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PATENT SPECIFICATION

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1778

PROVISIONAL SPECIFICATION

Improvements in the Cracking or Pressure Hydrogenation of Hydrocarbons

I, George William 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, organised under the Laws of Germany) to be as follows:—

My foreign correspondents have found that in the cracking and/or pressure hydrogenation of hydrocarbons rich in hydrogen which contain more than 15 grams of hydrogen per 100 grams of carbon, as for example hydrocarbons obtained by the reduction of carbon monoxide or other corresponding hydrocarbons rich in hydrogen, high yields of benzine, or under less strongly cracking conditions, of Diesel oil rich in hydrogen can be obtained and the formation of large amounts of gaseous hydrocarbons otherwise occurring in the cracking or cracking hydrogenation of hydrocarbons rich in hydrogen can be avoided, by using for the cracking or pressure hydrogenation catalysts known to be highly active, the activity of which has been considerably weakened by use in the cracking or pressure hydrogenation of carbonaceous substances poor in hydrogen in the liquid or, preferably, in the gaseous phase, in the latter case by using an oil pressure above the usual, preferably above 10 atmospheres, the total pressure being about 200 atmospheres or more, a temperature about 50° to 100° Centigrade above the optimum cracking or pressure hydrogenation temperature and/or by use for a very long time.

As highly active catalysts for the said treatment of carbonaceous substances poor in hydrogen there may be mentioned, especially for cracking, in particular substances containing silicic acid, preferably those simultaneously containing alumina, as for example natural aluminium hydrosilicates, such as bleaching earths or synthetically produced substances of the kind described for example in the specifications Nos. 23093 and 23340 A.D. 1937 (504,614 and 501,736), or catalysts of similar kinds. Highly active catalysts for the pretreatment pressure hydrogenation are in particular heavy metal sulphides, especially the sulphides of metals of the 5th and 6th groups of the periodic system or the iron group, or also the oxides of metals of the 5th to the 7th groups or mixtures of these substances.

The highly active catalysts are for example first used for cracking or for cracking or refining pressure hydrogenation of initial materials poor in hydrogen, such as tars, tar oils asphalt-basic or mixed-basic crude oils or their high boiling fractions or high boiling point pressure hydrogenation or extraction products of coals or peat in the liquid phase, at least for several hours and preferably for several days or even for longer periods. A decrease in the activity of the catalyst should thus take place without the deposition of asphalt on the catalyst.

Before using the catalysts for the substances rich in hydrogen, they may also be used in the working up of substances poor in hydrogen, as for example tar middle oils, in the gas phase, the oil partial pressure being more than is usual for cracking or pressure hydrogenation in the gas phase, preferably more than 10 atmospheres, as for example 15 atmospheres or more, the total pressure being about 200 atmospheres or more. The oil partial pressure may be adapted to the hydrogen content of the initial material in such a manner that initial materials richer in hydrogen can be worked up at higher oil partial pressure. When working up petroleum middle oils poor in hydrogen it preferably amounts to more than 20 atmospheres.

The catalyst is used in the said treatment of initial materials poor in hydrogen until its activity has been reduced to such an extent that even when the catalyst is used again for the cracking or pressure hydrogenation of other kinds of initial material it does not again attain its original value.

The oil partial pressure and the temperature in the pressure hydrogenation of initial materials poor in hydrogen may also be kept within the usual limits, but

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then a long period of use, for example six months or more, is necessary before the catalyst can be used for the working up of substances rich in hydrogen.

The catalysts used in the treatment of substances poor in hydrogen are used for the cracking or pressure hydrogenation of substances rich in hydrogen, as for example middle oils or lubricating oils. Such catalysts are especially suitable for the cracking or hydrogenation of the hydrocarbons obtained by the reduction of carbon monoxide with hydrogen which are known for example under the name "Kogasine". Thus, with a small formation of gaseous hydrocarbons, benzines are obtained in a good yield, or when working under less strongly cracking conditions, in particular while simultaneously supplying hydrogen under pressure, good Diesel oils rich in hydrogen are obtained. The catalysts used for the treatment of substances poor in hydrogen are also suitable for the refining pressure hydrogenation of impure hydrocarbons very rich in hydrogen, as for example of reduction products of carbon monoxide which contain small amounts of organic oxygen compounds.

