[Second Edition.]

PATENT SPECIFICATION

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322,284

PROVISIONAL SPECIFICATION.

Improvements in the Manufacture and Production of Unsaturated Hydrocarbons of Low Boiling Point.

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 is already known that hydrocarbons and other organic compounds are obtained by the treatment of oxides of carbon with hydrogen, in the presence of catalysts which contain metals of the eighth group of the periodic system, in particular iron or cobalt, as their active components, at elevated temperatures, and under any suitable pressures. Moreover it is also known that the capacity of these catalysts for causing the formation of liquid hydrocarbons and other compounds can be greatly increased by the addition of quite definite quantities, which quantities may only vary within narrow limits, of alkali metal compounds such for example as hydroxides, carbonates, acetates and the like.

My foreign correspondents have now found that the addition of small quantities of sulphur to the catalysts which also contain besides metals of the eighth group of the periodic system, alkali metal compounds, appreciably lengthens the life of the catalyst, reduces the proportion of hydrocarbons of high boiling point and strongly promotes the formation of unsaturated hydrocarbons. The amount of sulphur to be added to the catalyst, which is preferably combined with the alkali metal for example, as alkali metal sulphide or hydrosulphide, should advantageously be more than 0.15 part by weight, but in any case not appreciably more than 0.4 part by weight for each 100 parts of metal of the eighth group of the periodic system, and the alkali content should preferably be between 0.3 and 0.6 per cent reckoned as alkali metal and with reference to the metal of the eighth group which is to serve as the catalyst. In order to obtain the necessary content of alkali and sulphur the addition of suitable quantities of sulphides, hydrosulphides, if desired in admixture with oxides, hydroxides or carbonates of alkali metals to the catalyst is frequently to be recommended. Additions of tellurium or selenium and the corresponding compounds thereof, such as selenides or tellurides produce a similar action to those of sulphur.

The catalysts are preferably prepared by adding the corresponding quantities of alkali metal sulphide or hydrosulphide to the metal hydroxides, which latter are prepared by precipitation for example from aqueous metal salt solutions, acidified with nitric acid, by means of ammonia or alkalies and subsequent decantation and washing out of the ammonium nitrate or alkali nitrate. The catalysts may also be prepared by precipitating for example iron nitrate by means of ammonia which contains hydrogen sulphide, and by then adding the requisite quantity of alkali metal hydroxide or carbonate to the dried precipitate.

Such catalysts may also be prepared by treating a catalyst free from sulphur such as is described for example in the Specification No. 312,717 with gases containing sulphuretted hydrogen. The metals of the eighth group can be employed alone or in admixture with one another or with other substances such as copper, silver, gold, cadmium and the like. Other additions may be employed such as alkali metal chlorides or the like. Difficultly reducible oxides, other than those of the alkali metals, are preferably employed only in subordinate quantities or not at all.

The pressure to be employed may vary within wide limits, thus diminished, ordinary, comparatively high and also very high pressures for example 200 atmospheres or even 1000 atmospheres and more can be employed. The working temperature is chosen according to the products desired and the pressure employed. At ordinary pressures it is preferable that the temperature should not exceed 300° Centigrade and at 200 atmospheres it should not exceed 350° Centigrade. At low temperatures and elevated pressures, for example at from

250° to 260° Centigrade and 50 atmospheres the tendency is to form high molecular products such as solid or semi-solid paraffins and waxes. In this case the operation is generally speaking attended with difficulties owing to the clogging up of the conduits, particularly when employing high pressures. It is therefore preferable in this case to arrange the catalyst in a large autoclave, to reduce it therein, and then to pass in a mixture of carbon monoxide and hydrogen under pressure. The paraffins and waxes can then be directly drawn off in the liquid state without any appreciable quantity being carried along by the stream of gas on account of vaporisation. Under certain circumstances it is preferable to add an oil of very high boiling point to the autoclave before hand; this covers the catalyst and consequently ensures a good heat exchange of the same. Sometimes this oil must be renewed since it is removed in solution together with the reaction products.

