[Second Edition.]

PATENT SPECIFICATION

Application Date : Feb. 27, 1935. *No. 6258/35.* **449,274**

Complete Specification Left : Jan. 9, 1936.

Complete Specification Accepted : June 24, 1936.

PROVISIONAL SPECIFICATION.

Improvements in the Manufacture and Production of Hydrocarbons of High Boiling Point.

I, JAMES YATE JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organized under the Laws of Germany) to be as follows:—

A process has already been proposed for the carrying out of reactions with carbonaceous gases or liquids which are converted into vapours under the reaction conditions, without the formation of substances of high molecular weight at elevated temperatures and under pressures higher than 20 atmospheres, in particular for the conversion of middle oils into benzine-like hydrocarbons by destructive hydrogenation and for the production of oxygen derivatives of hydrocarbons by the interaction of the oxides of carbon with hydrogen, in which such large amounts of hydrocarbons which are liquid and stable under the reaction conditions and which do not take part in the reaction of the said carbonaceous materials are added before or during the reaction that the reaction proceeds within the said liquid substances. It has also been proposed to prepare alcohols of high molecular weight from carbon monoxide and hydrogen by treatment under pressure at about 400° Centigrade, the separation of solid substances on the catalyst being prevented by the addition of oils of high boiling point.

My foreign correspondents have now found that in the interaction of oxides of carbon with hydrogen valuable hydrocarbons having a higher molecular weight than benzine, in particular paraffins and lubricating oils, can be obtained by carrying out the reaction in the presence of the said hydrocarbons which are liquid under the reaction conditions and which do not take part in the reaction at pressures of more than 20 atmospheres and at temperatures below 375° Centigrade, advantageously at from 150° to 300° Centigrade.

[*Price* 1/-]

As catalysts may be mentioned those which are known to promote the formation of hydrocarbons and oxygen derivatives of hydrocarbons in the interaction of the oxides of carbon with hydrogen, such as the metals or oxides of the 6th group of the periodic system and of the iron group, and also, for example, titanium, zinc, copper, vanadium, aluminium, manganese or their oxides or mixtures of these substances. Thus for example mixtures of iron, copper and manganese; chromium, zinc and manganese; or iron, copper and zinc; or compounds of the said elements may be employed as catalysts. The sulphides of the heavy metals have also proved suitable. The catalysts are preferably activated, as for example by treatment with alkali or halogen or halogen hydrides or by the addition of rare earths or silver or their compounds. If desired, the said substances may be applied to carriers. The gases must be more or less purified before the reaction, depending on the sensitivity of the catalysts to poisoning.

The following Example will further illustrate the nature of this invention but the invention is not restricted to this Example.

EXAMPLE.

A mixture of hydrogen and carbon monoxide in which hydrogen is present in large excess is heated at 250° Centigrade under a pressure of 50 atmospheres together with anthracene oil in which a catalyst consisting of zinc oxide, magnesia and iron is suspended. After separation of the anthracene oil from the resulting products by distillation or by treatment with liquid sulphur dioxide or by other suitable methods a mixture of hydrocarbons of high molecular weight, consisting mainly of paraffin wax and lubricating oil, is obtained.

Dated this 27th day of February, 1935.

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

COMPLETE SPECIFICATION.

Improvements in the Manufacture and Production of Hydrocarbons of High Boiling Point.

We, COUTTS & COMPANY, a Company with unlimited liability, incorporated under the Companies' Act, of 440, Strand, in the County of London, and FREDERICK JOHNSON, a British Subject, of 218, Victoria Drive, Eastbourne, in the County of Sussex, legal representatives of JAMES YATE JOHNSON, deceased, late of 47, Lincoln's Inn Fields, in the County of London, do hereby declare the nature of this invention (which has been communicated from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organized under the Laws of Germany) and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

In the prior Specification No. 328,586 a process has already been proposed for the carrying out of reactions with carbonaceous gases or liquids which are converted into vapours under the reaction conditions, without the formation of substances of high molecular weight, at elevated temperatures and under pressures higher than 20 atmospheres, in particular for the conversion of middle oils into benzine-like hydrocarbons by destructive hydrogenation and for the production of oxygen derivatives of hydrocarbons by the interaction of the oxides of carbon with hydrogen, in which such large amounts of hydrocarbons which are liquid and stable under the reaction conditions and which do not take part in the reaction of the said carbonaceous materials are added before or during the reaction that the reaction proceeds within the said liquid substances. It has also been proposed to prepare alcohols of high molecular weight from carbon monoxide and hydrogen by treatment under pressure at about 400° Centigrade, the separation of solid substances on the catalyst being prevented by the addition of oils of high boiling point.

