Second Edition.]

PATENT SPECIFICATION

502,961

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1222

PROVISIONAL SPECIFICATION.

Improvements in the Manufacture and Production of Carbon Compounds poor in Hydrogen.

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 carbon compounds poor in hydrogen can be obtained from those richer in hydrogen by heating to sufficiently high temperatures in an advantageous manner by using catalysts which contain mixtures of alumina with a smaller amount of a metal of the 6th group or one of its compounds.

The metal of the 6th group or its compounds are preferably used in an amount of from 0.5 to 40 per cent. in particular from 2 to 30 per cent. calculated with reference to the mixture with alumina.

If the amount of the same is more than 40 per cent. in the total catalyst, there is a diminution in yield which becomes greater as the alumina content diminishes.

Metals of the 6th group include molybdenum and chromium and their oxides in particular. There may also be mentioned tungsten and uranium and their compounds, among the latter of which the oxides should be mentioned in particular. These may be regenerated in a very simple manner after use.

The alumina serving as the preponderating component of the catalyst is advantageously used in admixture with activated, water-soluble alumina obtained, for example, according to the British specification No. 441,384.

The catalyst may be applied to carriers, as for example active carbon, lignite small coke, bleaching earths, as for example Florida earth or fuller's earth, which if desired may have been pretreated with acids, such as halogen hydracids, as for example hydrofluoric acid, or also sulphuric acid or nitric acid.

As initial materials there may be mentioned in particular aliphatic hydrocarbons, such as pentane, hexane, heptane, octane and the like or mixtures of the same, and also benzines which have been obtained by reduction of carbon monoxide or from petroleums or by destructive hydrogenation of carbonaceous substances, or benzines which have been prepared from benzines poor in hydrogen by treatment with selective solvents for cyclic compounds. Aliphatic middle oils are also suitable.

The reaction is carried out at temperatures above about 250° Centigrade, preferably between 350° and 500° Centigrade. It may be carried out even at atmospheric pressure, but also at increased pressures, as for example from 3 to 50 atmospheres or more; the presence of hydrogen is not essential.

The reaction products obtained may be treated with selective solvents and the fractions rich in hydrogen again subjected to the present process.

By the said method of working it is possible to obtain benzene and its homologues, as for example toluene from heptane, by aromatisation from low-boiling aliphatic hydrocarbons.

The following Examples will further illustrate the nature of this invention but the invention is not restricted to these Examples. The parts are by weight.

EXAMPLE 1.

Granular active alumina, which has been obtained by mixing commercial alumina hydrate with watersoluble alumina and subsequent heating, is impregnated with an aqueous solution of chromic acid, dried and heated to 450° Centigrade for the purpose of decomposition. The finished catalyst contains 70 parts of Al_2O_3 and 30 parts of Cr_2O_3. Over the said catalyst there are led at 460° Centigrade the vapours of normal heptane (density = 0.686). The product obtained has a specific gravity of d = 0.735 and an octane value of 36. Its content of aromatic hydrocarbons amounts to about 30 per cent. The content of unsaturated hydrocarbons formed by side reactions in the product is very small. The gas obtained consists to the extent of

[*Price* 1/-]

from 85 to 90 per cent. of hydrogen.

By removing the highly condensed, coke-like substances deposited on the catalyst during the operation, by heating to temperatures of from about 500° to 600° Centigrade, the catalyst regains its original activity.

EXAMPLE 2.

Over a catalyst prepared, in a manner similar to that described in Example 1, by impregnating alumina with a solution of ammonium molybdate, drying and heating, which catalyst consists of 75 parts of Al_2O_3 and 25 parts of MoO_3, the vapours of normal heptane are led at a temperature of 460° Centigrade. A product having a specific gravity of 0.750 is obtained having a content of aromatic hydrocarbons of about 15 per cent. and an octane value of 52. The gas formed consists to the extent of 90 per cent. of hydrogen.

The original activity of the catalyst may be restored by heating it.

EXAMPLE 3.

