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PATENT SPECIFICATION

THE PATENT OFFICE LONDON

799,179

Date of Application and filing Complete Specification: July 20, 1955.

No. 20992/55.

Application made in Germany on Aug. 3, 1954.

Complete Specification Published: Aug. 6, 1958.

Index at acceptance:—Class 2(3), B1A.

International Classification:—C07c.

COMPLETE SPECIFICATION

Process for the Purification of Liquid Hydrocarbon Fractions

We, RUHRCHEMIE AKTIENGESELLSCHAFT, a German Company of Oberhausen-Holten, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the treatment or purification of a liquid hydrocarbon fraction for use in the production of polythene.

In the production of polythene having a molecular weight in excess of 100,000 by means of polymerisation catalysts comprising an organometallic compound at pressures of below 200 kg./sq. c.m. and at temperatures of below approximately 100°C. saturated aliphatic hydrocarbons boiling in the gasoline or diesel oil range are used as liquid medium within which the polymerisation catalysts are suspended or dissolved and the ethylene is polymerised. Hydrocarbon fractions of this kind may be obtained by cracking normally solid or other high molecular weight paraffins and subsequently hydrogenating the cracked products. It is also possible, however, to use hydrocarbon fractions from the Fischer-Tropsch synthesis, the unsaturated constituents in which have been converted into saturated hydrocarbons by hydrogenation. However, hydrocarbon fractions of this kind, particularly those from the Fischer-Tropsch synthesis, contain more or less appreciable proportions of oxygen-containing compounds such as alcohols, esters, or acids. The presence of an oxygen-containing compound, however, is deleterious in the polymerisation of ethylene by means of polymerisation catalysts of the kind referred to, for example, a catalyst consisting of a mixture of diethyl-aluminium monochloride and titanium tetrachloride, and the course of the reaction is severely hindered. These disturbing constituents must, therefore, be carefully removed. Hitherto this has been done by treating the hydrocarbon mixtures at elevated temperature with metallic sodium or with sodium-potassium alloys This necessitates a subsequent distillation step in order to separate the hydrocarbons from the reaction products produced by the treatment with alkali-metal. This method of operation is not entirely without danger and, moreover, is rather cumbersome and adds considerably to the costs by virtue of the consumption of sodium and/or other alkali-metal and the subsequent distillation.

It has now been found, according to the invention, that the purification of the mixtures of saturated aliphatic hydrocarbons containing olefins and oxygen-containing organic compounds as impurities to render them suitable for use as liquid media within which the polymerisation of ethylene can be carried out, can be effected in a simpler and more economic manner by first passing the hydrocarbon mixtures over a hydrogenation catalyst, preferably a nickel-containing catalyst, at a temperature in the range 230°-280°C. preferably at a temperature of about 250°C. subsequently subjecting them to an aftertreatment with solid aluminium chloride at temperatures of below 150°C. and preferably of below 100°C., and then filtering the hydrocarbon mixtures. The temperature of the treatment with the aluminium chloride is preferably not below about normal room temperature. The oxygen content of the hydrocarbon mixture is preferably reduced to below 0.008% (as determined by phenyl isopropyl potassium).

Of course, the hydrogenation of the olefinic constituents in the hydrocarbon fraction effected under the usual conditions can be omitted when applying the working method of the invention. It is expedient to effect a drying of the hydrocarbon mixture with, for example, calcium chloride between the hydrogenation step effected at about 250°C.

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and the treatment with aluminium chloride, in order to reduce the consumption of aluminium chloride.

By the hydrogenation effected at temperatures of about 250°C. all of the oxygen-containing organic compounds are destroyed to an extent such that proof of their presence cannot be obtained by the usual analytical methods (such as the determination of the neutralization number, hydroxyl number, carbonyl number and saponification number). Nevertheless, a hydrocarbon mixture of this kind disturbs the polymerisation of ethylene to a very marked degree. The extent of the adverse effect can be estimated by determining the content of oxygen-containing compounds in the hydrocarbon mixture by means of the highly sensitive reagent, phenylisopropyl potassium. This reagent is decolorised by oxygen compounds. Oxygen contents of as high as 0.01 % to 0.04% were shown by the hydrocarbons which had merely been pretreated by hydrogenation at 250°C., when the determination of the oxygen was carried out by means of phenyl-isopropyl potassium, whereas the oxygen contents of the hydrocarbons were given as zero when determined by the usual methods, such as the methods hereinbefore referred to. When, in contrast to this, a hydrocarbon mixture pre-purified by hydrogenation at 250° C. is treated with solid aluminium chloride, the oxygen content of the mixture is generally between 0.003% and 0.005% (as determined by phenyl-isopropyl potassium). Such an oxygen content does not deleteriously effect the course of the reaction in the polymerisation of ethylene.

The combination of the steps of hydrogenation at a temperature of about 250°C. with the treatment with aluminium chloride, results in only minor operational costs. The consumption of aluminium chloride is extremely low since only minor residual amounts of oxygen-containing compounds are to be removed. The method of operation in accordance with the invention results even in higher degrees of purity than those obtained by the known treatment of the hydrocarbon fraction with metallic sodium, in which the oxygen content has only been lowered to from 0.008% to 0.010%.