The products of olefinic character obtained in accordance with the present invention can be employed for a great variety of purposes, for example as anti-knock benzines as additions to other benzines in order to increase their resistance to knocking, for the manufacture of lubricating and insulating oils by condensation by means of aluminium chloride, boron fluoride and the like, for the catalytic manufacture of benzene hydrocarbons, and for the manufacture of alcohols, glycols and the like.

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

EXAMPLE 1.

A hydroxide mixture precipitated by means of ammonia and which contains iron and cobalt in the ratio of 4 to 1 by weight, is decanted several times, filtered off by suction and dried. After drying, the mixture is impregnated with a solution of potassium sulphide in such a quantity that the product contains 0.48 part of potassium and 0.2 part of sulphur to each 100 parts of the said metals, and the whole once more dried. The calculated quantity of potassium sulphide solution may also be added to the washed and still moist oxide or hydroxide mixture and then subjected to only one drying operation.

The catalyst so prepared is then reduced with hydrogen at 337° Centigrade. 200 cubic centimetres of this catalyst produce about 36 cubic centimetres of liquid hydrocarbons per cubic metre of a gas containing about 25 per cent of CO and 70 per cent of H_2 in a single passage of several weeks duration at 267° Centigrade and at ordinary pressure. The amount of constituents which boil above 180° Centigrade is about 10 per cent; the bromine value of the hydrocarbon mixture is from 130 to 135.

A catalyst which contains the corresponding quantity of potassium in the form of potassium hydroxide or potassium carbonate instead of potassium sulphide produces a hydrocarbon mixture under the same conditions which contains about 30 per cent of constituents boiling above 180° Centigrade, and which has a bromine value which lies between 90 and 100. Moreover the catalyst gradually becomes clogged up by the high-molecular products and also by the carbon which are formed. The yield after operating for 3 to 4 weeks has decreased to about half.

EXAMPLE 2.

Iron nitrate is precipitated with ammonia and the precipitate is decanted and washed until it is free from ammonium nitrate. The precipitate is then filtered off by suction and treated with an N-solution of potassium hydrosulphide in such quantity that the potassium content amounts to 0.4 per cent and the sulphur content to 0.32 per cent with reference to the iron metal. 200 cubic centimetres of the catalyst dried at from 170° to 180° Centigrade are reduced at 350° Centigrade. From each cubic metre of a gas containing 25 per cent of CO and 70 per cent of H_2, by a single passage over this catalyst at 200° Centigrade and at ordinary pressure 25 cubic centimetres of liquid hydrocarbons containing about 20 per cent of constituents which boil above 180° Centigrade are obtained. The same iron catalyst containing 0.4 per cent of potassium in the form of potassium hydroxide and no sulphur yields about the same quantity of hydrocarbons under the same reaction conditions, but the constituents which boil above 180° Centigrade amount to about 55 per cent. The bromine value of the hydrocarbon mixture obtained with the iron catalyst containing sulphur and alkali is 140 and that of the mixture obtained with the contact containing no sulphur is only 95.

In addition to hydrocarbons which are liquid at ordinary temperatures, a more or less large quantity of unsaturated and saturated hydrocarbons which are gaseous or readily volatile at ordinary temperatures and which mostly contain from 3 to 5 carbon atoms in the molecule is also obtained. By appropriate choice of the reaction conditions it is possible to favour or hinder the formation of these hydrocarbons.

Dated this 11th day of October, 1928.

JOHNSONS & WILLCOX,
47, Lincoln's Inn Fields, London,
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COMPLETE SPECIFICATION.

Improvements in the Manufacture and Production of Unsaturated Hydrocarbons of Low Boiling Point.

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 has already been proposed to obtain hydrocarbons and other organic compounds by the treatment of oxides of carbon with hydrogen, in the presence of catalysts, which contain metals of the eighth group of the periodic system, in particular iron or cobalt, as their active components at elevated temperatures, and under any suitable pressures. It has further been proposed to increase the capacity of these catalysts for causing the formation of liquid hydrocarbons and other compounds by the addition of quite definite quantities, which quantities may only vary within narrow limits, of alkali metal compounds such for example as hydroxides, carbonates, acetates and the like.

