PATENT SPECIFICATION

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1616

PROVISIONAL SPECIFICATION.

Method of Operating with Gases Containing Carbon Monoxide at Elevated Temperatures.

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 organised under the Laws of Germany) to be as follows:—

A process has already been proposed in Specification No. 231,285 for producing oxygenated organic compounds by the catalytic reduction of carbon monoxide with hydrogen at an elevated temperature and under pressure, the operation being carried out in apparatus in which the parts coming into contact with carbon monoxide are lined, coated or made of copper, silver or aluminium, or their alloys, or special steels having a large content of chromium, manganese, tungsten, vanadium or molybdenum, or are provided with coatings of chromium, manganese, tungsten, vanadium or molybdenum. At the same time, less refractory metals, such as tin, zinc, lead or the like may be employed for the less hot or cold parts of the apparatus which come into contact with the carbon monoxide, or resistant non-metallic coatings may be employed in such parts. The object of these precautionary measures is to prevent, as far as possible, the formation of iron carbonyl, as otherwise poisoning of the catalysts, deposition of iron from the gases containing iron carbonyl at undesired places, obstructions, and deposition of carbon may occur.

My foreign correspondents have now found that these precautionary measures are not absolutely essential in the case of those parts of the apparatus, which have a comparatively high temperature, such as from 350 to 500 degrees Centigrade and also the cold parts, because at these temperatures iron is only corroded by carbon monoxide, with the formation of iron carbonyl to a negligible extent, and, under certain circumstances, the iron is not attacked at all, whereas the said measures are necessary for those parts which have a medium temperature, as for example from 180 to 200 degrees Centigrade. Hence, the highly heated parts of the apparatus may be of iron, but such parts as are at temperatures of from 180 to 200 degrees Centigrade and which come into contact with the gases containing carbon monoxide, must in any event be made of some other material than carbonyl-forming iron, and of one which is able to resist carbon monoxide, such as copper, aluminium or highly alloyed special steel, or else must be lined with such material.

In order to ensure more reliable working, and especially when operating with high partial pressure of carbon monoxide, it is advisable to broaden the range of temperature within which no carbonyl-forming iron may be used, beyond the limits of from 180 to 200 degrees Centigrade, namely from 150 to 250 degrees Centigrade.

The method of working according to the present invention is applicable to operations with high temperatures, with gases containing carbon monoxide, as for example in the synthesis of methanol and other organic compounds or in the destructive hydrogenation of coals, tars, mineral oils and other carbonaceous materials, since, in these cases the gases are always admitted to and discharged from the heat exchangers, reaction vessels and the like, at low temperatures, so that the said gases must traverse zones having medium temperatures in which no carbonyl-forming iron should be present. Consequently, according to the present invention, in the catalytic treatment of gases containing carbon monoxide especially in the synthesis of methanol and other organic compounds certain parts of the apparatus, which are at temperatures between 180 and 200 degrees Centigrade, or better still, between 150 and 250 degrees Centigrade, should be constructed of other, insensitive materials, and not of ordinary iron.

The result of the foregoing consideration is that it is advisable that the said apparatus for operations with gases containing carbon monoxide, as for example in the synthesis of methanol, in so far as the hot parts consist of iron, should not be

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heated from a temperature lying below the mean banned temperature range or cooled from a temperature above the said range to a temperature below the said range in the presence of carbon monoxide, but only in the presence of other gases, in particular hydrogen, in order to prevent the contact of carbon monoxide with iron within the banned range of temperature.

The following example will further illustrate the nature of the said invention which however is not limited thereto.

EXAMPLE.

The reaction vessel for the synthesis of methanol from a gaseous mixture, consisting of 20 per cent of carbon monoxide and 80 per cent of hydrogen, at a pressure of 200 atmospheres, consists of a high-pressure tube composed entirely of iron and heated to 400 degrees Centigrade by internal means. The reaction gases are subjected to a mutual exchange of heat by admitting the incoming gases into the heat exchanger at a temperature of 25° Centigrade and discharging therefrom with a temperature of about 280° Centigrade whereupon they are led into the reaction vessel direct. The gases issuing from the reaction vessel enter the heat exchanger with a temperature of 400° Centigrade and leave it with a temperature of about 100° Centigrade. The heat exchanger is wholly constructed of manganese copper, whilst all other parts of the apparatus especially the connections between the heat exchanger and the reaction vessel which have temperatures between 280 and 400 degrees Centigrade, are of iron, as are also the circulation pipes, with temperatures up to 100° Centigrade, and the reaction vessel itself, which is maintained at 400° Centigrade.

