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PATENT SPECIFICATION

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507,999

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1212

(Samples have been furnished in this case under Section 2, sub-section 5, of the Patents and Designs Acts, 1907 to 1938.)

PROVISIONAL SPECIFICATION

Improvements in Non-knocking Motor Fuels

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:—

In the conversion of low molecular weight paraffin hydrocarbons, such as ethane, propane, butane or low-boiling liquid paraffin hydrocarbons, into non-knocking motor fuels, there is the difficulty that considerable amounts of low molecular weight hydrocarbons, in particular the lowest member of the series, methane, are formed and that when using methane itself very high temperatures are necessary. In every case there also takes place considerable deposition of carbon.

My foreign correspondents have now found that paraffin hydrocarbons can be employed in a very advantageous manner for the preparation of valuable non-knocking fuels by subjecting them together with light boiling aromatic or hydroaromatic hydrocarbons or both in the vapour phase to a thermal treatment at temperatures above 300° Centigrade, preferably in the presence of rigidly arranged catalysts.

As paraffin hydrocarbons there may be mentioned for example benzines or middle oils from paraffin-basic petroleums or from destructive hydrogenation products of coals, such as brown coals, or of tars, in particular brown coal tars, or of mineral oils, or fractions of the products obtained by the reduction of carbon monoxide, and also corresponding fractions of hydrocarbons rich in hydrogen which have been obtained by the treatment of oils with selective solvents. Of the gaseous paraffinic hydrocarbons, pentane, butane and propane are especially suitable for the treatment. As light boiling aromatic hydrocarbons there may be employed preferably benzene or its homologues; hydrogenation products of these substances or naphthalene or its hydrogenation products are also suitable. In the mixtures to be treated, the proportion of the aromatic and/or hydroaromatic hydrocarbons advantageously amounts to between about 10 and 50 per cent; in many cases it may be even greater. The aromatic and/or hydroaromatic hydrocarbons should boil substantially in the boiling range of the benzines.

The paraffinic hydrocarbons may be mixed with the aromatic and/or hydroaromatic hydrocarbons in the liquid or vapour phase. The mixture is then subjected in the vapour phase to the thermal treatment at temperatures of between 300° and 700°, advantageously between 450° and 650° Centigrade and preferably in the presence of catalysts.

The liquid mixture or the single components may also be heated before the catalytic treatment to temperatures which are higher than necessary for their evaporation. Thus for example the initial materials may be heated to about 500° Centigrade and then led at the said temperature over the catalysts.

Of the light boiling paraffinic hydrocarbons, liquid and gaseous hydrocarbons may be present at the same time. In this case it is advantageous to heat the mixture of the liquid paraffins with the aromatics for example to about 480° Centigrade and to heat the gaseous hydrocarbons separately therefrom, for example to from 500° to 700° Centigrade, the hot vapours then being united with the heated gases and the whole treated at from 450° to 700° Centigrade, preferably in the presence of catalysts.

The nature of the catalysts to be used depends on the conditions used, in particular on the temperature, and also on the nature of the paraffinic hydrocarbons. The paraffinic hydrocarbons are advantageously treated in the presence of catalysts having a splitting or dehydrogenating action. Catalysts may also be used, however, which have, in addition to a splitting action, also a polymerising

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action, or there may be added to splitting catalysts larger or smaller proportions of catalysts having a polymerising action. The latter may also be brought into reaction separately from the catalysts having a splitting or dehydrogenating action in a second, closed reaction vessel.

At least one of the said actions is exerted by most metals of the 2nd to the 8th groups of the periodic system or their compounds. For example the sulphides, oxides, phosphates, halides or sulphates of iron, cobalt, nickel, chromium, venadium, aluminium, zinc, tin, manganese, titanium, magnesium, tungsten and molybdenum are suitable as catalysts for the said treatment.

The said metals or metal compounds are advantageously applied to carriers, as for example to bodies having large surfaces, such as Fuller's earth, bleaching earths, silicates and silica gel, or active carbons, lignite small coke which may if desired be pretreated with acid substances in particular hydrogen fluoride.

In many cases it is preferable to carry out the reaction in the presence of halogens or volatile compounds of halogens or other non-metals, as for example volatile sulphur or phosphorus compounds, or of hydrogen, preferably with a low partial pressure of the hydrogen (up to about 30 per cent. of the total pressure).

The reaction may be carried out at atmospheric or increased pressure, as for example at from 20 to 200 atmospheres or more.

The gases formed may be led back again to the reaction. The liquid products obtained may be subjected to a refining, as for example a refining destructive hydrogenation.

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

EXAMPLE.

