PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Improvements in the Manufacture and Production of Oxygenated Organic Compounds.

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 the Badische Anilin & Soda Fabrik, of Ludwigshafen-on-Rhine, Germany, a company incorporated according to German laws) to be as follows:—

The catalytic production of methanol and other oxygenated organic compounds by the interaction of oxides of carbon and hydrogen, has already been described; it has also been stated that the capacity of the contact masses for the production of these oxygenated compounds is considerably diminished or even entirely destroyed by the presence of iron, nickel or cobalt in the said contact masses. It has also been recommended to exclude the said metals, or compounds thereof, from the gases which are to be brought into reaction as well as from the contact vessel itself and other parts of the apparatus.

My foreign correspondents have now discovered that iron, nickel and cobalt, hereinafter for brevity referred to as "iron metals," not only lose their injurious property in the production of oxygenated organic compounds, but actually exert a high catalytic activity in the said production, when the said iron metals or their oxides are employed in a chemical combination or in the form of alloys or solid solutions. For example suitable contact masses containing iron, nickel or cobalt may consist of an oxide of such metals of the iron group or other compounds thereof in conjunction with a difficultly reducible oxygen compound for example an oxide of chromium, vanadium, tungsten, zirconium, aluminium, titanium or others suitable to form chemical compounds, or solid solutions, with the said compounds of the metals of the aforesaid iron group. Or the said metals themselves may be used in a state of an alloy or compound with one or more suitable elements such for example as manganese, chromium, tungsten, tin, zinc, silicon, boron, sulphur, phosphorus, arsenic or other metalloids other than carbon, and the like. It is, however, necessary that such contact masses contain the metal of the iron group saturated or even super-saturated with the dissolved or compounded element. For example, an iron alloy must consist of mixed crystals only with no free iron crystals. In accordance with this invention, the catalysts consisting of iron and a sufficient amount of sulphur, phosphorus, arsenic or other metalloids, except carbon, give rise to ample quantities of oxygenated organic compounds such as alcohols, ketones, acids, esters, and the like, whereas a contact mass containing free iron does not allow of organic compounds containing oxygen being produced in any substantial amount from mixtures of carbon oxide and hydrogen, but only methane and water and at the same time a deposit of carbon. The efficiency of the above-mentioned contact masses is further improved by the addition of an alkali or alkali metal compounds. In many cases the nature of the products will be more or less different as compared with those produced with contact masses free from the said iron metals, for example higher alcohols, ketones, acids, and the like are formed in the present case in larger amounts.

[Price

Generally it is advisable in order to keep the said contact masses active for a long period of time, to cause them always to contain a certain amount of combined oxygen, and a small addition of oxygen may be made to the gases for this purpose, or part or even all of the hydrogen may be replaced by water vapour or steam. Hydrocarbons, for example methane, may also be present in addition to or instead of part or all of the hydrogen. Accordingly, water vapour, or steam, or hydrocarbons constitute equivalents of hydrogen for the purpose of the present invention. With an increased percentage of carbon monoxide the formation of higher molecular products is generally increased and the formation of water lowered, whereas with a preponderating volume of hydrogen the relative production of methanol is increased. The gases to be subjected to the reaction must also be free from iron carbonyl which would be decomposed by the contact masses and produce a coating thereon of free metallic iron which would give rise to undesirable reactions. Such an iron-coated contact mass would however be made effective again by binding the said free iron for example with sulphur or arsenic. Also care should be taken to avoid the formation of volatile compounds of the iron metals by a contact of the gases with surfaces of free iron metals, in the apparatus, and this may be effected by lining the said apparatus with, or making it of, suitable non-ferrous metals, such as copper, aluminium, silver, manganese, chromium or other non-ferrous metals or of a suitable iron alloy, such as steel V2A of the firm of Krupp, or iron combined, or saturated, at least superficially, with sulphur, arsenic or with other of the aforesaid elements, when however attention must be given to the fact that sulphur or some other elements would be extracted by the action of the reducing gases at high temperatures, say above about 400 degrees Centigrade.

The following examples are given to illustrate further the nature of this invention, the parts being by weight unless otherwise stated, but the invention is not confined to these examples which may be varied within wide limits.

EXAMPLE 1.

One part of manganese nitrate and one part of nickel chloride are dissolved in water and precipitated with a solution of two parts of potassium carbonate. The mixture is evaporated without filtration and dried at 120 degrees Centigrade. The contact mass thus obtained gives rise, with a gas mixture composed of one volume of carbon dioxide, one volume of carbon monoxide, and two volumes of hydrogen, at 320 degrees Centigrade and with a pressure of 300 atmospheres, to a product containing methanol and other alcohols, organic acids, esters and ketones.

