[Second Edition.]

PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Improvements in the manufacture and production of Non-knocking Motor Fuels.

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:—

My foreign correspondents have found that motor fuels having quite unusual non-knocking properties are obtained by subjecting oxygen-containing hydrogenation products of oxides of carbon, which contain, besides methyl alcohol, mainly isobutyl alcohol and other higher alcohols, either directly or after previous separation by distillation to a splitting off of water, the resulting iso-olefines being wholly or partly polymerised to give the di-iso- or tri-iso-olefines which may then be mixed again, or which may be combined with the monomeric higher iso-olefines if the corresponding higher alcohols have been separated from the isobutyl alcohol and the olefines formed therefrom have not been subjected to polymerisation. Thus for example the isobutylene obtained by splitting off water from the hydrogenation product or from the fractions thereof containing isobutyl alcohol may be polymerised to give di-isobutylene or tri-isobutylene, then mixed with mono- or di-isoamylenes and the higher homologues, such as isohexylene to isodecylene, and employed as motor fuels.

The non-knocking properties of the motor fuels thus obtained are of a quality hitherto unknown. The octane value of such a motor fuel is above 100.

The preparation of the oxygen-containing initial material consisting of isobutyl alcohol and higher alcohols is effected by the catalytic hydrogenation of oxides of carbon in such manner that in addition to methanol, mainly isobutyl alcohol and higher aliphatic alcohols are formed. The process is carried out under pressure in the presence of catalysts, as for example catalysts of zinc oxide and chromium oxide, for example according to the specification No. 238,319. The constituents of the hydrogenation products thus obtained which boil at a higher temperature than methanol are then together or, preferably, after having been separated by fractional distillation subjected to the splitting off of water; this may be effected for example catalytically by leading over catalysts, such as aluminium oxide, at 300° Centigrade. In this stage of the process isobutylene is mainly obtained, and also isoamylene (2-methylbutene (1)) and higher iso-olefines. The following polymerisation of the iso-olefines to dimers and trimers is advantageously carried out while employing sulphuric acid of suitable concentration at elevated temperatures. For example di-isobutylene may be obtained by means of sulphuric acid of from 50 to 60 per cent. strength according to the specification No. 322,102, while tri-isobutylene may be obtained by means of more concentrated sulphuric acid, as for example of about 70 per cent. strength. If it is desired that the higher homologues of isobutylene should also be present in the fuel in the form of their dimers, they may be polymerised together with the isobutylene. A content in the fuel of such low polymers of higher homologues of isobutylene is desirable when the product is to be employed as a "safety fuel," that is when it is to have a high flashpoint.

It has also been found that the new fuels have quite an unusual non-knocking property when they are wholly or only partly subjected to a more or less complete hydrogenation to form saturated hydrocarbons. Even in the driving of aeroplane engines, the hydrogenated fuels have surprisingly high non-knocking properties in spite of the high temperatures prevailing in such engines. The isoamylene and isohexylene are preferably added in a non-hydrogenated condition because in this case the starting of the engine is promoted.

The new fuels may also be employed in admixture with other fuels. When mix-

[*Price* 1s.]

ing methanol with the fuels it is preferable to add a dissolving agent, as for example isobutyl alcohol.

The known anti-knock agents, such as iron carbonyl, lead tetraethyl or monomethylaniline, or the so-called "upper lubricating oils" may also be added to the fuels if desired. The latter may be advantageously obtained by polymerising the olefines obtained in the course of the process, if desired together with aromatic hydrocarbons. A certain lubricating effect is also obtained by the addition of the alcohols of high molecular weight contained in the initial material, but by reason of the changing composition of these higher fractions of the initial material it is necessary to subject these additional materials to a test of their suitability and, in some cases, to purify them. Dyestuffs and substances imparting odour may also be incorporated with the fuels.

The process according to this invention offers the possibility of starting from watergas and obtaining a motor fuel of a high quality hitherto unattainable in any fuel used in practice. The new fuels are also far superior to all fuels hitherto prepared from oxygen-containing hydrogenation products of oxides of carbon as regards non-knocking properties.