Butane is heated to 530° Centigrade under a pressure of 250 atmospheres and at a speed of throughput of 2 kilograms per litre of heated spiral volume in an externally heated tubular spiral. With each kilogram of the butane thus heated there are mixed 0.25 kilogram of benzene and 40 litres of hydrogen. The mixture is then led at 530° Centigrade over a sulphurised mixture of molybdic acid, zinc oxide and magnesia as a catalyst. There is thus frmed a product the fraction of which boiling up to 180° Centigrade may be used very advantageously as an addition for improving the non-knocking properties of motor fuels. By subjecting the product to hydrogenating refining, a valuable motor fuel having very good non-knocking properties is obtained.

Dated this 23rd day of September, 1937.

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

COMPLETE SPECIFICATION

Improvements in Non-knocking Motor Fuels

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:—

In the conversion of low molecular weight paraffin hydrocarbons, such as ethane, propane, butane or low-boiling liquid paraffin hydrocarbons, into non-knocking motor fuels, there is the difficulty that considerable amounts of low molecular weight hydrocarbons, in particular the lowest member of the series, methane, are formed and that when using methane itself very high temperatures are necessary. In every case there also takes place considerable deposition of carbon.

My foreign correspondents have now found that paraffin hydrocarbons can be employed in a very advantageous manner for the preparation of valuable non-knocking fuels by subjecting them together with benzene and/or its light boiling homologues and/or with light boiling hydroaromatic hydrocarbons in the vapour phase to a thermal treatment at temperatures above 300° Centigrade, preferably in the presence of rigidly arranged catalysts. By light boiling homologues of benzene and light boiling hydroaromatic hydrocarbons is meant those boiling in the boiling range of benzines, i.e. up to 225° Centigrade.

As paraffin hydrocarbons there may be mentioned for example benzines or middle oils from paraffin-basic petroleums or from destructive hydrogenation products of coals, such as brown coals, or of tars, in particular brown coal tars, or of mineral oils, or fractions of the gaseous, liquid or solid products obtained by the reduction of carbon monoxide, and also liquid fractions of hydrocarbons rich in hydrogen which have been obtained by the treatment of oils with selective solvents. Of the gaseous paraffinic hydrocarbons, pentane, butane and propane are especially suitable for the treatment. They may be taken from any source, as for example from cracking gases or from the gaseous portions of the products obtained by the reduction of carbon monoxide with hydrogen and the like. As light boiling hydroaromatic hydrocarbons there may be employed preferably hydrogenation products of benzene or its homologues or of naphthalene. In the mixtures to be treated the proportion of the benzene and/or its homologues and/or the hydroaromatic hydrocarbons advantageously amounts to between about 10 and 50 per cent; in many cases it may be even greater.

The paraffinic hydrocarbons may be mixed with the aromatic and/or hydroaromatic hydrocarbons in the liquid or vapour phase. The mixture is then subjected in the vapour phase to the thermal treatment at temperatures of between 300° and 700°, advantageously between 450° and 650° Centigrade and preferably in the presence of catalysts.

The liquid mixture or the two components may also be heated before the catalytic treatment to temperatures which are higher than necessary for their evaporation. Thus for example the initial materials may be heated to about 500° Centigrade and then led at the said temperature in the vapour phase over the catalysts.

Of the paraffinic hydrocarbons, liquid and gaseous hydrocarbons may be present at the same time. In this case it is advantageous to heat the mixture of the liquid paraffins with the aromatics for example to about 480° Centigrade and to heat the gaseous hydrocarbons separately therefrom, for example to from 500° to 700° Centigrade, the hot vapours then being united with the heated gases and the whole treated at from 450° to 700° Centigrade, preferably in the presence of catalysts.

The nature of the catalysts to be used depends on the conditions used, in particular on the temperature, and also on the nature of the paraffinic hydrocarbons, but in any case the catalysts should have a splitting action. In some cases it is of advantage to use catalysts which have, in addition to a splitting action, also a pronounced polymerising action, or there may be added to splitting catalysts larger or small proportions of catalysts having a polymerising action. The latter may be brought into reaction separately from the catalysts having a splitting action in a second, closed reaction vessel.

The said splitting action is exerted by most metals of the 2nd to the 8th groups of the periodic system or their compounds. For example the sulphides, oxides, phosphates, halides or sulphates of iron, cobalt, nickel, chromium, vanadium, aluminium, zinc, tin, manganese, titanium, magnesium, tungsten and molybdenum are suitable as catalysts for the said treatment, insofar as they remain substantially solid under the conditions of the operation.

The said metals or metal compounds are advantageously applied to carriers, as for example to bodies having large surfaces, such as Fuller's earth, bleaching earths, silicates and silica gel, or active carbons, or lignite small coke which may if desired be pretreated with acid substances in particular hydrogen fluoride.

In many cases it is preferable to carry out the reaction in the presence of hydrogen, preferably with a low partial pressure of the hydrogen (up to about 30 per cent. of the total pressure).

The reaction may be carried out at atmospheric or increased pressure, as for example at from 20 to 200 atmospheres or more.

