

PATENT SPECIFICATION

Application Date: June 11, 1935. No. 16,823 / 35.

458,035

Complete Specification Left: May 16, 1936.

Complete Specification Accepted: Dec. 11, 1936.

PROVISIONAL SPECIFICATION.



Improvements in the Reaction of Oxides of Carbon with 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—

In the reduction of oxides of carbon, in particular of carbon monoxide, by means of hydrogen to form gaseous, liquid and solid hydrocarbons, or to form oxygen-containing compounds in the presence of catalysts, the reactions are frequently strongly exothermic and effect an undesirable rise in the temperature when provision is not made for a careful withdrawal of the heat of reaction. Several proposals have already been made for withdrawing the said undesirable heat. For example it has been proposed to charge the catalysts into pockets or narrow tubes of material having good thermal conductivity around which flows a cooling agent, and it has also been proposed to spread the catalysts on flat plates capable of being cooled.

All these devices have the great drawback that the direct withdrawal of heat from the single particles of catalyst, i.e. from those places at which the heat is set free, takes place very incompletely and that the major portion of the excess heat is first transferred from the catalyst to the reaction gases and is then withdrawn from the latter by the cooling devices.

My foreign correspondents have now found that in the reaction of oxides of carbon in particular carbon monoxide and hydrogen, very good catalytic actions are obtained by employing as catalysts metallic parts of the apparatus which are etched, if desired with an addition of activators, on the surfaces coming into contact with the reacting gases and through or around which at the same time flows a heating or cooling agent. In this manner an intimate and therefore very efficient combination of the surface rendered catalytically active and the cooling system is obtained.

[Price 1/-]

As suitable metals for the parts of the apparatus which after etching, if desired with an addition of activators, form useful catalysts may be mentioned for example ingot steel, iron, special steels, nickel, copper and their alloys with other metals, and also metals coated with zinc, nickel or cobalt. The application of the active metals to the parts of the apparatus may be effected galvanically by electrolysis, by bringing up and burning in the active metal, by bringing up metal plates by soldering or otherwise, care being taken, however, that a junction of good thermal conductivity is obtained.

For example a suitable catalyst may be a spiral tube of ingot steel which has been pretreated according to this invention and through which the cooling or heating medium flows or a bundle of narrow tubes may be employed, the gas either flowing past the tubes while the cooling or heating medium flows through them, or the gas flowing through the tubes while the cooling or heating medium flows around them. The tubes may also be provided with ribs or other devices for increasing the surface area.

The etching of the surface of the catalyst may be effected in any suitable manner for example by suitable acids. Acetic and nitric acids have proved especially suitable for etching ingot steel. Activators, as for example compounds of uranium, alkali metals, copper, silver, magnesium, mercury, manganese, or chromium and in particular uranyl nitrate, copper nitrate, magnesium nitrate or potassium nitrate, may be added to the acids serving for etching. Other acids, such as lactic acid, formic acid or picric acid are also suitable. Alkalies, in particular aqueous ammonia or salts, may also be employed for etching many metals.

The etching may also be effected by the use of electrolysis, as for example in aqueous solutions of suitable acids, salts or bases, if desired in the presence of activators. The etching may also be effected with suitable gases capable of attacking the metals, as for example with hydrogen chloride, oxides of nitrogen, or

vapours or fused substances. The various methods of etching may also be used simultaneously or consecutively.

5 Suitable heating or cooling agents are gases, superheated or saturated steam, hot water, oils, or melts of metals or salts.

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

EXAMPLE.

15 A steel tubular spiral having 46 windings, the diameter of the windings being about 50 millimetres is arranged within a high pressure tube having an internal diameter of 90 millimetres and a length of 800 millimetres which is lined with copper. The steel tube, which is 8 metres in length, consists of the ingot steel known under the trade name of Mannesmann-SII-ingot steel; it is 5 millimetres in internal diameter and 8 millimetres in external diameter.

25 The outer surface of the spiral is etched for 48 hours with a solution of 1000 cubic centimetres of glacial acetic acid, 100 grams of uranyl nitrate and 10 grams of potassium nitrate. The solution is painted on every 2 hours and allowed to dry. The resulting rust is wiped off.