My foreign correspondents have now found that the addition of small quantities of sulphur in a free or preferably combined state to the catalysts which also contain besides metals of the eighth group of the periodic system, for example metals of the iron group, alkali metal compounds, appreciably lengthens the life of the catalyst; reduces the proportion of hydrocarbons of high boiling point and strongly promotes the formation of liquid unsaturated hydrocarbons from gaseous mixtures comprising oxides of carbon and hydrogen by treatment with the said catalysts at an elevated temperature and under any desired pressure. The amount of sulphur to be added to the catalysts, which is preferably combined with the alkali metal for example, as alkali metal sulphide or hydrosulphide, should advantageously be more than 0.15 part by weight, but in any case not appreciably more than 0.4 part by weight for each 100 parts by weight of metal of the eighth group of the periodic system and the alkali content should preferably be between 0.3 and 0.6 part by weight. In order to obtain the necessary content of alkali and sulphur the addition of suitable quantities of sulphides, hydrosulphides, if desired in admixture with oxides, hydroxides or carbonates of alkali metals to the catalyst is frequently to be recommended. Additions of tellurium or selenium or the corresponding compounds thereof, such as selenides or tellurides produce a similar action to that of sulphur in a free or combined state and may be used in place of the same.

The catalysts are preferably prepared by adding the corresponding quantities of alkali metal sulphide or hydrosulphide to the metal hydroxides, which latter are prepared by precipitation for example from aqueous metal salt solutions, acidified with nitric acid, by means of ammonia or alkalies and subsequent decantation and washing out of the ammonium nitrate or alkali nitrate. The catalysts may also be prepared by precipitating for example iron nitrate by means of ammonia which contains hydrogen sulphide, and by then adding the requisite quantity of alkali metal hydroxide or carbonate to the dried precipitate.

Such catalysts may also be prepared by treating a catalyst free from sulphur for example of the nature described in the introductory paragraph with gases containing sulphuretted hydrogen. The metals of the eighth group can be employed alone or in admixture with one another or with other substances such as copper, silver, gold, cadmium and the like in a free or combined state. Other additions may be employed such as alkali metal chlorides or the like. Difficultly reducible oxides, other than those of the alkali metals, are preferably employed only in subordinate quantities or not at all.

The pressure to be employed may vary within wide limits; thus, diminished, ordinary, comparatively high and also very high pressures for example 200 atmospheres or even 1000 atmospheres and more can be employed. The working temperature is chosen according to the products desired and the pressure employed. At ordinary pressures it is preferable that the temperature should not exceed 300° Centigrade and at 200 atmospheres it should not exceed 350° Centigrade. At low temperatures and elevated pressures, for example at from 250° to 260° Centigrade and 50 atmospheres the tendency is to form high molecular bye-products such as solid or semi-solid paraffins and waxes. In this case the operation is generally speaking attended with difficulties owing to the clogging up of the conduits, particularly when employing high pressures. It is therefore preferable in this case to arrange the catalyst in a large autoclave, to reduce it therein, and then to pass in a mixture of carbon monoxide and hydrogen under pressure. The paraffins and waxes can then be directly drawn off in the liquid state without any appreciable quantity being carried along by the stream of gas on account of vaporisation. Under certain circumstances it is preferable to add an oil of very high boiling point to the autoclave beforehand; this covers the catalyst and consequently ensures a good heat exchange of the same. Sometimes this oil must be renewed since it is removed in solution together with the reaction products.

The liquid products of olefinic character obtained in accordance with the present invention can be employed for a great variety of purposes, for example as anti-knock benzines as additions to other benzines in order to increase their resistance to knocking, for the manufacture of lubricating and insulating oils by condensation by means of aluminium chloride, boron fluoride and the like, for the catalytic manufacture of benzene hydrocarbons, and for the manufacture of alcohols, glycols and the like.

The following Examples will further illustrate how the said invention may be carried out in practice but the invention is not restricted to these Examples. The parts are by weight.

Example 1.