EXAMPLE 2.

Ten parts of metallic iron are melted with ten parts of zinc, and twenty parts of tungstic acid introduced into the melt. With such contact mass a gas mixture containing 40 per cent. of carbon monoxide and 60 per cent. of hydrogen produces, at 200 atmospheres pressure and 460 degrees Centigrade, a mixture of methyl alcohol and higher molecular, oxygenated organic compounds.

EXAMPLE 3.

Ferric hydroxide is kneaded with 10 per cent. its weight of chromium hydroxide, dried and reduced to grains. The mass is then soaked with a solution of 40 per cent. its weight of zinc nitrate and 40 per cent. its weight of potassium permanganate. A gas mixture composed of coal gas and carbon monoxide is first passed over a methane forming catalyst at a temperature of about 500 degrees Centigrade and a pressure of 800 atmospheres; the gas mixture produced containing about 30 per cent. carbon monoxide, 30 per cent. methane, 30 per cent. hydrogen and 10 per cent. nitrogen, carbon dioxide and other gases is then passed at the aforesaid pressure and at a temperature of 380 degrees Centigrade over the before described catalytic mass whereby a mixture of methanol, ethyl alcohol, propyl alcohol, acetone, acids and so on is produced. A contact mass composed of iron, manganese and arsenic acts in a similar manner.

EXAMPLE 4.

A contact mass composed of 80 per cent. nickel oxide and 20 per cent. chromium oxide may be used for producing from a mixture of one volume of carbon monoxide and two volumes of hydrogen at 320 degrees Centigrade and at 800 atmospheres pressure, methyl alcohol and water and considerable amounts of higher alcohols. The yield of higher alcohol is further increased and the formation of water diminished by adding methane to the gas mixture, which addition has also the advantage of reducing the risk of a sudden superheating of the contact mass. An addition of steam acts in a similar way.

EXAMPLE 5.

A contact mass containing 60 parts of zinc oxide and 30 parts of chromium oxide which is very suitable for producing methanol from carbon monoxide and hydrogen, would be much damaged by an addition of 10 parts of free iron oxide and would yield practically exclusively water and hydrocarbons with a heavy deposition of carbon. If, however, 5 parts of sulphur are further added to the mass, it produces, when a mixture of carbon monoxide and hydrogen is passed over it, at 400 degrees Centigrade and 200 atmospheres pressure, ample quantities of methanol and higher molecular products. A similar action is exerted by other metalloids such for example as tellurium, phosphorus, arsenic, or other metalloids related thereto, such as tin, antimony, bismuth or the like.

EXAMPLE 6.

Manganese steel is dissolved in an acid, the solution evaporated to dryness and the residue mixed with a solution of 20 per cent. its weight of vanadic acid and 20 per cent. its weight of chromic acid. The mass is dried at 120 degrees Centigrade, and when a mixture of 20 per cent. of carbon dioxide and 80 per cent. of hydrogen is passed over this contact mass at 200 atmospheres pressure and 350 degrees Centigrade, the formation of oxygenated organic compounds takes place.

EXAMPLE 7.

100 parts of zinc oxide are soaked in the order named with solutions of 10 parts of chromic acid, 10 parts of ferric nitrate, 10 parts of potassium carbonate and 5 parts of arsenic pentoxide, and dried at 150 degrees Centigrade. A gas mixture composed of 60 per cent. carbon monoxide and 40 per cent. of hydrogen, completely dry and free from iron carbonyl, when passed over the said mass at 350 degrees Centigrade and 200 atmospheres pressure gives rise to a product composed of methyl alcohol and small amounts of ethyl-, propyl-, isobutyl- and other alcohols and acids, for example formic and acetic acid.

EXAMPLE 8.

Three parts of cobalt hydroxide are kneaded with one part of uranium oxide and one part of manganese oxide, dried and reduced to grains and then soaked with a concentrated potash solution.

Illuminating gas, freed from sulphur compounds and benzene hydrocarbons by treatment with active carbon or silica gel and having about the composition:—50 per cent. hydrogen, 30 per cent. methane, 12 per cent. carbon monoxide, 4 per cent. ethylene and 4 per cent. nitrogen, is then passed over the said contact mass at 400 degrees Centigrade and 800 atmospheres pressure.