When, deviating from the method of operation according to the invention, the hydrocarbon mixture is only given a treatment with aluminium chloride without the preceding hydrogenation, then not only is the consumption of aluminium chloride be considerably increased, but, also, the olefinic hydrocarbons would be lost by the formation of polymers. Moreover the hydrocarbon mixture treated in this manner, as in the treatment with sodium, would then have to be separated from these polymers by distillation since the polymers would otherwise be introduced into the polyethylene from which they could be removed only with great difficulty. Similar conditions would also be encountered if the olefinic hydrocarbons, deviating from the method according to the invention, were previously to be converted into saturated hydrocarbons by means of a hydrogenation effected in the conventional manner with, for example, nickel catalysts at temperatures of about 150°C. Although, by such a hydrogenation at elevated temperatures, the olefins are quantitatively hydrogenated, the oxygen-containing organic compounds undergo practically no change so that polymer formation and an increased consumption of aluminium chloride is again encountered in the subsequent treatment with aluminium chloride. This results in higher costs due to the consumption of aluminium chloride and the distillation, so that no improvement is obtained as compared with the known pretreatment with sodium.

The hydrogenation step according to the invention may be effected with the conventional hydrogenation catalysts, such as with cobalt or nickel-containing catalysts. It is possible to operate with suspended catalysts, but the hydrogenation is preferably effected with stationary catalysts through which the hydrocarbon mixture is passed upwardly or downwardly. The hydrogenation may be effected at pressures of as low as normal atmospheric pressure. It is advantageous, however, to use somewhat elevated pressures such as 20-50 kg./sq. cm. No advantage is obtained by the use of still higher pressures.

The treatment with solid aluminium chloride may be effected in any suitable manner. The hydrocarbon mixture may, for example, be treated with solid pulverulent aluminium chloride in a vessel provided with a stirrer. It is more convenient, however, to pass the hydrocarbon mixture upwardly through a tower filled with solid, lumpy aluminium chloride. After the treatment with aluminium chloride, the hydrocarbon mixture must be filtered. No distillation of the product is required.

The invention is illustrated by the following example.

EXAMPLE

A saturated aliphatic hydrocarbon fraction from the Fischer-Tropsch synthesis, containing olefins and oxygen-containing organic compounds as impurities and boiling between 100°C. and 200°C., was passed upwardly through a pressure-resistant tube of a diameter 50 mm. and a length 6 metres packed with a solid nickel catalyst. The composition of the catalyst was:

100 parts Ni
50 parts kieselguhr
10 parts MgO

The tube was heated by means of an oil jacket, the temperature being adjusted to 250°C. The experiment was carried out at a hydrogen pressure of 30 kg./sq. cm. with the hydrocarbon mixture being passed through at a rate of 5 litres per hour. The pressure on the hydrocarbon mixture issuing from the tube was released, and the mixture was cooled to about 20°C. Thereafter, it was dried by passing it upwardly through a tube of 100 mm. diameter and 4 metres in length filled with solid lumpy calcium chloride. The dried mixture was then passed upwardly through a tube of 100 mm. diameter and 4 metres length filled with solid lumpy aluminium chloride, after which the hydrocarbon mixture was filtered. The determination of oxygen content of the hydrocarbon mixture by means of phenyl-isopropyl potassium gave the following results:

1) After hydrogenation and drying and before treatment with aluminium chloride: 0.020%

2) After treatment with aluminium chloride 0.004%

WHAT WE CLAIM IS:—

1. A process for the treatment of a saturated aliphatic hydrocarbon fraction containing olefins and oxygen-containing organic compounds as impurities, which comprises subjecting the hydrocarbon fraction to hydrogenation in the presence of a hydrogenation catalyst at a temperature in the range 230°-280°C., treating the hydrocarbon fraction with solid aluminium chloride at a temperature below 150°C. and thereafter filtering the hydrocarbon fraction.

2. A process for the purification of a liquid mixture of saturated aliphatic hydrocarbons containing olefins and oxygen-containing organic compounds as impurities prior to use as a liquid medium within which ethylene is polymerised, which comprises passing the hydrocarbon mixture together with hydrogen over a nickel-containing hydrogenation catalyst at a temperature in the range 230°-280°C. subjecting the hydrocarbon mixture to treatment with solid aluminium chloride at a temperature below 150°C., and thereafter filtering the hydrocarbon mixture.

3. A process according to Claim 1 or Claim 2, in which the first step is effected at a temperature of about 250°C.

4. A process according to any one of the preceding claims, in which the treatment with aluminium chloride is effected at a temperature below 100°C.

5. A process according to any one of the preceding claims, in which the treatment with aluminium chloride is effected at a temperature not below about normal room temperature.

6. A process according to any one of the preceding claims, in which the first step is effected at a pressure in the range 20-50 kg./sq. cm.

7. A process according to any one of the preceding claims, in which the hydrocarbon mixture of fraction from the first step is dried prior to the treatment with aluminium chloride.

8. A process according to Claim 7, in which the drying is effected with calcium chloride.

9. A process for the treatment of a saturated hydrocarbon fraction boiling in the gasoline and/or diesel oil range and containing oxgen-containing organic compounds as impurities, which comprises subjecting the fraction to hydrogenation in the presence of a hydrogenation catalyst at a temperature in the range 230°-280°C. and thereafter contacting the fraction with solid aluminium chloride at a temperature below 150°C., to lower the oxygen content of the fraction to below 0.008%.

10. A process for the treatment of a saturated aliphatic hydrocarbon fraction, substantially as hereinbefore described with reference to the Example.

11. A hydrocarbon fraction whenever treated by the process claimed in any one of the preceding claims.

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Printed for Her Majesty's Stationery Office by Wickes & Andrews, Ltd., E.C.4. 684/2.—1958.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.