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PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in the Cracking of Hydrocarbon Mixtures

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:—

It is already known that in the cracking of oils waste by the formation of coke frequently takes place, which is partly attributable to the impurities contained in the oils and partly to the small hydrogen content of the initial materials. In order to avoid this drawback it has already been proposed to free the initial materials from asphalt and impurities containing sulphur or nitrogen and the like and to take care that they contain sufficient hydrogen.

My foreign correspondents have now found that in cracking the fractions boiling above 250° Centigrade of the mixture of hydrocarbons prepared synthetically from carbon monoxide and hydrogen under well known conditions i.e. in the presence of catalysts at atmospheric or slightly elevated pressures and at temperatures below 250° Centigrade, large amounts of coke are formed although the fraction referred to is prepared from carefully purified gases free from substances known to lead to the formation of coke, and is very rich in hydrogen, containing about 18 parts of hydrogen for each 100 parts of carbon. Thus for example an oil boiling above 325° Centigrade which has been prepared by reduction of carbon monoxide and which has been freed from paraffin wax gives a coke residue of about 14 per cent. when cracked at from 550° to 600° Centigrade. This is the more surprising because other substances of quite similar composition, even when they are not so pure and are poorer in hydrogen, as for example petrolatum which contains only 15 parts of hydrogen for each 100 parts of carbon give only quite a small formation of coke when cracked.

My foreign correspondents have now found that such deleterious formation of coke is avoided by subjecting the said hydrocarbon fraction, prior to the cracking treatment, to refining by means of a chemical refining agent, or by means of selective solvents, or by a refining hydrogenation.

As chemical refining agents there may be mentioned in particular concentrated sulphuric acid, metal halides, as for example aluminium chloride, iron chloride, boron fluoride, zinc chloride and titanium chloride. When using the said substances it is preferable subsequently to carry out an aftertreatment with bleaching earths or alkali.

Substances having a physical action may also be used for the pretreatment of the oils, as for example selective solvents, such as phenols, keto acids, glycol acetate, liquid sulphur dioxide and liquid ammonia.

Contrary to expectation, the initial oils, in spite of their very high hydrogen content, are changed by a pretreatment with hydrogen in such manner that a considerably smaller formation of coke takes place in the subsequent cracking. This treatment with hydrogen may be carried out by leading the oils of high boiling point prepared from carbon monoxide and hydrogen, preferably directly after the separation of the constituents of lower boiling point, together with the residual gas formed in the reduction of the carbon monoxide or with fresh hydrogen, over known hydrogenation catalysts, such as metal compounds of the 5th to the 8th groups of the periodic system, in particular the sulphides or oxides, and especially those of the 6th group, at atmospheric or, preferably, at increased pressure, as for example from 20 to 200 atmospheres or more, and at temperatures of from 250° to 475° Centigrade.

As initial materials there may be mentioned the higher fractions, in particular those boiling above 250°, and preferably above 325° Centigrade, of products which have been prepared from carbon monoxide and hydrogen at temperatures of from 150° to 250° Centigrade at atmospheric or increased pressure, as for example 1 to 20 atmospheres, in

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the presence of catalysts, as for example a substance containing cobalt. It is preferable to free the said oils from solid paraffin wax before the treatment with the said substances. The cracking of the pretreated oils is carried out at atmospheric or increased pressure at temperatures of from about 500° to 700° Centigrade or more, preferably in the presence of catalysts, as for example metals, oxides, halides, phosphates, sulphides, metalloid halides, halogens or hydrogen halides or mixtures of the said substances. The cracking products thus obtained, in particular the benzine and middle oil fractions, constitute especially good initial materials for the production of high quality lubricating oils by polymerisation or condensation.

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

EXAMPLE.

A mixture of carbon monoxide and hydrogen in the ratio of 1:2 is led at 200° Centigrade over a catalyst containing cobalt, thorium and bleaching earths. The fraction boiling above 320° Centigrade of the oil thus obtained is freed from paraffin wax and then treated with about 2 per cent. sulphuric acid and subsequently with bleaching earth. The oil thus prepared is cracked at from 550° to 600° Centigrade while returning the products of high boiling point; in this way 72 per cent. of oil, consisting to the extent of 58 per cent. of benzine and middle oil, 27 per cent. of gaseous hydrocarbons and 0.5 per cent. of coke are obtained. If the pretreatment of the oil be carried out with phenol, the formation of coke amounts to 0.9 per cent.

If the same initial oil be cracked under the same conditions but without the pretreatment, 52 per cent. of oil, 33 per cent. of gaseous hydrocarbons and 14 per cent. of coke are obtained.

Dated this 21st day of August, 1936.

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

COMPLETE SPECIFICATION

Improvements in the Cracking of Hydrocarbon Mixtures

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 cracking of oils, loss by the formation of coke is frequently encountered which is partly attributable to the impurities contained in the oils and partly to the small hydrogen content of the initial materials. In order to avoid this drawback it has been proposed to free the initial materials from asphalt and impurities containing sulphur or nitrogen and the like and to provide that they contain sufficient hydrogen.