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

EXAMPLE 1.

A purified gas mixture consisting of 2 parts of hydrogen and 1 part of carbon monoxide is led slowly at 200 atmospheres and at a temperature of from 450° to 500° Centigrade in an apparatus lined with copper over a catalyst which has been prepared by introducing zinc oxide into fused potassium bichromate and subsequently reducing with hydrogen. The reaction product is freed from methyl alcohol and water and then split up into single alcohol fractions by distillation; the main fraction consists of isobutyl alcohol. The single fractions are led at about 300° Centigrade over precipitated aluminium oxide, the corresponding olefines thus being obtained.

The isobutylene is absorbed in an about 55 per cent. sulphuric acid and the solution heated to 100° Centigrade. An upper layer is formed which consists mainly of di-isobutylene. The higher members simultaneously formed may be reconverted by catalytic splitting into isobutylene and polymerised afresh.

The isoamylene may be converted into the dimer in a similar manner, or it may be added as such to be di-isobutylene. The higher olefines formed may, up to about decylene, be added to the fuel in the amounts in which they are obtained.

Having regard to the requirements of the motor, a complete or partial hydrogenation of the mixture or of its single components may be carried out when desired. The fuel is an excellent motor fuel, especially for aeroplane engines.

EXAMPLE 2.

The alcohols and then the olefines are prepared in the manner described in Example 1. The isobutylene is then treated at room temperature with a 70 per cent. sulphuric acid. Two layers are thus formed, the upper of which consists mainly of tri-isobutylene. By heating the lower layer to about 100° Centigrade, more tri-isobutylene and also di-isobutylene are formed; the latter is separated and may be catalytically split up with the aid of an aluminium oxide catalyst at from 200° to 300° Centigrade into isobutylene which may be polymerised afresh. The isoamylene, isohexylene and isoheptylene are converted by means of a from 60 to 70 per cent. sulphuric acid into the dimeric hydrocarbons and then mixed with the tri-isobutylene.

A fuel having very good non-knocking properties is obtained which has a high flashpoint and which is therefore suitable as so-called "safety fuel." If a specially high flashpoint is desired, the addition of di-isoamylene may be omitted. The fuel may be partially or completely hydrogenated, depending on the requirements of the motor. The said fuel also has an octane value of about 100.

Dated this 8th day of October, 1934.

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 Fuels.

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

Our foreign correspondents have found that motor fuels having quite unusual non-knocking properties are obtained by subjecting gas mixtures containing hydrogen and carbon monoxide to a heat-treatment under superatmospheric pressure in such a manner that besides methyl alcohol, mainly isobutyl alcohol and other higher alcohols are formed, then subjecting these alcohols, after separation of the methyl alcohol, to a treatment effecting the splitting off of water, and polymerising the resulting iso-olefines as a whole or in part to give the di-iso- or tri-iso-olefines which may then be mixed again, or which may be combined with monomeric higher iso-olefines. Thus, for example, the isobutylene present in the product obtained by splitting off water from the product formed by the interaction of hydrogen with carbon monoxide may be polymerised to give di-isobutylene or tri-isobutylene, whereupon such polymerisation product may be mixed with mono- or di-isoamylene and/or higher homologues, such as isohexylene to isodecylene.

It has also been found that the new fuels have quite an unusual non-knocking property when they are subjected to a more or less complete hydrogenation to form saturated hydrocarbons. Even in the driving of aeroplane engines, the hydrogenated fuels have surprisingly high non-knocking properties in spite of the high temperatures prevailing in such engines. The said motor fuels are considerably superior as regards non-knocking properties to the motor fuels hitherto generally used for the driving of aeroplane engines.