Our foreign correspondents have now found that in the interaction of carbon monoxide with hydrogen, valuable hydrocarbons having a higher molecular weight than benzine, in particular paraffin waxes and lubricating oils, can be obtained by carrying out the reaction in the presence of the said hydrocarbons which are liquid under the reaction conditions and which do not take part in the reaction, such as hydrocarbons of high boiling point of an aromatic character, as for example anthracene oil, at pressures of more than 20 atmospheres and at temperatures below 375° Centigrade, advantageously at from 150° to 300° Centigrade. Pressures of 50, 70, 100, 150, 200 or even more atmospheres may be employed.

As catalysts may be mentioned those which are known to promote the formation of hydrocarbons and oxygen derivatives of hydrocarbons in the interaction of the oxides of carbon with hydrogen, such as the metals or oxides of the 6th group of the periodic system and of the iron group, and also, for example, titanium, zinc, copper, vanadium, aluminium, manganese or their oxides or other compounds or mixtures of these substances. Thus for example mixtures of iron, copper and manganese; chromium, zinc and manganese; or iron, copper and zinc; or of the compounds of the said elements may be employed as catalysts. The sulphides of the heavy metals have also proved suitable. The catalysts are preferably activated, as for example by treatment with alkali or halogen or halogen hydrides or by the addition of rare earths or silver or their compounds. If desired, the said substances may be applied to carriers. The gases must be more or less purified before the reaction, depending on the sensitivity of the catalysts to poisoning.

The process may be carried out by adding the catalyst in a state of fine dispersion to the liquid medium. The catalyst may also be arranged in a fixed position for example in tubes or pockets of wire gauze which may be fixed to a stirring device.

Care should preferably be taken that the liquid medium is vigorously stirred and that there is always a fresh supply of liquid medium in the reaction chamber.

It is advantageous to work in such manner that the liquid in the reaction chamber is continuously removed therefrom and conducted back again into the same while avoiding cooling, and in this manner, if desired, a greater quantity of reaction gas can also be pumped in with it. The sulphur and oxygen contents of the circulating liquid are thus very small since these elements are carried away in the form of volatile compounds by the effluent gases. A hot gas cycle may also be employed. The quantity of products leaving with the unused

gases may be readily regulated by the quantity of gas introduced.

The initial gases are suitably introduced into the reaction chamber in a state of fine dispersion, for example through fine nozzles or through solid porous masses.

The liquid medium may be renewed continuously or at intervals, for example by removing the liquid from the reaction chamber through a filter so that the catalyst remains in the reaction chamber, separating any undesirable substances from the liquid medium and then recycling the latter into the reaction chamber or by partially or wholly removing the liquid mass from the reaction chamber, separating the catalyst from the liquid and returning the former to the reaction chamber, if desired after a regeneration which may be carried out with or without the employment of pressure for example by grinding in a high speed mill.

The added liquid medium may be separated from the resulting products by distillation or by extraction with a selective solvent, such as sulphur dioxide, or by any other suitable method.

The ratio of hydrogen to carbon monoxide in the initial gas is that usually employed for the conversion of these gases into hydrocarbons. The duration of treatment, which depends on the particular conditions of catalysts, pressure and temperature employed, is also of the same order as that commonly used for the conversion of carbon monoxide and hydrogen into hydrocarbons.

The following Example will further illustrate how this invention may be carried out in practice but the invention is not restricted to this Example.

EXAMPLE.

A mixture of hydrogen and carbon monoxide in which hydrogen is present in large excess is heated at 250° Centigrade under a pressure of 50 atmospheres together with anthracene oil in which a catalyst consisting of zinc oxide, magnesia and iron is suspended. After separation of the anthracene oil from the resulting products by distillation or by treatment with liquid sulphur dioxide or by other suitable methods a mixture of hydrocarbons of high molecular weight, consisting mainly of paraffin wax and lubricating oil, is obtained.

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 conversion of mixtures of carbon monoxide and hydrogen into valuable hydrocarbons having a higher molecular weight than benzine which comprises heating such mixtures in the presence of catalysts promoting the conversion of carbon monoxide and hydrogen into hydrocarbons and under a pressure of more than 20 atmospheres to a temperature below 375° Centigrade, preferably between 150° and 300° Centigrade, while within a medium of hydrocarbons which remain liquid under the reaction conditions.

2. In the process as claimed in claim 1, operating in the presence of a hydrocarbon of high boiling point of aromatic character, preferably anthracene oil, as the medium remaining liquid under the reaction conditions.

3. The process for the conversion of mixtures of carbon monoxide and hydrogen into valuable hydrocarbons substantially as described in the foregoing Example.

4. Hydrocarbon mixtures when obtained by the process as particularly described and ascertained.

Dated this 9th day of January, 1936.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
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Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 8138.—50/5/1939.]