

22 APR. 1933

AMENDED SPECIFICATION.

Reprinted as amended under Section 8 of the Patents and Designs Acts 1907 to 1932.

PATENT SPECIFICATION



Application Date: July 24, 1929. No. 22,792/29.

338,854

Complete Left: May 19, 1930.

Complete Accepted: Nov. 24, 1930.

PROVISIONAL SPECIFICATION.

Improvements in the Manufacture of Oxygenated Organic Compounds.

I, HENRY DREYFUS, a citizen of the Swiss Republic, of Celanese House, 22 & 23, Hanover Square, London, W. 1, do hereby declare the nature of this invention to be as follows:—

This invention relates to the manufacture of oxygenated organic compounds from oxides of carbon and hydrogen, or alternatively from compounds synthesised therefrom, e.g. methyl alcohol, mixed or not with oxides of carbon and/or hydrogen.

In a series of researches upon the production of organic compounds by the hydrogenation of oxides of carbon I have found that valuable products are obtainable by utilising catalysts consisting of alkali or alkaline earth or copper borates, silicates or phosphates, or salts of other oxy acids of phosphorus.

Initially the basic radicle, e.g. sodium, potassium, calcium, barium, or copper, may be present in the form of a salt of any of the oxy acids referred to above, for example in the form of ortho, pyro or meta phosphates, or in the form of phosphites or hypophosphites or in the form of ortho or meta silicates.

The compounds may contain the basic and the acid radicles in any convenient proportion. An excess of basic radicle over acid radicle or of acid radicle over basic radicle sometimes materially alters the direction of the reaction. The proportion may for example be one molecular proportion of basic radicle to two proportions of acid radicle, or equal molecular proportions may be used, or one molecular proportion of acid radicle may be used to two molecular proportions of basic radicle. Furthermore intermediate proportions or proportions outside those indicated may be used. The excess of basic or acid radicle may be present in a combined state, as for example in a basic or acid

salt, or the excess of the base or of the acid may be present merely in admixture or association with the normal salt.

Copper containing catalysts are advantageously used in conjunction with compounds of the alkalies or alkaline earth metals, for instance compounds of the oxy acids referred to above. Here again the relative proportion of alkali or alkaline earth metal to copper may be varied as desired. For example proportions of 1:2, 1:1 or 2:1 molecules of alkali or alkaline earth metal to copper may be employed.

Reacting gases of varying composition may be employed for the purpose of the present invention, for example reacting gases containing two or more volumes of carbon monoxide or dioxide to one volume of hydrogen, or equal volumes of the oxide of carbon and of hydrogen, or one volume of carbon monoxide or dioxide to two or more volumes of hydrogen, or mixtures containing intermediate proportions. Mixtures of carbon monoxide and dioxide may of course be employed. It is not necessary to utilise pure reacting gases since mixtures containing the desired reacting gases may be employed, for example coke oven gas, producer gas, water gas and the like. The proportions of reacting gases in such industrial gases may be adjusted, if desired, by suitable additions. The reacting gases may contain inert gases, such as nitrogen, or they may contain hydrocarbons, for example methane or other paraffins.

The actual hydrogenation of the oxides of carbon may be conducted at any suitable temperatures, for example temperatures ranging from 200 to 250° C. to 400 or 500 or even 600° C. or more, but preferably the temperatures used are between 250° and 400° C. and particularly 250° to 300° to 350° C. The reaction is

[Price 1/-]

preferably carried out under pressure, for example pressures of 50, 100, 200, 300 or 500 atmospheres or more.

According to a modification of the invention instead of employing oxides of carbon in conjunction with hydrogen the oxygenated organic compounds obtained from such a synthesis, for example methyl or ethyl alcohol or other alcohols, may be used. The alcohols or other compounds may be used alone or in conjunction with carbon monoxide, carbon dioxide and/or hydrogen. The vapours of the methyl alcohol or other compound may be passed with or without carbon monoxide or dioxide and with or without hydrogen over the catalysts of the present invention contained in a heated reaction vessel. The methyl or ethyl alcohol or other compound may furthermore be prepared in a preliminary operation continuously with its use according to the present invention. For such continuous operation mixtures of carbon monoxide or dioxide and hydrogen or gases containing them may, for example, be passed through the reaction

chamber containing zinc oxide or basic zinc chromate or other catalysts or catalyst mixtures capable of producing the methyl alcohol or other compound, and the resulting gases or vapours passed directly over the catalysts or catalyst mixtures of the present invention. Instead of using methyl alcohol or other compound obtainable from carbon monoxide or dioxide and hydrogen, compounds capable of yielding the methyl alcohol or other compound may be used, for example methyl formate, methyl acetate or dimethyl ether.

