PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in the Manufacture and Production of Hydrocarbons and more especially Liquid Hydrocarbons.

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), and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

It is already known that liquid hydrocarbons can be obtained catalytically from oxides of carbon by the action of hydrogen, or gases rich in hydrogen, such as methane, under high pressures and at high temperatures. The contact masses employed, however, are frequently easily damaged owing to sooting and the formation of methane.

My foreign correspondents have now found that relatively high yields of hydrocarbons and more especially liquid hydrocarbons may be continuously obtained, under ordinary, moderately elevated or high pressure and at elevated temperature, if contact masses be used which contain in addition to copper, silver, gold, zinc in the metallic state or mixtures or alloys of the same, or oxides of copper, silver or gold, which are reduced to metals under the conditions of working elements of the 8th group of the periodic system or compounds of the same and, if desired, other elements or compounds in small quantities, substantially in the absence of carriers of low heat conductivity.

Gaseous or liquid hydrocarbons, or both, may, according to this invention, be obtained according to the conditions chosen for working. In some cases, there are obtained, in addition to hydrocarbons, methanol and other oxygen-containing organic compounds. The liquid hydrocarbons are rich in constituents of low boiling point, and are well adapted for use as fuel for internal combustion engines. Inasmuch as they are, for the most part, unsaturated, they do not, generally speaking, require any additions of anti-knocking agents when used in high-compression engines.

A large variety of metals or metallic compounds may be used as additions to the contact masses containing the elements of the 8th group of the periodic system or compounds of the same, as described in the foregoing, as for example, manganese, cerium, chromium, molybdenum, tungsten, titanium, antimony, bismuth, zirconium and the like. Sometimes it may be advantageous to use as additions to the said contact masses mixtures of two or three of these latter additional substances. The amount of the additions should be considerably less than that of the principal metal, preferably being in most cases only a few units per cent. In most cases it will be less than 20 per cent.

The contact masses may be prepared in a great variety of ways. For example, copper oxide may be intimately mixed with the additions and then charged into the reaction vessel preferably in the form of small pressed lumps.

A porous metallic copper, such as may be prepared by reducing copper oxide at temperatures below 400° to 500° Centigrade may be impregnated with solutions of the substances to be added.

Copper oxide may also be fused in conjunction with the additions, or metallic copper, for example, may be fused and oxidised, in conjunction with a small percentage of magnesium and cobalt, in a current of oxygen.

Another method of preparing the catalysts according to the present invention consists in producing a very fine deposit of metals such as iron, cobalt, antimony and the like on copper or silver, by conducting gaseous compounds of the said metals—and more especially organic compounds, such as the carbonyls—over the heated metals, these gaseous compounds being preferably diluted with other gases.

The initial gas may consist, for example, of water gas, which has preferably been freed from carbon dioxide, sulphur and iron carbonyl; or coal or hydrocarbons such as natural gas and the like, or tar oils and the like, may be incom-

[Price 1/-]

pletely burned with oxygen or mixtures of oxygen and steam, the resulting gas being used after purification and, if desired, after a portion of the carbon monoxide has been catalytically transformed into carbon dioxide and hydrogen by means of steam. Producer gas, coke-oven gas or similar gas mixtures of any kind, may also be used.

The hydrogen needed for the reaction may also be generated in the reaction vessel itself, as for example by wholly or partially replacing the hydrogen in the initial gas mixtures by water vapour, light hydrocarbons such as methane, or mixtures thereof.

In order to prevent the deposition of carbon, the hot parts of the apparatus, with which the reaction gases come in contact, are preferably made of copper, manganese, bronze, aluminium, silver, chromium steels or the like, and not of iron.

The formation of the hydrocarbons proceeds at ordinary pressure, but generally speaking increases as the pressure is raised. Thus, for example, the operations may be carried on, with perfect security, at pressures as high as 200 atmospheres, or even higher, up to 1000 atmospheres, or more. The process is generally carried out at temperatures between 150° and 500° Centigrade; the most suitable range of temperatures is from 200° to 400° Centigrade.

The operation may be carried on with the gases employed, in a circulatory system or several reaction vessels may be arranged in series.

The following examples will further illustrate how the said invention may be carried into practical effect but the invention is not restricted to these examples. The parts are by weight.

EXAMPLE 1.

Water gas is passed, under a pressure of 200 atmospheres and at a temperature of 350° Centigrade over a contact mass prepared by mixing 100 parts of copper and 1 part of cobalt, in the form of their oxides. A continuous and abundant yield of hydrocarbons, boiling between 40° and 120° Centigrade and mainly of unsaturated character, is obtained. Methane, ethane, propane and butane are formed only in traces, if at all.

EXAMPLE 2.

Copper oxide, in the form of wire, such as is used in combustion analyses, is reduced and is then soaked with 1 to 2 per cent. of iron oxide, and 1 per cent. of zirconium oxide, in the form of a solution of their nitrates. 10 cubic centimetres of this contact mass are supplied into a pressure-resistant tube lined with copper. Water gas is passed through it at about 300° Centigrade and under a pressure of 20 atmospheres, after having been passed over an activated copper contact mass prepared by reducing copper oxide with 10 per cent. of chromic anhydride at from 400° to 450° Centigrade and then freed from carbon dioxide and sulphuretted hydrogen by extraction with water under pressure, and from the iron carbonyl present by means of active charcoal. Abundant quantities of liquid hydrocarbons boiling at between 30° and 120° Centigrade are formed. A similar effect is obtained with a contact mass containing potassium antimonate in place of iron oxide and zirconium oxide.

EXAMPLE 3.

50 parts of copper oxide, 30 parts of silver oxide, 8 parts of cobalt oxide and 2 parts of chromic acid are intimately mixed with a little water, and then dried. Over this contact mass is passed a mixture of 50 parts, by volume, of carbon monoxide and 50 parts, by volume, of hydrogen, at 300° Centigrade and under ordinary pressure. Liquid benzines are recovered from the effluent gases, by means of activated charcoal or strongly cooling. The gas also contains low, gaseous hydrocarbons, especially ethylene, propane, and butane. Similar results are obtained by passing the initial gases, under ordinary pressure, through a long, heated copper tube, the inner side of which is activated with small quantities of iron.

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 by the catalytic conversion of oxides of carbon with hydrogen, or gases rich in hydrogen, such as methane, or steam, which consists in the use of contact masses which contain—in addition to copper, silver, gold, zinc in the metallic state or mixtures of alloys of the same or oxides of copper, silver or gold, which are reduced to metals under the conditions of working—elements of the 8th group of the periodic system, or compounds of the same and, if desired, other elements or compounds, in small quantities and substantially in the absence of carriers of low heat conductivity, ordinary, moderately elevated or high pressures and elevated temperatures being employed.

2. The process for the manufacture and production of hydrocarbons claimed in the preceding claim substantially as described in each of the foregoing examples

3. Hydrocarbons and more especially liquid hydrocarbons, when prepared in accordance with the preceding claiming clauses.

Dated this 9th day of June, 1927.
JOHNSONS & WILLCOX,
47, Lincoln's Inn Fields, London, W.C. 2,
Agents.

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