The preparation of the oxygen-containing initial material containing, in addition to methanol, mainly isobutyl alcohol and higher alcohols, by the interaction of hydrogen with carbon monoxide, is carried out under pressure, usually above 50 atmospheres, as for example 200 atmospheres or preferably still higher pressures, in the presence of catalysts, as for example catalysts of zinc oxide and chromium oxide, for example according to the specification No. 238,319. The constituents of the products thus obtained which boil at a higher temperature than methanol are then together subjected to the splitting off of water; this may be effected for example catalytically by leading over catalysts, such as aluminium oxide, at 300° Centigrade. In this stage of the process isobutylene is mainly obtained as dehydration product of isobutyl alcohol and isoamylene (2-methylbutene (1)) and higher iso-olefines as dehydration products of the corresponding higher alcohols. The following polymerisation of the iso-olefines to dimers and trimers is advantageously carried out while employing sulphuric acid of suitable concentration at elevated temperatures. For example di-isobutylene may be obtained by means of sulphuric acid of from 50 to 60 per cent. strength according to the specification No. 322,102, while tri-isobutylene may be obtained by means of more concentrated sulphuric acid, as for example of about 70 per cent. strength. In a similar manner the dimers and trimers of isoamylene and higher iso-olefines may be prepared. If it is desired that the higher homologues of isobutylene should also be present in the fuel in the form of their dimers, they may be polymerised alone and then added to the polymerised isobutylene or they may also be polymerised together with the isobutylene. A content in the fuel of such low polymers of higher homologues of isobutylene is desirable when the product is to be employed as a "safety fuel," that is when it is to have a high flashpoint.

The new fuels may also be employed in admixture with other fuels. When mixing methanol with the fuels it is preferable to add a dissolving agent, as for example isobutyl alcohol.

Other anti-knock agents, such as iron carbonyl, lead tetraethyl or monoethylaniline, or the so-called "upper lubricating oils" may also be added to the fuels if desired. A certain lubricating effect is also obtained by the addition of the alcohols of high molecular weight contained in the product formed by the interaction of hydrogen and carbon monoxide, but by reason of the changing composition of these higher fractions of the said product it is necessary to subject these additional materials to a test of their suitability and, in some cases, to purify them. Dyestuffs and substances imparting odour may also be incorporated with the fuels.

Fuels which may be prepared according to the process of the present invention are the following: Di-isobutylene or tri-isobutylene (obtained by separating isobutylene from the mixture of iso-olefines resulting from the dehydration of the mixture of alcohols from which methanol has previously been separated and then polymerising the said isobutylene); a mixture of dimers or trimers of isobutylene and higher boiling iso-olefines (obtained for example by separating methanol from the product resulting from the interaction of hydrogen and carbon monoxide and then either dehydrating and subsequently polymerising as a whole the said product freed from methanol, or dehydrating the product freed from methanol as a whole, separating into fractions the resulting iso-olefines, polymerising the latter separately and mixing the resulting polymerisation products); compositions of di-isobutylene with amylene or hexylene or heptylene or mixtures thereof (the said iso-olefines being obtained by separation from the mixture of the iso-olefines resulting from the dehydration of the mixture of alcohols); or compositions of di-isobutylene with pentane or hexane or heptane or mixtures thereof (the said pentane or hexane or heptane or mixtures thereof being prepared by hydrogenation of the beforementioned amylene, hexylene, heptylene or mixtures thereof); or compositions of di-isobutylene with at least one of the iso-olefines amylene, hexylene and heptylene and at least one of the saturated hydrocarbons pentane, hexane and heptane prepared by hydrogenation of the said iso-olefines, or iso-octane (obtained by hydrogenation of di-isobutylene); or compositions of the said iso-octane with amylene, hexylene or heptylene or with mixtures of these iso-olefines or with pentane, hexane, or heptane or mixtures of these saturated hydrocarbons or with at least one of the said iso-olefines and at least one of the said saturated hydrocarbons; or compositions of tri-isobutylene with di-isoamylene or di-isohexylene or di-isoheptylene or mixtures thereof (the said dimers resulting from the polymerisation of iso-olefines boiling higher than isobutylene which in turn are obtained by separation of the mixture of iso-olefines formed in the dehydration of the alcohols freed from methanol); or compositions of tri-isobutylene with decane or dodecane or tetradecane or mixtures of these saturated hydrocarbons (the said saturated hydrocarbons or mixtures thereof resulting from the hydrogenation of the corresponding di-iso-olefines obtained as described above) or dodecane (obtained by hydrogenation of tri-isobutylene); or compositions of the said dodecane with the abovementioned di-isoamylene or di-isohexylene or di-isoheptylene or mixtures thereof or with the decane or dodecane or tetradecane resulting from the hydrogenations of those di-iso-olefines. It is, however, to be understood that the present invention is not restricted to the preparation of these particular compounds and compositions but that many other valuable fuels may be obtained in the above described manner.