The vapours of a benzine fraction (80° to 150° Centigrade, d = 0.750) freed from aromatic hydrocarbons by a solvent are led at a temperature of 460° Centigrade over the catalyst described in Example 2. A product having a specific gravity of 0.780 is obtained containing 31 per cent. of aromatic hydrocarbons which contain about 35 per cent. of benzene and 45 per cent. of toluene. The knocking value of the fraction increases from an octane value of 70 to one of 81.

EXAMPLE 4.

The fraction boiling between 80° and 160° Centigrade of a benzine, obtained in the benzine synthesis from carbon monoxide and hydrogen, having its specific gravity of 0.700 and an octane value of 34 is led at 460° Centigrade over the catalyst of Example 2. A product is obtained having a specific gravity of from 0.750 to 0.755, an octane value of 60 and a content of aromatic hydrocarbons of about 35 per cent.

Dated this 27th day of July, 1937.

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

COMPLETE SPECIFICATION

Improvements in the Manufacture and Production of Carbon Compounds poor in Hydrogen.

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 hydrocarbons poor in hydrogen can be obtained in an advantageous manner from benzines obtained by reduction of carbon monoxide, by heating them to temperatures of between 350° and 500° Centigrade in the presence of catalysts containing mixtures of alumina with a smaller amount of a metal of the 6th group of the periodic system or a compound thereof.

The metal of the 6th group or its compounds are preferably used in an amount of from 0.5 to about 40 per cent. in particular from 2 to 30 per cent. calculated with reference to the mixture with alumina.

If the amount of the metal or metal compound is more than about 40 per cent. in the catalyst, there is a diminution in yield which becomes greater as the alumina content diminishes.

Metals of the 6th group include molybdenum and chromium and their oxides in particular. There may also be mentioned tungsten and uranium and their compounds, among the latter of which the oxides should be mentioned in particular. These may be regenerated in a very simple manner after use.

The alumina serving as the preponderating component of the catalyst is advantageously used in admixture with activated, watersoluble alumina obtained for example according to the British Specification No. 441,384.

The catalyst may be applied to carriers, as for example active carbon, lignite small coke, bleaching earths, as for example Florida earth or Fuller's earth, which if desired may have been pretreated with acids, such as halogen hydracids, as for example hydrofluoric acid, or sulphuric acid or nitric acid.

The reaction may be carried out even at atmospheric pressure, but also at increased pressures, as for example from 3 to 50 atmospheres or more; the presence of hydrogen is not essential.

The reaction products obtained may be treated with selective solvents and the fractions rich in hydrogen again subjected to the present process.

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. The parts are by weight.

EXAMPLE.

The fraction boiling between 80° and 160° Centigrade of a benzine, obtained by the catalytic conversion of carbon monoxide with hydrogen, having a specific gravity of 0.700 and an octane number of 54 is led at 460° Centigrade over a catalyst which has been prepared by impregnating alumina with a solution of ammonium molybdate, drying and heating, and which consists of 75 parts of Al_2O_3 and 25 parts of MoO_3. A product is obtained having a specific gravity of from 0.750 to 0.755, an octane number of 60 and a content of aromatic hydrocarbons of about 35 per cent.

I am aware that the use of catalysts of the nature described for the dehydrogenation of hydrocarbons is described in the specification No. 485,178 as open to public inspection and the use of the said catalysts for the conversion of aliphatic hydrocarbons into cyclic hydrocarbons is claimed in specification No. 488,189. The use of benzines obtained by a reduction of carbon monoxide is not mentioned in the said specifications; by their use the octane number is improved to a much greater extent than by using as initial materials, benzines of other origin.

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 manufacture and production of hydrocarbons poor in hydrogen which consists in heating benzines richer in hydrogen obtained by a reduction of carbon monoxide to temperatures between 350° and 500° Centigrade in the presence of catalysts which contain mixtures of alumina with a smaller amount of a metal of the 6th group of the periodic system or a compound thereof.

2. In the process as claimed in claim 1 using as a catalyst a mixture of alumina with from 2 to 30 per cent. of a metal of the 6th group of the periodic system or a compound thereof.

3. The process for the manufacture and production of hydrocarbons poor in hydrogen from benzines obtained by reduction of carbon monoxide, substantially as described in the foregoing Example.

4. Hydrocarbons poor in hydrogen when prepared by the process particularly described and ascertained.

Dated this 27th day of June, 1938.

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

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