[Second Edition.]

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

1355

Improvements in the Manufacture and Production of Non-knocking Motor Fuel by the Catalytic Reaction of Carbon Monoxide and Hydrogen.

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:—

It has already been proposed to prepare motor fuel of low boiling point by the catalytic reaction of carbon monoxide and hydrogen at temperatures of from 150° to 250° Centigrade.

My foreign correspondents have now found that the said constituents of low boiling point can be recovered from the reaction products in a simple manner and their non-knocking properties can be improved by treating them or their fractions rich in olefines with condensing agents at elevated temperatures. By "fractions" is meant not only fractions obtained by condensation (by compression or cooling) but also portions obtained by other separating operations, as for example selective absorption or washing out or the like.

In order to carry out the process according to this invention, the gases and vapours leaving the reaction chamber may for example first be freed from constituents of high boiling point by cooling, the products of low boiling point then being separated in a suitable manner, as for example by compression. The reaction gases may be compressed in three or more stages, advantageously for example at 3, 8, 24 and, if desired, 50 atmospheres. The benzine constituents of high boiling point obtained in the first two stages, which only contain slight amounts of olefines, may be directly employed, preferably in admixture with benzine fractions of low boiling point. The products obtained in the third and higher stages (if any) are subjected to a polymerising treatment. For this purpose the products after separation of the gases or also together with the same, are treated at from 20° to 250° Centigrade, preferably without releasing the pressure, with condensing agents, such as halogen, sulphur, halides, such as boron fluoride, aluminium chloride, zinc chloride, titanium chloride or tin chloride, or advantageously with bleaching earths which have been impregnated with phosphoric acid or halides, or mixtures of the said substances. In this manner the olefines contained in large amounts in the benzine fractions or low boiling point are polymerised with the formation of a non-knocking motor fuel which is advantageously mixed with the benzine fractions of higher boiling point separated in the first stage of the compression.

The condensing treatment may be carried out with the whole of the benzine obtained by compression, and the benzine may be recovered by absorption or washing instead of by compression. During the condensing treatment, olefines from other sources may be added, whereby they are converted into non-knocking hydrocarbons in the same operation.

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

EXAMPLE.

A gas mixture consisting of 2 parts of hydrogen and 1 part of carbon monoxide is led at 190° Centigrade over a catalyst consisting of cobalt, manganese and kieselguhr. The mixture leaving the reaction chamber is cooled to 20° Centigrade, the fraction boiling above about 180° Centigrade thus being separated. The remaining gaseous mixture then passes into a three-stage compressor. The condensate obtained in the first stage at 3 atmospheres is not further treated. The benzine fractions of low boiling point obtained in the second and third stages at 8 and 24 atmospheres are treated under the same pressure at 235° Centigrade with bleaching earth which has been impregnated with phosphoric acid. The treat-

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ment of the separated benzine fractions may be carried out in the presence of the gas present under pressure in the single compression stages.

The benzine obtained is mixed with the fraction obtained in the first stage. The mixture has an octane value of 65 and is accordingly capable of use in the usual manner.

Dated this 5th day of April, 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 Non-knocking Motor Fuel by the Catalytic Reaction of Carbon Monoxide and Hydrogen.

We, COUTTS & COMPANY, a Company with unlimited liability, incorporated under the Companies Acts, 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 :—

It has already been proposed to prepare motor fuels of low boiling point by the catalytic reaction of carbon monoxide and hydrogen at elevated temperatures, in particular at temperatures of from 150° to 350° Centigrade and under atmospheric pressure or pressures above atmospheric pressure.

Our foreign correspondents have now found that the constituents of low boiling point can be recovered in a simple manner from the products of the said reaction and that their non-knocking properties can be improved by treating them or their fractions rich in olefines with condensing agents at elevated temperatures. By "fractions" are meant not only fractions obtained by condensation (by compression or cooling) but also portions obtained by other separating operations, as for example selective absorption or washing out or the like.