The process according to this invention offers the possibility of starting from watergas and obtaining a motor fuel of a high quality hitherto unattainable in any fuel used in practice. The new fuels are also far superior to all fuels hitherto prepared from oxygen-containing products obtained by the said interaction of hydrogen with carbon monoxide as regards non-knocking properties.

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 1.

A purified gas mixture consisting of 2 parts of hydrogen and 1 part of carbon monoxide is led slowly at 200 atmospheres and at a temperature of from 450° to 500° Centigrade in an apparatus lined with copper over a catalyst which has been prepared by introducing zinc oxide into fused potassium bichromate and subsequently reducing with hydrogen. The reaction product is freed from methyl alcohol and water. The remainder mainly consists of isobutyl alcohol; amyl-, hexyl-, heptyl-alcohol as well as higher alcohols are present in smaller amounts; also small amounts of aldehydes and ketones of different molecular weight are present in the said remainder.

This mixture is then dehydrated at a temperature of 300° Centigrade in the presence of a catalyst comprising aluminium oxide (in the form of precipitated aluminium hydroxide or the oxide formed by burning aluminium hydroxide or of burnt bauxite).

The resulting mixture of olefines is treated with a sulphuric acid having a suitable concentration and at a suitable temperature (as for example with a 55 per cent. sulphuric acid at 100° Centigrade) for such a long time that only the low molecular olefines, in particular the isobutylene, are polymerised to their dimers and trimers. When working with a stronger sulphuric acid (as for example a 70 per cent. sulphuric acid) also the higher molecular weight olefines, such as hexylene and heptylene may be polymerised to their dimers.

The resulting polymerisation products which are also olefines may be converted by treatment with hydrogen in the presence of a hydrogenating catalyst (as for example nickel deposited on silica gel or pumice) and at a temperature of about 150° Centigrade into completely or partially saturated products depending on the duration of treatment and hydrogen pressure employed.

The said mixture of olefines may also be divided into its single constituents or groups of constituents which may then be polymerised separately.

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 which comprises treating a mixture of hydrogen and carbon monoxide at an elevated temperature and at superatmospheric pressure in such a manner that a product containing besides methyl alcohol, mainly isobutyl alcohol and other higher alcohols is formed, separating methyl alcohol from the said product, then dehydrating the mixture of alcohols contained in this product freed from methyl alcohol, iso-olefines thus being formed and thereupon polymerising at least part of the said iso-olefines with the formation of polymers selected from the group consisting of dimers and trimers of the said iso-olefines.

2. In the process as claimed in Claim 1, dehydrating the product freed from methyl alcohol, separating the dehydrated product into a lower boiling and a higher boiling portion, polymerising the lower boiling portion and adding to the polymerised substance at least part of the said higher boiling portion.

3. In the process as claimed in Claim 1, dehydrating the product freed from methanol, dividing the dehydrated product into a lower boiling and a higher boiling portion, polymerising the said lower boiling portion, polymerising at least part of the said higher boiling portion, and then combining the resulting polymerisation products.

4. In the process as claimed in Claim 1, hydrogenating at least part of the polymerisation products with the formation of at least partly saturated products.

5. In the process as claimed in Claim 1, adding to the polymerisation products a substance obtained by the hydrogenation of part of the non-polymerised product resulting from the dehydration of the alcohols formed from the initial gas mixture.

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

Dated this 5th day of September, 1935.

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