The reactions according to the present invention may be effected in any suitable reaction chambers or vessels, for example copper vessels or copper lined vessels or steel vessels, and particularly vessels made of steel containing molybdenum, tungsten, manganese, cobalt, nickel or the like.

Dated this 24th day of July, 1929.
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London, W. 1.

COMPLETE SPECIFICATION (AMENDED).

Improvements in the Manufacture of Oxygenated Organic Compounds.

I, HENRY DREYFUS, a citizen of the Swiss Republic, of Celanese House, 22 & 23, Hanover Square, London, W. 1, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:

This invention relates to the manufacture of oxygenated organic compounds from oxides of carbon and hydrogen, or alternatively from compounds synthesised therefrom, e.g. methyl alcohol, mixed or not with oxides of carbon and/or hydrogen.

In a series of researches upon the production of organic compounds by the hydrogenation of oxides of carbon I have found that valuable products are obtainable by utilising catalysts consisting of alkali or alkaline earth or copper borates, silicates or phosphates or salts of other oxy-acids of phosphorus.

Initially the basic radicle, e.g. sodium, potassium, calcium, barium, or copper, is present in the form of a salt of any of the oxy acids referred to above, for example in the form of ortho, pyro or meta phosphates, or in the form of phosphites or hypophosphites or in the form of ortho or meta silicates.

The borates, silicates or phosphates or salts of other oxy-acids of phosphorus may contain the basic and the acid radicles in any convenient proportion. An excess of basic radicle over the acid radicle or of acid radicle over basic radicle sometimes materially alters the direction of the reaction. Generally excess of the acid radicle tends to produce products of higher degree of oxidation than alcohols, whereas excess of the basic radicle tends to confine the reaction to the production of aliphatic alcohols. The proportion may for example be one molecular proportion of basic radicle to two proportions of acid radicle, or equal molecular proportions may be used, or one molecular proportion of acid radicle may be used to two molecular proportions of basic radicle. Furthermore intermediate proportions or proportions outside those indicated may be used. The excess of basic or acid radicle may be present in a combined state, as for example in a basic or acid salt, or the excess of the base or of the acid may be present merely in admixture or association with the normal salt.

Copper containing catalysts are advantageously used in conjunction with compounds of the alkalis or alkaline earth metals, for instance compounds of the oxy

acids referred to above. Here again the relative proportion of alkali or alkaline earth metal to copper may be varied as desired. For example proportions of 1:2, 1:1 or 2:1 molecules of alkali or alkaline earth metal to copper may be employed.

Reacting gases of varying composition may be employed for the purpose of the present invention, for example reacting gases containing two or more volumes of carbon monoxide or dioxide to one volume of hydrogen, or equal volumes of the oxide of carbon and of hydrogen, or one volume of carbon monoxide or dioxide to two or more volumes of hydrogen, or mixtures containing intermediate proportions. Mixtures of carbon monoxide and dioxide may of course be employed. It is not necessary to utilise pure reacting gases since mixtures containing the desired reacting gases may be employed, for example coke oven gas, producer gas, water gas and the like. The proportions of reacting gases in such industrial gases may be adjusted, if desired, by suitable additions. The reacting gases may contain inert gases, such as nitrogen, or they may contain hydrocarbons, for example methane or other paraffins.

The actual hydrogenation of the oxides of carbon may be conducted at any suitable temperatures, for example temperatures ranging from 200 to 250° C. to 400 or 500 or even 600° C. or more, but preferably the temperatures used are between 250° and 400° C. and particularly 250° to 300° to 350° C. The reaction is preferably carried out under pressure, for example pressures of 50, 100, 200, 300 or 500 atmospheres or more.