The reaction gases when cooled while under pressure yield a liquid condensate containing methanol, ethyl and higher alcohols, saturated and unsaturated ketones and other organic compounds. The remainder of gas is passed through other contact furnaces or returned to the same contact mass by means of a circulating pump. The gas may be replenished by adding fresh purified coal gas or such gases as are consumed by the reaction.

Dated this 2nd day of February, 1925.

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

COMPLETE SPECIFICATION.

Improvements in the Manufacture and Production of Oxygenated Organic Compounds.

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 the Badische Anilin & Soda Fabrik, of Ludwigshafen-on-Rhine, Germany, a corporation organized according to German laws) and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The catalytic production of methanol and other oxygenated organic compounds by the interaction of oxides of carbon and hydrogen, has already been described; it has also been stated that the capacity of the contact masses for the production of these oxygenated compounds is considerably diminished or even entirely destroyed by the presence

of iron, nickel or cobalt in the said contact masses. It has also been recommended to exclude the said metals, or compounds thereof, from the gases which are to be brought into reaction as well as from the contact vessel itself and other parts of the apparatus.

My foreign correspondents have now discovered that iron, nickel and cobalt, hereinafter for brevity referred to as "iron metals," not only lose their injurious property in the production of oxygenated organic compounds, but actually exert a high catalytic activity in the said production, when the said iron metals or their oxides are employed in a chemical combination or in the form of alloys or solid solutions (which latter terms do not mean mere agglomerates or mixtures of separate particles but an entirely homogeneous mass, such for example as the materials known as spinels which consist of two or more metal oxides homogeneously combined, which in some cases may even be regarded as chemical compounds). The said compounds, alloys, or solid solutions should be such as contain the components in proportions that admit of the characteristic properties of the individual components being no longer present. For this purpose the iron metals should also not be combined with copper or silver alone and the combination should be stable and not allow the formation of free iron metal either by reduction or by decomposition under the conditions of working, that is, under the influence of a stream of reducing gas containing carbon monoxide and hydrogen, at a temperature of generally between about 200° and 600° Centigrade, and generally also under a considerable pressure. For example suitable contact masses containing iron, nickel or cobalt may consist of an oxide of an iron metal or another compound thereof in conjunction with a difficultly reducible oxygen compound such as oxides of chromium, vanadium, tungsten, zirconium, aluminium, titanium or others suitable to form chemical compounds or solid solutions with the said compounds of the iron metals. Or the said metals themselves may be used in a state of an alloy with one or more suitable metals such for example as manganese, chromium, tungsten, tin, zinc, and the like, the latter being sufficient in quantity to leave no free iron and the like present, or in the state of a compound with one or several metalloids, such as silicon, boron, sulphur, phosphorus, arsenic or other metalloids other than carbon. It is, however, necessary that such contact masses contain the metal of the iron group saturated or even supersaturated with the dissolved or compounded element. For example, an iron alloy must contain the iron as a solid solution only with no free iron crystals.

In accordance with this invention, the catalysts consisting of iron and a sufficient amount of another metal or of sulphur, phosphorus, arsenic or other metalloids, except carbon, give rise to ample quantities of oxygenated organic compounds such as alcohols, ketones, acids, esters, and the like, whereas a contact mass containing free iron does not allow or organic compounds containing oxygen being produced in any substantial amount from mixtures of carbon oxide and hydrogen, but only methane and water and at the same time a deposit of carbon. For example in a gas mixture consisting of carbon monoxide and hydrogen at a temperature of about 450 degrees Centigrade or higher, iron oxide even when mixed with a small percentage of chromium oxide is largely reduced. When such a catalyst is employed for the catalytic hydrogenation of carbon oxides, only water and methane are formed. When, however, so much chromium oxide is added as will transform all the iron to iron chromium spinel ($FeO.Cr_2O_3$) which is not reduced under the said conditions of working, organic reaction products containing oxygen are formed as well as some water resulting from the condensation of organic compounds containing oxygen of low molecular weight. The efficiency of the above mentioned contact masses is further improved by the addition of an alkali or alkali metal compound. In many cases the nature of the products will be more or less different as compared with those produced with contact masses free from the said iron metals, for example higher alcohols, ketones, acids, and the like are formed in the present case in larger amounts. For example, pure methanol is produced when a purified mixture of 20 per cent. of carbon monoxide and 80 per cent. of hydrogen is passed at a pressure of 200 atmospheres and at 380 degrees Centigrade over a contact mass prepared from 20 per cent. of chromic acid, 10 per cent. of cupric oxide and 70 per cent. of zinc oxide; when, however, 0.01 per cent. of iron oxide is added to the contact mass which iron oxide is bound by the chromic acid or chromic oxide and therefore is not reduced to metallic iron, the total yield is not diminished, but the product consists of 96 per cent. to 97 per cent. of methanol and about 3 per cent. to 4 per

cent. of higher alcohols, especially of normal propyl and isobutyl alcohol.