In order to carry out the process according to this invention, the gases and vapours leaving the reaction chamber may for example first be freed from constituents of high boiling point, in particular those having a boiling point higher than benzine, by cooling, the products of low boiling point then being separated in a suitable manner, as for example by compression. The reaction gases may be compressed in three or more stages, advantageously for example at 3, 8, 24 and, if desired, 50 atmospheres. The benzine constituents of high boiling point (boiling for example above 100° Centigrade, such as those boiling between above 150° and 200° Centigrade) obtained in the first two stages, and which only contain slight amounts of olefines, may be directly employed, preferably in admixture with benzine fractions of low boiling point. The products obtained in the third and higher stages (if any) are subjected to a polymerising treatment. For this purpose the products, after separation of the gases or also together with the same, are treated at from 20° to 250° Centigrade, preferably without releasing the pressure, with condensing agents, as for example halogen, sulphur or halides, such as boron fluoride, aluminium chloride, zinc chloride, titanium chloride or tin chloride, or advantageously with bleaching earths which have been impregnated with phosphoric acid or halides, or mixtures of the said substances. The particular temperatures employed depend upon the nature of the condensing agents and upon the duration of treatment. With agents having a strong condensing action the temperatures are lower than with agents having a weaker action, and when working for longer periods of time lower temperatures are necessary than when working only for short periods of time. The polymerisation is preferably carried to such an extent that mainly hydrocarbons boiling within the boiling point range of benzine are formed. In this manner the olefines contained in large amounts in the benzine fractions of low boiling point are polymerised with the formation of a non-knocking motor fuel which is advantageously mixed with the benzine fractions of higher boiling point separated in the first stage of the compression. Accordingly the treatment with condensing agents is carried so far that hydrocarbons are formed which through boiling higher than the initial

olefines, do not boil substantially above the end boiling point of benzine.

The condensing treatment may also be carried out with the whole of the benzine obtained by compression. The benzine may also be recovered by absorption or washing instead of by compression. During the condensing treatment, olefines from other sources may be added, whereby they are converted into non-knocking hydrocarbons in the same operation.

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 volume.

EXAMPLE.

A gas mixture consisting of 2 parts of hydrogen and 1 part of carbon monoxide is led at 190° Centigrade over a catalyst consisting of cobalt, manganese, and kieselguhr. The mixture leaving the reaction chamber is cooled so that the fraction boiling above about 180° Centigrade is separated. The remaining gaseous mixture then passes into a three-stage compressor. The condensate obtained in the first stage at 3 atmospheres and boiling between about 150° and 180° Centigrade is not further treated. The benzine fractions of low boiling point obtained in the second and third stages at 8 and 24 atmospheres (the said fractions boiling between about 100° and 150° Centigrade and between about 70° and 100° Centigrade respectively) are treated under the same pressures at 235° Centigrade with bleaching earth which has been impregnated with phosphoric acid. The treatment of the separated benzine fractions may be carried out in the presence of the gas present under pressure in the single compression stages.

The benzine obtained is mixed with the fraction obtained in the first stage. The mixture has an octane value of 65 and is accordingly capable of use in the usual manner.

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 manufacture and production of non-knocking motor fuels from the hydrocarbons formed by the catalytic conversion of carbon monoxide with hydrogen which comprises treating the constituents of low boiling point of the said hydrocarbons or their fractions rich in olefines preferably after separation of the higher boiling constituents, at an elevated temperature with agents having a condensing action under such conditions of time, temperature and activity of the catalyst that hydrocarbons boiling higher than the said constituents of low boiling point but not substantially above the end boiling point of benzine are formed.

2. In the process as claimed in claim 1, subjecting only the portion of the liquid hydrocarbons, boiling below 150° Centigrade, to a polymerising treatment.

3. In the process as claimed in claim 1 or 2, passing a gaseous mixture of carbon monoxide and hydrogen through a space maintained under conditions under which conversion of the said mixture into liquid hydrocarbons takes place, recovering from the products leaving the said space the hydrocarbons of high boiling point by cooling and the hydrocarbons of lower boiling point by compression, and subjecting at least part of the said hydrocarbons of lower boiling point to a polymerising treatment in the presence of a condensing agent under such conditions of time, temperature and activity of the catalyst that hydrocarbons boiling higher than the said constituents of low boiling point but not substantially above the end boiling point of benzine are formed.

4. The process for the manufacture and production of valuable motor fuels substantially as described in the foregoing Example.

5. Motor fuels when obtained by the process particularly described and ascertained.

Dated this 26th day of February, 1936.

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