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

EXAMPLE.

A tar oil boiling from about 200° to 400° Centigrade is led at 410° Centigrade together with hydrogen under a pressure of 200 atmospheres with a partial pressure of tar oil of 13 atmospheres over tungsten disulphide rigidly arranged in a reaction vessel for three days. The activity of the catalyst is thus reduced by about 25 per cent. A hydrocarbon mixture obtained by the reduction of carbon monoxide and boiling between 200° and 325° Centigrade is then led over the same catalyst at the same temperature and at the same pressure. A product consisting to the extent of 70 per cent. of benzine is obtained. Only 6 per cent. of the initial material are converted into gaseous hydrocarbons.

Dated this 8th day of April, 1938.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

COMPLETE SPECIFICATION

Improvements in the Cracking or Pressure Hydrogenation of Hydrocarbons

I, GEORGE WILLIAM 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, organised 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:—

My foreign correspondents have found that in the cracking and/or pressure hydrogenation of hydrocarbons rich in hydrogen which contain more than 15 grams of hydrogen per 100 grams of carbon, as for example hydrocarbons obtained by the reduction of carbon monoxide or other corresponding hydrocarbons rich in hydrogen, high yields of benzine, or under less strongly cracking conditions, of Diesel oil rich in hydrogen can be obtained and the formation of large amounts of gaseous hydrocarbons otherwise occurring in the cracking or cracking hydrogenation of hydrocarbons rich in hydrogen can be avoided, by using for the cracking or pressure hydrogenation catalysts known to be highly active, the activity of which has been considerably weakened, for example by about 25 per cent., by use in the cracking or pressure hydrogenation of carbonaceous substances poor in hydrogen. The initial treatment with hydrocarbons poor in hydrogen to reduce the activity of the catalyst may be carried out in the liquid or, preferably, in the gaseous phase. In the latter case the treatment is preferably carried out with partial pressures of oil vapour higher than those normally used for carrying out the hydrogenation of such materials and preferably above 10 atmospheres and at a total pressure of about 200 atmospheres, or more, at temperatures about 50° to 100° Centigrade above the temperatures normally used for the cracking or pressure hydrogenation of such materials and/or continuing the treatment for a sufficient time until the activity of the catalyst is reduced to a suitable degree, for example by about 25 per cent.

As highly active catalysts which may have their activity reduced by this pretreatment there may be mentioned, especially for cracking, in particular substances containing silicic acid, preferably those simultaneously containing alumina, as for example natural aluminium hydrosilicates, such as bleaching earths or artificially produced substances of a similar kind. Highly active catalysts which may have their activity reduced by the pretreatment pressure hydrogenation are in particular heavy metal sulphides, especially the sulphides of metals of the 5th and 6th groups of the periodic system or the iron group, or also the oxides of metals of the 5th to the 7th groups or mixtures of these substances.

The highly active catalysts are for example first used for a cracking process or for a cracking or refining pressure hydrogenation of initial materials poor in hydrogen, such as tars, tar oils, asphalt-basic or mixed basic crude oils or their high boiling fractions or high boiling point pressure hydrogenation or extraction products of coals or peat in the liquid phase, the time of use continuing for at least several hours or better for several days or even for longer periods. The conditions under which the cracking or pressure hydrogenation is carried out should be such that a decrease in the activity of the catalyst takes place without the deposition of asphalt on the catalyst.