30 Superheated steam under a pressure of 12 atmospheres is led through the spiral

as a heating and cooling medium. After hydrogen alone has been led through the chamber under a pressure of 100 atmospheres for 24 hours at 394° Centigrade a mixture of 50 per cent. of carbon monoxide and 50 per cent. of hydrogen under a pressure of 100 atmospheres is led in an amount of 2 cubic metres per hour at a reaction temperature of from 368° to 412° Centigrade through the chamber for 17 days without interruption. 1 cubic metre per hour of final gas is obtained which contains 127 grams of oil and readily volatile hydrocarbons. The final gas has the composition:—

CO ₂	-	-	-	36.9 per cent.	
C _n H _{2n}	-	-	-	3.9 " "	50
CO	-	-	-	15.3 " "	
H ₂	-	-	-	20.9 " "	
C ₂ H ₆	-	-	-	5.2 " "	
CH ₄	-	-	-	13.9 " "	
N ₂	-	-	-	3.9 " "	55

The surface of the catalyst amounts to 2000 square centimetres so that the throughput is 1 litre per hour per square centimetre of catalytic surface.

Dated this 11th day of June, 1935.

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

COMPLETE SPECIFICATION.

Improvements in the Reaction of Oxides of Carbon with Hydrogen.

60 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 Frankfurt-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:—

80 In the reduction of oxides of carbon, in particular of carbon monoxide, by means of hydrogen to form in particular gaseous, liquid and solid hydrocarbons containing more than one carbon atom or to form oxygen-containing compounds in the presence of catalysts, the heat evolved by the conversions (which are exothermic)

is frequently very considerable and effects an undesirable rise in the temperature when provision is not made for a careful withdrawal of the heat of reaction. Several proposals have already been made for withdrawing the said undesirable heat. For example it has been proposed to charge the catalysts into pockets or narrow tubes of material having good thermal conductivity around which flows a cooling agent, and it has also been proposed to spread the catalysts on flat plates capable of being cooled.

100 All these devices have the great drawback that the direct withdrawal of heat from the single particles of catalyst i.e. from those places at which the heat is set free, takes place very incompletely and that the major portion of the excess heat is first transferred from the catalyst to the reaction gases and is then withdrawn from the latter by the cooling devices.

110 Our foreign correspondents have now found that in the reaction of oxides of carbon, in particular carbon monoxide and hydrogen, very good catalytic actions are obtained and that at the same time a

very easy and sufficiently rapid withdrawal or supply of heat is secured by employing as catalysts internal metallic surfaces of the apparatus itself which are etched, if desired, with an addition of activators, at the parts coming into contact with the reacting gases and through or around which at the same time preferably flows a heating or cooling agent. In this manner an intimate and therefore very efficient combination of the surface rendered catalytically active and the cooling system is obtained.

As suitable metals for the parts of the apparatus which after etching, if desired with an addition of activators, form useful catalysts may be mentioned for example iron metals, such as ingot steel, iron, special steels, nickel, cobalt or also copper and their alloys with other metals, and also metals coated with zinc, nickel or cobalt. Other metals, may, however, also be employed. Metals having a melting point below the temperature at which the conversion takes place are, of course, unsuitable. If the active metals are applied as coatings to the parts of the apparatus coming into contact with the reacting gases the application may be effected galvanically by electrolysis, by bringing up and burning in the active metal, by bringing up metal plates by soldering or otherwise, care being taken, however, that a junction of good thermal conductivity is obtained.

For example a suitable catalyst may be a spiral tube of ingot steel which has been pretreated according to this invention and through which the cooling or heating medium flows, or a bundle of narrow tubes consisting of or coated with any of the aforesaid metals may be employed the gas either flowing past the tubes while the cooling or heating medium flows through them, or the gas flowing through the tubes while the cooling or heating medium flows around them. The tubes may also be provided with ribs or other devices for increasing the surface area.

The etching of the surface of the catalyst may be effected in any manner which is known as suitable for etching metals, as for example by suitable acids. Acetic and nitric acids have proved especially suitable for etching ingot steel. Activators, as for example compounds of uranium, alkali metals, copper, silver, magnesium, mercury, manganese, or chromium and in particular uranyl nitrate, copper nitrate, magnesium nitrate or potassium nitrate, may be added to the acids or other agents serving for etching. Other acids, such as lactic acid, formic acid or picric acid are also suitable. Alkalies, in particular aqueous

ammonia or salts, may also be employed for etching many metals, as for example for etching zinc or iron, if desired by subjecting the said metals to electrolysis in an alkaline aqueous solution, as for example in caustic potash solution. Salts, such as nitrates of alkali metals or ammonium chloride or copper sulphate may also be employed as etching agents.