The employment of a catalyst containing zinc and chromium enables a good yield of very pure methanol to be obtained in a continuous manner and without interruption due to defects in the plant. If, on the other hand, the manganese copper heat exchanger of the apparatus be replaced by one of iron, troubles become apparent in a short time. The iron parts of the heat exchanger are attacked by carbon monoxide, with the formation of iron carbonyl, and the tubes of the heat exchanger are ruined, in a shorter or longer period depending on their thickness. Moreover, the upper part of the catalyst becomes contaminated by large deposits of iron, giving rise to the deposition of carbon and formation of methane, the catalyst being gradually spoiled completely.

Dated this 30th day of December, 1927.

JOHNSONS & WILLCOX,
47, Lincoln's Inn Fields, London, W.C. 2,
Agents.

COMPLETE SPECIFICATION.

Method of Operating with Gases Containing Carbon Monoxide at Elevated Temperatures.

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 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:—

A process has already been proposed in Specification No. 231,285 for producing oxygenated organic compounds by the catalytic reduction of carbon monoxide with hydrogen at an elevated temperature and under pressure, the operation being carried out in apparatus in which the parts coming into contact with carbon monoxide are lined, coated or made of copper, silver or aluminium, or their alloys, or special steels having a large content of chromium, manganese, tungsten, vanadium or molybdenum, or are provided with coatings of chromium, manganese, tungsten, vanadium or molybdenum. At the same time, less refractory metals, such as tin, zinc, lead or the like may be employed for the less hot or cold parts of the apparatus which come into contact with the carbon monoxide, or resistant non-metallic coatings may be employed in such parts. The object of these precautionary measures is to prevent, as far as possible, the formation of iron carbonyl, as otherwise poisoning of the catalysts, deposition of iron from the gases containing iron carbonyl at undesired places, obstructions, and deposition of carbon may occur. A process has further been proposed for manufacturing formaldehyde by the interaction of carbon monoxide and water in which the reaction vessel is provided internally with an aluminium or other inert metal casing or is constructed of aluminium and the like, reaction temperatures of 220° and 340°

Centigrade being mentioned. It has further been proposed to manufacture formates by the action of carbon monoxide or gases containing the same on solutions of sodium or potassium hydroxide or on suspensions of the hydroxides of calcium, barium or strontium in water under pressures of more than 300 atmospheres and at temperatures of about 400° Centigrade in reaction vessels the inner wall of which is constructed of copper and the pressure bearing wall being constructed of iron or nickel steel. It has further been proposed to produce formaldehyde or methyl alcohol from carbon monoxide and hydrogen in a reaction vessel constructed of copper, iron or iron provided with stone or pottery or lined with platinum or other contact substance, temperatures of between about 100° and 250° to 300° Centigrade being mentioned as suitable for the process.

My foreign correspondents have now found that these precautionary measures are not absolutely essential in the case of those parts of the apparatus which have a comparatively high temperature, such as from 350 to 500 degrees Centigrade and also the cold parts, because at these temperatures iron is only corroded by carbon monoxide, with the formation of iron carbonyl to a negligible extent, and, under certain circumstances, the iron is not attacked at all, whereas the said measures are necessary for those parts which have a medium temperature, as for example from 180 to 200 degrees Centigrade. Hence, the highly heated parts of the apparatus may be of iron, but such parts as are at temperatures of from 180 to 200 degrees Centigrade and which come into contact with the gases containing carbon monoxide, must in any event be made of some other material than carbonyl-forming iron, and of one which is able to resist carbon monoxide, such as copper, aluminium or highly alloyed special steel, or else must be lined with such material.