A hydroxide mixture precipitated by means of ammonia and which contains iron and cobalt in the ratio of 4 to 1 by weight, is decanted several times, filtered off by suction & dried. After drying, the mixture is impregnated with a solution of potassium sulphide in such a quantity that the product contains 0.48 part of potassium and 0.2 part of sulphur to each 100 parts of the said metals, and the whole once more dried. The calculated quantity of potassium sulphide solution may also be added to the washed and still moist oxide or hydroxide mixture and then subjected to only one drying operation.

The catalyst so prepared is then reduced with hydrogen at 337° Centigrade. 200 cubic centimetres of this catalyst produce about 36 cubic centimetres of liquid hydrocarbons per cubic metre of a gas containing about 25 per cent of CO and 70 per cent of H_2 in a single passage of several weeks duration at 267° Centigrade and at ordinary pressure. The amount of constituents which boil above 180° Centigrade is about 10 per cent; the bromine value of the hydrocarbon mixture is from 130 to 135.

A catalyst which contains the corresponding quantity of potassium in the form of potassium hydroxide or potassium carbonate instead of potassium sulphide produces a hydrocarbon mixture under the same conditions which contains about 30 per cent of constituents boiling above 180° Centigrade, and which has a bromine value which lies between 90 and 100. Moreover the catalyst gradually becomes clogged up by the high molecular products and also by the carbon which are formed. The yield after operating for 3 to 4 weeks has decreased to about half.

Example 2.

Iron nitrate is precipitated with ammonia and the precipitate is decanted and washed until it is free from ammonium nitrate. The precipitate is then filtered off by suction and treated with an N-solution of potassium hydrosulphide in such quantity that the potassium content amounts to 0.4 per cent and the sulphur content to 0.32 per cent with reference to the iron metal. 200 cubic centimetres of the catalyst dried at from 170° to 180° Centigrade are reduced at 350° Centigrade in a current of gas. From each cubic metre of a gas containing about 25 per cent of CO and about 70 per cent of H_2, by a single passage over this catalyst at about 260° Centigrade and at ordinary pressure 25 cubic centimetres of liquid hydrocarbons containing about 20 per cent of constituents which boil above 180° Centigrade are obtained. The same iron catalyst containing 0.4 per cent of potassium in the form of potassium hydroxide and no sulphur yields about the same quantity of hydrocarbons under the same reaction conditions, but the constituents which boil above 180° Centigrade amount to about 55 per cent. The bromine value of the hydrocarbon mixture obtained with the iron catalyst containing sulphur and alkali is 140 and that of the mixture obtained with the contact containing no sulphur is only 95.

In addition to hydrocarbons which are liquid at ordinary temperatures, a more or less large quantity of unsaturated and saturated hydrocarbons which are gaseous or readily volatile at ordinary temperatures and which mostly contain from 3 to 5 carbon atoms in the molecule is also obtained. By appropriate choice of the reaction conditions it is possible to favour or hinder the formation of these 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 manufacture and production of low boiling and unsaturated hydrocarbons from gaseous mixtures comprising oxides of carbon and hydrogen which consists in treating the said mixtures at an elevated temperature and under any desired pressure with catalysts, which contain besides metals of the eighth group of the periodic system, alkali metal compounds and which are provided with an addition of small quantities of sulphur in a free or combined state.

2. In the process as claimed in claim 1, the use of catalysts containing for each 100 parts by weight of a metal of the eighth group of the periodic system in a free or combined state, 0.3 to 0.6 part by weight of an alkali metal and between 0.15 and 0.4 part by weight of sulphur in a free or combined state.

3. In the process as claimed in claims 1 and 2 the use of selenium or tellurium or the corresponding compounds thereof in place of sulphur in a free or combined state.

4. The process for the manufacture and production of low boiling and unsaturated hydrocarbons from gaseous mixtures comprising oxides of carbon and hydrogen substantially as described in each of the foregoing Examples.

5. Low boiling and unsaturated hydrocarbons when obtained according to the preceding claiming clauses.

Dated this 8th day of July, 1929.

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