The etching may also be effected by the use of electrolysis, as for example in aqueous solutions of suitable acids, salts or bases, if desired in the presence of activators. The etching may also be effected with suitable gases capable of attacking the metals, as for example with hydrogen chloride, oxides of nitrogen, or vapours or fused substances. The various methods of etching may also be used simultaneously or consecutively.

Suitable agents for heating or cooling the gases to be converted are gases, superheated or saturated steam, hot water, oils, or melts of metals or salts.

The aforesaid conversion of the oxides of carbon with hydrogen are effected at temperatures above 150°, preferably between 200° and 450° Centigrade, and at any desired pressure, as for example atmospheric pressure or slightly elevated pressures, such as 2, 3, 5 or 10 atmospheres, or still higher pressures, such as 50 to 100 or more atmospheres. The duration of treatment usually ranges between some seconds and several days, as for example 8 or 24 or 48 hours.

For each volume of carbon monoxide, one volume of hydrogen may be employed, but other ratios, such as 2 to 3 or also 4 to 1 or 1 to 8 are also suitable. Usually between 10 and 80 per cent. and preferably between 40 and 60 per cent. of carbon monoxide are present in the initial gaseous mixture.

The following Example will further illustrate how one of the modifications of the process according to this invention may be carried out in practice but the invention is not restricted to this Example.

EXAMPLE.

A steel tubular spiral having 46 windings, the diameter of the windings being about 50 millimetres, is arranged with a high pressure tube having an internal diameter of 90 millimetres and a length of 800 millimetres which is lined with copper. The steel tube, which is 8 metres in length, consists of the ingot steel known under the trade name of Mannesmann-Sil-ingot steel; it is 5 millimetres in internal diameter and 8 millimetres external diameter.

The outer surface of the spiral is etched for 48 hours with a solution of 1000 cubic

centimeters of glacial acetic acid, 100 grams of uranyl nitrate and 10 grams of potassium nitrate. The solution is painted on every 2 hours and allowed to dry. The resulting rust is wiped off.

5 Superheated steam which may have a temperature between 200° and 400° Centigrade is led under a pressure of 12 atmospheres through the spiral as a heating and cooling medium. After hydrogen alone has been led through the chamber under a pressure 100 atmospheres for 24 hours at 394° Centigrade a mixture of 50 per cent. of carbon monoxide and 50 per cent. of hydrogen under a pressure of 100 atmospheres is led in an amount of 2 cubic metres per hour at a reaction temperature of from 368° to 412° Centigrade through the chamber for 17 days without interruption. 1 cubic metre per hour of final gas is obtained which contains 127 grams of oil and readily volatile hydrocarbons. The final gas has the composition:—

25	CO_2	36.9	per cent.
	C_nH_{2n}	3.9	" "
	CO	15.3	" "
	H_2	20.9	" "
	C_2H_6	5.2	" "
30	CH_4	13.9	" "
	N_2	3.9	" "

The surface of the catalyst amounts to 2000 square centimetres so that the throughput is 1 litre per hour per square centimetre of catalytic surface.

35 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 conversion of oxides of carbon with hydrogen at an elevated temperature into gaseous, liquid or solid hydrocarbons or their oxygen-containing derivatives, which comprises passing a mixture of such oxide of carbon, in particular carbon monoxide, and hydrogen at an elevated temperature through an apparatus in which the conversion is catalytically promoted by the internal surfaces of the apparatus itself which at the parts coming into contact with the said mixture comprises an etched metal, in particular an etched iron metal, such as an etched metallic substance essentially comprising iron.

2. In the process as claimed in claim 1, passing the mixture of carbon monoxide and hydrogen at a temperature above 150° , preferably between 200° and 450° Centigrade, through the apparatus.

3. In the process as claimed in Claim 1 or 2 passing the carbon monoxide and hydrogen at an elevated temperature through the apparatus in which apart from the catalytic internal surfaces of the apparatus itself no further catalyst is present.

4. The process for the conversion of oxides of carbon with hydrogen substantially as described in the foregoing Example.

5. Gaseous, liquid and solid hydrocarbons and their oxygen-containing derivatives, when obtained by the process particularly described and ascertained.

Dated this 16th day of May, 1936.

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