight are desired, while temperatures up to 100° F. may be used for the production of viscous lubricating oil.

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 improving oils and liquid hydrocarbons of the kind hereinbefore indicated by the addition of polymerisation products obtained by treating gases containing ethylene and propylene with polymerising agents, such as aluminium chloride, iron chloride, zinc chloride, and boron fluoride, with or without substances which accelerate or retard the reaction, characterised in that polymerisation is carried out at temperatures lying below 0° C.

2. A process according to claim 1, characterised in that the gases containing mixtures of propylene and ethylene are extracted from industrial gases.

3. A process according to claim 1, characterised in that the gases treated are in such condition or of such composition that they comprise mixtures of ethylene and propylene in a practically pure state.

4. A process for improving hydrocarbon oils, characterised by the polymerisation, in the presence of the oils to be improved, of the propylene and the ethylene in gases which contain propylene and ethylene by the action of catalysts such as aluminium chloride, iron chloride, zinc chloride, boron fluoride and the like at temperatures lying below 0° C. with or without the use of super-pressure.

5. A process according to claim 4, characterised by the use of a return-flow cooler cooled to a low temperature without the use of pressure in the polymerisation of the unsaturated hydrocarbons.

6. A process according to claims 4 and 5, characterised in that the mass is vigorously stirred during the whole reaction while the unsaturated hydrocarbons are being polymerised.

7. A process according to claim 6, characterised in that the reaction mixture is heated to normal temperature after the main reaction has ceased.

Dated this 10th day of July, 1935.
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