According to a modification of the invention instead of employing oxides of carbon in conjunction with hydrogen the oxygenated organic compounds obtained from such a synthesis, for example methyl or ethyl alcohol or other alcohols, may be used. In this modification of the invention methyl alcohol, for example, can be converted into compounds of higher order, for example into ethyl alcohol, acetaldehyde, acetic acid etc. The alcohols or other compounds are employed under pressure and may be used alone or in conjunction with carbon monoxide, carbon dioxide and/or hydrogen. The use of hydrogen generally tends to produce higher alcohols, e.g. ethyl alcohol, propyl alcohol and higher alcohols to the exclusion of compounds of a higher order of oxidation, e.g. aldehydes, acids, ketones, whilst the use of carbon dioxide is effective in promoting the formation of such bodies of higher order of oxidation. In cases, however, where the catalyst con-

tains excess or substantial excess of acid radicle over basic radicle the reaction tends to produce products of a higher order of oxidation, e.g. acids and aldehydes even in the presence of hydrogen. The vapours of the methyl alcohol or other compound may be passed with or without carbon monoxide or dioxide and with or without hydrogen over the catalysts of the present invention contained in a heated reaction vessel. The methyl or ethyl alcohol or other compound may furthermore be prepared in a preliminary operation continuously with its use according to the present invention. For such continuous operation mixtures of carbon monoxide or dioxide and hydrogen or gases containing them may, for example, be passed through the reaction chamber containing zinc oxide or basic zinc chromate or other catalysts or catalyst mixtures capable of producing the methyl alcohol or other compound, and the resulting gases or vapours passed directly over the catalysts or catalyst mixtures of the present invention. Instead of using methyl alcohol or other compound obtainable from carbon monoxide or dioxide and hydrogen, compounds capable of yielding the methyl alcohol or other compound may be used, for example methyl formate, methyl acetate or dimethyl ether.

The reactions according to the present invention may be effected in any suitable reaction chambers or vessels, for example copper vessels or copper lined vessels or steel vessels, and particularly vessels made of steel containing molybdenum, tungsten, manganese, cobalt, nickel or the like.

The following examples serve to illustrate convenient forms of execution of the invention, it being understood that they are given only by way of illustration and are in no way limitative.

EXAMPLE 1.

Water gas containing about 65% of hydrogen and 30% carbon monoxide is passed under a pressure of between 50 and 150 atmospheres in contact with a catalyst composed of a mixture of copper meta phosphate and sodium phosphate (e.g. containing about 5-10% sodium phosphate) heated to a temperature between 250° and 350° C.

There results a copious yield of ethanol and other higher aliphatic alcohols.

EXAMPLE 2.

Methanol or a mixture of methanol and carbon monoxide are passed under a pressure of between 100 and 200 atmospheres in contact with copper meta borate heated to a temperature between 250° and 350° C.

There results a copious yield of ethanol

and other higher aliphatic alcohols, together with aldehydes, acids, and ketones.

If, in the above example, the carbon monoxide is wholly or partly replaced by hydrogen and particularly if the carbon monoxide is wholly replaced, the reaction products are substantially free from acids, aldehydes and ketones. If, however, the carbon monoxide is replaced by carbon dioxide, formation of the compounds of a higher order of oxidation is materially increased, whilst if, besides replacing the carbon monoxide with carbon dioxide, there is employed a catalyst containing an excess of acid radicle over basic radicle, e.g. a mixture of 1 molecular equivalent of copper meta borate and 1 molecular equivalent of phosphoric acid, the reaction product consists largely or entirely of acetic acid, methyl acetate, acetaldehyde and higher acids, aldehydes and esters.

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. Process for the manufacture of oxygenated organic compounds other than acids from oxides of carbon and hydrogen, characterised in that the reaction is performed in presence of catalysts consisting of alkali or alkaline earth or copper borates, silicates or phosphates, or salts of other oxy acids of phosphorus.

2. Process for the manufacture of oxygenated organic compounds, characterised in that oxygenated organic compounds obtainable by synthesis from oxides of carbon and hydrogen and

especially methyl, ethyl or other aliphatic alcohols, are brought to reaction under pressure in presence of catalysts consisting of alkali or alkaline earth or copper borates, silicates or phosphates or salts of other oxy acids of phosphorus and in presence or absence of carbon monoxide, carbon dioxide and/or hydrogen.

3. Process according to claim 1 or 2 and wherein the catalysts contain an excess of basic radicle or an excess of acid radicle over the normal content, and particularly wherein the excess of acid radicle is present either in the form of an acid salt or in the free state in admixture with or association with the normal salt.

4. Process according to Claim 1, 2 or 3 and wherein the reaction is performed at temperatures between 200° and 600° C., and especially at temperatures between 250° and 400° C.

5. Process according to claim 1, 2, 3 or 4 and wherein the reaction is performed under pressures of 50—200 or more atmospheres.

6. Process for the manufacture of aliphatic alcohol substantially as described in Example 1.

7. Process for the manufacture of oxygenated organic compounds substantially as described in Example 2.

8. Oxygenated organic compounds whenever produced by the process claimed in any of the preceding claims.

Dated this 17th day of May, 1930.

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