Generally it is advisable in order to keep the said contact masses active for a long period of time, to cause them always to contain a certain amount of combined oxygen, and a small addition of oxygen may be made to the gases for this purpose. Part or in the case of carbon monoxide, even all of the hydrogen may be replaced by water vapour or steam. Hydrocarbons, for example methane, may also be present in addition to or instead of part or all of the hydrogen. Accordingly, water vapour, or steam, or hydrocarbons constitute equivalents of hydrogen for the purpose of the present invention. With an increased percentage of carbon monoxide the formation of higher molecular products is generally increased and the formation of water lowered whereas with a preponderating volume of hydrogen the relative production of methanol is increased. The gases to be subjected to the reaction must also be free from iron carbonyl which would be decomposed by the contact masses and produce a coating thereon of free metallic iron which would give rise to undesirable reactions. Such an iron-coated contact mass would however be made effective again by binding the said free iron for example with sulphur or arsenic. Also care should be taken to avoid the formation of volatile compounds of the iron metals by a contact of the gases with surfaces of free iron metals, in the apparatus, and this may be effected by lining the said apparatus with, or making it of, suitable non-ferrous metals such as copper, aluminium, silver manganese, chromium or other non-ferrous metals or of a suitable iron alloy, such as steel V2A of the firm of Krupp, or iron combined, or saturated, at least superficially, with sulphur, arsenic, or with other of the aforesaid elements, when however attention must be given to the fact that sulphur or some other elements would be extracted by the action of the reducing gases at high temperatures, say above about 400 degrees Centigrade.

The following examples are given to illustrate how the invention may be carried into practical effect, the parts being by weight unless otherwise stated, but the invention is not confined to these examples which may be varied within wide limits.

EXAMPLE 1.

One part of manganese nitrate and one part of nickel chloride are dissolved in water and precipitated with a solution of two parts of potassium carbonate. The mixture is evaporated without filtration and dried at 120 degrees Centigrade. The contact mass thus obtained (consisting of a sort of spinel and insofar as part of the oxide is reduced in working, of an alloy) gives rise, with a gas mixture composed of one volume of carbon dioxide, one volume of carbon monoxide and two volumes of hydrogen, at 320 degrees Centigrade and with a pressure of 300 atmospheres to a product containing methanol and other alcohols, organic acids, esters and ketones.

EXAMPLE 2.

Ten parts of metallic iron are melted with ten parts of zinc, and twenty parts of tungstic acid introduced into the melt. With such contact mass consisting of a solid solution of oxides and partly of an alloy a gas mixture containing 40 per cent. of carbon monoxide and 60 per cent. of hydrogen produces, at 200 atmospheres pressure and 460 degrees Centigrade, a mixture of methyl alcohol and higher molecular, oxygenated organic compounds.

EXAMPLE 3.

Ferric hydroxide is kneaded with 10 per cent. its weight of chromium hydroxide, dried and reduced to grains. The mass is then soaked with a solution of 40 per cent. its weight of zinc nitrate and 40 per cent. its weight of potassium permanganate. A gas mixture composed of coal gas and carbon monoxide is first passed over a methane forming catalyst at a temperature of about 500 degrees Centigrade and a pressure of 800 atmospheres; the gas mixture produced containing about 30 per cent. carbon monoxide, 30 per cent. methane, 30 per cent. hydrogen and 10 per cent. nitrogen, carbon dioxide and other gases is then passed at the aforesaid pressure and at a temperature of 380 degrees Centigrade over the beforedescribed catalytic mass consisting of a solid solution of a spinel character whereby a mixture of methanol, ethyl alcohol, propyl alcohol, acetone, acids and so on is produced. A contact mass composed of iron, manganese and arsenic acts in a similar manner.

EXAMPLE 4.

A contact mass composed of 80 per cent. nickel oxide and 20 per cent. chromium oxide which under the conditions of working combine with each other and in which contact mass the water formed in the reaction prevents the reduction of nickel oxide, may be used for producing from a mixture of

one volume of carbon monoxide and two volumes of hydrogen at 320 degrees Centigrade and at 800 atmospheres pressure, methyl alcohol and water and considerable amounts of higher alcohols. The yield of higher alcohol is further increased and the formation of water diminished by adding methane to the gas mixture, which addition has also the advantage of reducing the risk of a sudden superheating of the contact mass. An addition of steam acts in a similar way.