In order to ensure more reliable working, and especially when operating with high partial pressure of carbon monoxide, it is advisable to broaden the range of temperature within which no carbonyl-forming iron may be used, beyond the limits of from 180 to 200 degrees Centigrade, and according to this invention the limits comprise 150° to 250° Centigrade.

The method of working according to the present invention is applicable to operations with high temperatures and under pressure, with gases containing carbon monoxide, as for example in the synthesis of methanol and other organic compounds, or in the destructive hydrogenation of coals, tars, mineral oils and other carbonaceous materials, since, in these cases the gases are always admitted to and discharged from the heat exchangers, reaction vessels and the like, at low temperatures, so that the said gases must traverse zones having medium temperatures in which no carbonyl-forming iron should be present. Consequently, according to the present invention, in the catalytic treatment of gases containing carbon monoxide especially in the synthesis of methanol and other organic compounds certain parts of the apparatus, which are at temperatures between 180 and 200 degrees Centigrade, or better still between 150 and 250 degrees Centigrade, should be constructed of other, insensitive materials, and not of ordinary iron.

The result of the foregoing considerations is that it is advisable that the said apparatus for operations with gases containing carbon monoxide, as for example in the synthesis of methanol, in so far as the hot parts consist of iron, should not be heated from a temperature lying below the mean banned temperature range or cooled from a temperature above the said range to a temperature below the said range in the presence of carbon monoxide, but only in the presence of other gases, in particular hydrogen, in order to prevent the contact of carbon monoxide with iron within the banned range of temperature.

The following Example will further illustrate how the said invention may be carried into practical effect but the said invention is not restricted thereto.

EXAMPLE.

The reaction vessel for the synthesis of methanol from a gaseous mixture, consisting of 20 per cent of carbon monoxide and 80 per cent of hydrogen, at a pressure of 200 atmospheres, consists of a high-pressure tube composed entirely of iron and heated to 400 degrees Centigrade by internal means. The reaction gases are subjected to a mutual exchange of heat by admitting the incoming gases into the heat exchanger at a temperature of 25 degrees Centigrade and discharging therefrom with a temperature of about 280 degrees Centigrade whereupon they are led into the reaction vessel direct. The gases issuing from the reaction vessel enter the heat exchanger with a temperature of 400 degrees Centigrade and leave it with a temperature of about 100 degrees Centigrade. The heat exchanger is wholly constructed of manganese copper, whilst all other parts of the apparatus especially the connections between the heat exchanger and the reaction vessel which have temperatures between 280 and 400 degrees Centigrade, are of iron, as are also the circulation pipes, with temperatures up to 100 degrees Centigrade, and the reaction vessel itself, which is maintained at 400 degrees Centigrade.

The employment of a catalyst containing zinc and chromium enables a good yield of very pure methanol to be obtained in a continuous manner and without interruption due to defects in the plant. If, on the other hand, the manganese copper heat exchanger of the apparatus be replaced by one of iron, troubles become apparent in a short time. The iron parts of the heat exchanger are attacked by carbon monoxide, with the formation of iron carbonyl, and the tubes of the heat exchanger are ruined, in a shorter or longer period depending on their thickness. Moreover, the upper part of the catalyst becomes contaminated by large deposits of iron, giving rise to the deposition of carbon and formation of methane, the catalyst being gradually spoiled completely.

I am aware of Specifications Nos. 277,273, 249,155, 203,812, 247,217 and 240,955 and do not claim anything described or claimed therein. I am also aware of Specifications Nos. 286,010 and 300,294 and make no claim to what is claimed therein.

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. The process for operating with gases containing carbon monoxide at an elvated temperature and pressure in particular in the production of oxygenated organic compounds by the catalytic reduction of carbon monoxide which consists in the exclusion of iron only from those parts of the apparatus having temperatures of between about 180° and 200° Centigrade and preferably of between about 150° and 250° Centigrade.

2. A specific manner of carrying out the process according to claim 1, which consists in the exclusion of carbon monoxide and preferably working in the presence of hydrogen when heating the apparatus up to the reaction temperature and cooling it down.

3. The process for operating with gases containing carbon monoxide substantially as described in the foregoing Example.

Dated this 7th day of August, 1928.

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