My foreign correspondents have now found that in cracking the fractions boiling above 250° Centigrade of the mixture of hydrocarbons prepared synthetically from carbon monoxide and hydrogen under well known conditions i.e. in the presence of catalysts at atmospheric or slightly elevated pressures and at temperatures below 300° Centigrade, large amounts of coke are formed although the fraction referred to is prepared from carefully purified gases free from substances known to lead to the formation of coke, and is very rich in hydrogen, containing about 18 parts of hydrogen for each 100 parts of carbon.

Thus for example an oil boiling above 325° Centigrade which has been prepared by reduction of carbon monoxide and which has been freed from paraffin wax gives a coke residue of about 14 per cent. when cracked at from 550° to 600° Centigrade. This is the more surprising because other substances of quite similar composition, even when they are not so pure and are poorer in hydrogen, as for example petrolatum which contains only 15 parts of hydrogen for each 100 parts of carbon give only quite a small formation of coke when cracked.

My foreign correspondents have now found that such deleterious formation of coke is avoided by subjecting the said hydrocarbon fraction, prior to the cracking treatment, to refining by means of a chemical refining agent, or by means of selective solvents, or by a refining hydrogenation.

As chemical refining agents there may be mentioned in particular concentrated sulphuric acid, metal halides, as for example aluminium chloride, ferric chloride, boron fluoride, zinc chloride and titanium chloride. When using the said substances it is preferable subsequently to carry out an aftertreatment with bleaching earths or alkali.

Substances having a refining effect by physical action may also be used for the pretreatment of the oils, as for example selective solvents, such as phenols, keto acids, glycol acetate liquid sulphur dioxide and liquid ammonia.

In spite of their very high hydrogen content, the initial oils are also changed by a pretreatment with hydrogen in such manner that a considerably smaller formation of coke takes place in the subsequent cracking. This treatment with hydrogen may be carried out by leading the oils of high boiling point prepared from carbon monoxide and hydrogen, preferably directly after the separation of the constituents of lower boiling point, together with the residual gas formed in the reduction of the carbon monoxide or with fresh hydrogen, over known hydrogenation catalysts, such as metal compounds of the 5th to the 8th groups of the periodic system, in particular the sulphides or oxides, and especially those of the 6th group, at atmospheric or, preferably, at increased pressure, as for example from 20 to 200 atmospheres or more, and at temperatures of from 250° to 475° Centigrade.

The refining with agents having a chemical action, such as sulphuric acid, metal halides or hydrogen, as well as with agents having a physical action is effected under conditions of temperature and duration of time such as may be used for the refining of other hydrocarbon mixtures, such as mineral oils or tars or their distillation products and the like.

As initial materials there may be mentioned the higher fractions, in particular those boiling over 250° Centigrade and preferably above 325° Centigrade, of products which have been prepared from carbon monoxide and hydrogen at temperatures of from 150° to 250° Centigrade at atmospheric or increased pressure, as for example 1 to 20 atmospheres or higher, in the presence of catalysts, as for example a substance containing cobalt or iron or nickel. It is preferable to free the said oils from paraffin wax before the treatment with the said substances. The cracking of the pretreated oils is carried out at atmospheric or increased pressure at temperatures of from about 500° to 700° Centigrade or more, preferably in the presence of catalysts, as for example metals, oxides, halides, phosphates, sulphides of metals, metalloid halides, halogens or hydrogen halides or mixtures of the said substances. The cracking products thus obtained, in particular the benzine and middle oil fractions, constitute especially good initial materials for the production of high quality lubricating oils by polmerisation or condensation.

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.

EXAMPLE.

A mixture of carbon monoxide and hydrogen in the ratio of 1:2 is led at 200° Centigrade over a catalyst containing cobalt, thorium and bleaching earths. The fraction boiling above 320° Centigrade of the oil thus obtained is freed from paraffin wax and then treated with about 2 per cent. sulphuric acid and subsequently with bleaching earth. The oil thus prepared is cracked at from 550° to 600° Centigrade while returning the products of high boiling point; in this way 72 per cent. of oil, consisting to the extent of 58 per cent. of benzine and middle oil, 27 per cent. of gaseous hydrocarbons and 0.5 per cent. of coke are obtained. If the pretreatment of the oil be carried out with phenol, the formation of coke amounts to 0.9 per cent.

If the same initial oil be cracked under the same conditions but without the pretreatment, 52 per cent. of oil, 33 per cent. of gaseous hydrocarbons and 14 per cent. of coke are obtained.

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 cracking the fractions boiling above 250° Centigrade of hydrocarbon mixtures obtained synthetically from carbon monoxide and hydrogen under known conditions as hereinbefore specified in which the said hydrocarbon mixtures are refined, prior to the cracking, by treatment with chemical refining agents, or by treatment with selective solvents, or by a refining hydrogenation.

2. In the process as claimed in Claim 1, treating a hydrocarbon mixture resulting from the reduction of carbon monoxide which boils at a temperature above 325° Centigrade.

3. In the process as claimed in Claim 1, using as refining agent acid agents as concentrated sulphuric acid or metal halides.

4. In the process as claimed in Claim 1, the further step of removing paraffin wax from the initial materials before pretreating them with a refining agent.

5. The process for the cracking of hydrocarbon mixtures substantially as

described in the foregoing Example.

6. Cracking products when obtained by the process particularly described and ascertained.

Dated the 20th day of August, 1937.
J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Agents.

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