EXAMPLE 5.

A contact mass containing 60 parts of zinc oxide and 30 parts of chromium oxide which is very suitable for producing methanol from carbon monoxide and hydrogen, would be much damaged by an addition of 10 parts of free iron oxide and would yield practically exclusively water and hydrocarbons with a heavy deposition of carbon. If, however, 5 parts of sulphur which combines chemically with free iron metal formed by reduction of the iron oxide are further added to the mass, it produces when a mixture of carbon monoxide and hydrogen is passed over it, at 400 degrees Centigrade and 200 atmospheres pressure, ample quantities of methanol and higher molecular products. A similar action is exerted by other metalloids such for example as tellurium, phosphorus, arsenic, or by certain metals related to the metalloids such as tin, antimony, bismuth or the like.

EXAMPLE 6.

Manganese steel is dissolved in an acid, the solution evaporated to dryness and the residue mixed with a solution of 20 per cent. its weight of vanadic acid and 20 per cent. its weight of chromic acid. The mass is dried at 120 degrees Centigrade, and when a mixture of 20 per cent. of carbon dioxide and 80 per cent. of hydrogen is passed over this contact mass consisting of a solid solution of a spinel character at 200 atmospheres pressure and 350 degrees Centigrade, the formation of oxygenated organic compounds takes place.

EXAMPLE 7.

100 parts of zinc oxide are soaked in the order named with solutions of 10 parts of chromic acid, 10 parts of ferric nitrate, 10 parts of potassium carbonate and 5 parts of arsenic pentoxide, and dried at 150 degrees Centigrade. A gas mixture composed of 60 per cent. of carbon monoxide and 40 per cent. of hydrogen, completely dry and free from iron carbonyl, when passed over the said mass in which the arsenic pentoxide chemically reacts and combines with any iron formed in the course of the operation at 350 degrees Centigrade and 200 atmospheres pressure gives rise to a product composed of methyl alcohol and small amounts of ethyl-, propyl-, iso-butyl- and other alcohols and acids, for example formic and acetic acid.

EXAMPLE 8.

Three parts of cobalt hydroxide are kneaded with one part of uranium oxide and one part of manganese oxide, dried and reduced to grains and then soaked with a concentrated potash solution. A difficultly reducible mixture of a spinel character is formed.

Illuminating gas, freed from sulphur compounds and benzene hydrocarbons by treatment with active carbon or silica gels and having about the composition:— 50 per cent. hydrogen, 30 per cent. methane, 12 per cent. carbon monoxide, 4 per cent. ethylene and 4 per cent. nitrogen, is then passed over the said contact mass at 400 degrees Centigrade and 800 atmospheres pressure.

The reaction gases when cooled while under pressure yield a liquid condensate containing methanol, ethyl and higher alcohols, saturated and unsaturated ketones and other organic compounds. The remainder of gas is passed through other contact furnaces or returned to the same contact mass by means of a circulating pump. The gas may be replenished by adding fresh purified coal gas or such gases as are consumed by the reaction.

I do not claim the use of a contact mass containing cobalt in combination with one or more of the elements, copper, silver, gold, zinc, cadmium and lead as described in the Specification of my previous Patent No. 229,715.

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 of converting oxides of carbon into methanol or other oxygenated organic compounds by means of hydrogen at an elevated temperature and pressure with the aid of a contact mass, which comprises iron, nickel or cobalt in a chemical combination or in the form of alloys or solid solutions, but not combined with copper or silver alone, which combination must be stable and should not allow the formation of free iron metal either by reduction or by decomposition under the conditions of

working, in the absence of volatile compounds of iron, nickel and cobalt from the gases and in the absence of free iron metals on the surface of the apparatus exposed to the gases.

2. In the process defined in the preceding claiming clause, the addition to the gas mixture of a restricted quantity of oxygen.

3. In the process defined in the foregoing claiming clauses, the employment of water vapour or steam or hydrocarbons instead of part or all of the hydrogen, the complete substitution of hydrogen by water vapour or steam being only possible in the case of carbon monoxide.

4. The process of manufacturing or producing methanol or other oxygen-containing organic compounds substantially as described in each of the foregoing examples.

5. Methanol or other oxygen-containing compounds when prepared in accordance with the preceding claiming clauses.

Dated this 24th day of October, 1925.

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