The catalysts may also be reduced in activity by employment in the working up of substances poor in hydrogen, as for example tar middle oils, in the gas phase with a greater oil vapour partial pressure than is usual for cracking or pressure hydrogenation in the gas phase, preferably of more than 10 atmospheres, as for example 15 atmospheres or more. The oil vapour partial pressure varies directly with the hydrogen content of the initial material so that the higher the hydrogen content of the initial materials, the greater are the partial pressures of oil vapours used. Thus when working up petroleum middle oils (gas oils) poor in hydrogen it preferably amounts to more than 20 atmospheres.

The catalyst is used in the said treatment of initial materials poor in hydrogen until its activity has been reduced to such an extent that even when the catalyst is used again for the cracking or pressure hydrogenation of other kinds of initial materials it does not again attain its original value.

When the oil vapour partial pressure and the temperature in the pressure hydrogenation of initial materials poor in hydrogen is kept within the usual limits, a long period of use, for example six months or more, is necessary before the catalyst activity is so much reduced that the catalyst becomes suitable for use for the working up of substances rich in hydrogen in accordance with this invention.

The catalysts of reduced activity obtained by the treatment of substances poor in hydrogen may be used subsequently according to the present invention for the cracking or pressure hydrogenation of substances rich in hydrogen, as for example middle oils or lubricating oils, and are especially suitable for the cracking or hydrogenation of the hydrocarbons obtained by the reduction of carbon monoxide with hydrogen, as for example the so-called "Kogasine". Thus, with a small formation of gaseous hydrocarbons, benzines are obtained in a good yield, or when working under less strongly cracking conditions, in particular while simultaneously supplying hydrogen under pressure, good Diesel oils rich in hydrogen are obtained. The catalysts are also suitable for use in the refining pressure hydrogenation of impure hydrocarbons very rich in hydrogen, as for example reduction products of carbon monoxide which contain small amounts of organic oxygen compounds.

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

EXAMPLE.

A tar oil boiling from about 200° to 400° Centigrade is led at 410° Centigrade together with hydrogen under a pressure of 200 atmospheres with a partial pressure of tar oil of 13 atmospheres over tungsten disulphide rigidly arranged in a reaction vessel for three days. The activity of the catalyst is thus reduced by about 25 per cent., which means that in order to obtain the original result the speed of the vapours and gases led through the vessel must be reduced by about 25 per cent. A fraction of a hydrocarbon mixture boiling between 200° and 325° Centigrade of an oil obtained by the reduction of carbon monoxide is then led over the same catalyst at the same temperature and at the same pressure. A product consisting to the extent of 70 per cent. of benzine is obtained. Only 6 per cent. of the initial material are converted into gaseous hydrocarbons.

It has already been known in the aromatising hydrogenation of middle oils for the production of high grade anti-knock benzines, to submit the material first to a non-aromatising hydrogenation treatment and to use as catalyst for the second stage of aromatising destructive hydrogenation, catalysts which have been used for the previous non-aromatising hydrogenation stage for such a time that their activity has been reduced by a considerable amount.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. A process for the catalytic conversion of hydrocarbons containing more than 15 grams of hydrogen per 100 grams of carbon, comprising subjecting them to a cracking treatment or to a hydrogenation treatment under pressure in the presence of an initially highly active catalyst the activity of which has been reduced for example by about 25 per cent. by its employment in a cracking or pressure hydrogenation treatment of carbonaceous substances poor in hydrogen.

2. A process as claimed in claim 1, in which the hydrocarbon containing more than 15 grams of hydrogen per 100 grams of carbon is a product of a catalytic reduction of carbon monoxide with hydrogen.

3. A process as claimed in claim 1, in which the activity of the initially highly active catalyst has been reduced by cracking or pressure hydrogenation of a hydrocarbon oil poor in hydrogen under a total pressure of at least about 200 atmospheres and an oil-vapour partial pressure of more than 10 atmospheres at a temperature of 50° to 100° Centigrade above the normal temperature for cracking such materials and/or for a considerable time.

4. The process for converting hydrocarbons substantially as described in the foregoing Example.

5. Hydrocarbons when obtained by the process particularly described and ascertained.

Dated this 4th day of April, 1939.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

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