The gases formed may be led back again to the reaction. The liquid products obtained may be subjected to a refining, as for example a refining destructive hydrogenation.

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.

Butane is heated to 530° Centigrade under a pressure of 250 atmospheres and at a speed of throughput of 2 kilograms per litre of heated spiral volume and per hour in an externally heated tubular spiral. With each kilogram of the butane thus heated there are mixed 0.25 kilogram of preheated benzene and 40 litres (measured under normal conditions of temperature and pressure) of preheated hydrogen. The mixture is then led at 530° Centigrade and under a pressure of 250 atmospheres over a sulphurised mixture of molybdic acid, zinc oxide and magnesia, as a catalyst having a splitting and a polymerising action, with a velocity of flow of 1.5 kilograms of the mixture of butane and benzene per hour and per litre of catalyst. There is thus formed per each kilogram of benzene 1.6 kilograms of a liquid product the fraction of which boiling up to 180° Centigrade may be used very advantageously as an addition for improving the non-knocking properties of motor fuels. By subjecting the product to hydrogenating refining at 210° Centigrade under a hydrogen pressure of 50 atmospheres in the presence of a catalyst consisting of a mixture of two molecular proportions of nickel sulphide with one molecular proportion of tungsten sulphide and with a velocity of flow of 1 kilogram of the product per litre of catalyst and per hour, the amount of hydrogen employed being 1.5 cubic metres per each kilogram of the product, a valuable motor fuel having very good non-knocking properties is obtained.

Samples have been furnished under Section 2(5) of the Acts, which samples have been prepared in the following manner:—

SAMPLE A.

Benzine boiling up to 180° Centigrade, obtained by mixing 2 parts of a fraction boiling between 160 and 220° Centigrade of the liquid hydrocarbons, obtained by the conversion of carbon monoxide with hydrogen, with 1 part of tetrahydronaphthalene and passing the mixture at 450° Centigrade and under 20 atmospheres over a catalyst consisting of molybdenum oxide and zinc oxide with a velocity of flow of 0.5 litre of the said mixture (measured as a liquid) per litre of catalyst and per hour. (The benzine is obtained in a yield of 45 per cent. The catalyst has a splitting and polymerizing action).

SAMPLE B.

Benzine boiling up to 180° Centigrade, obtained by mixing 4 parts of petrolatum with 1 part of crude benzol and passing the mixture at 430° Centigrade under atmospheric pressure over a catalyst consisting of artificially prepared aluminium silicate with a velocity of flow of 1 litre of the said mixture (measured as a liquid) per litre of catalyst and per hour. (The benzine is obtained in a yield of 40 per cent. The catalyst has a splitting action).

SAMPLE C.

Benzine boiling up to 180° Centigrade, obtained by mixing a heavy benzine fraction of a paraffin basic mineral oil with 15 per cent by volume of crude benzol and passing the mixture at 500° Centigrade and under 70 atmospheres through a heated tubular coil with a velocity of flow of 0.3 litre of the said mixture (measured as a liquid) per litre of the heated tubular coil space and per hour. (The benzine is obtained in a yield of 90 per cent).

I am aware that it has already been proposed to subject mixtures of tar acids or coal distillation products containing tar acids with a mineral oil to a thermal treatment at about 350—650° Centigrade in finely divided or vapour condition whereby the tar acids become converted into benzol and its homologues. In the said process, however, only distillates having a higher boiling range than benzines, for example those boiling between 250 and 270° Centigrade or between 200 and 425° Centigrade, are employed.

It has also been proposed to carry out the destructive hydrogenation of high boiling hydrocarbons rich in open-chain compounds with the formation therefrom of hydrocarbons having a lower boiling point while stabilising the reaction temperature by destructively hydrogenating a blend of the hydrocarbon rich in open-chain compounds with high boiling hydrocarbon material rich in closed-chain compounds. As set forth above, the present invention is only concerned with benzene and/or its light boiling homologues and/or with light boiling hydroaromatic hydrocarbons.

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 production of valuable non-knocking motor fuels which comprises subjecting paraffin hydrocarbons together with benzene and/or its light boiling homologues and/or light boiling hydroaromatic hydrocarbons as herein defined in the vapour phase to a thermal treatment at a temperature between 300° and 700° Centigrade, preferably in the presence of a rigidly arranged catalyst having a splitting action and, if desired, in the presence of hydrogen.

2. In the process as claimed in claim 1, operating at temperatures between 450° and 650° Centigrade.

3. A process as claimed in claim 1 or 2, which comprises carrying out the thermal treatment in the presence of a catalyst having besides the splitting action also a polymerising action.

4. The process for the production of non-knocking motor fuels substantially as described in the foregoing Example.

5. Non-knocking motor fuels when obtained by the process particularly described and ascertained.

Dated this 28th day of February, 1939.

J. Y. & G. W. JOHNSON,
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