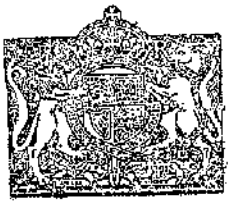
[Second Edition.]

PATENT SPECIFICATION



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PROVISIONAL SPECIFICATION.

Improvements in or relating to the Manufacture of Acetic Acid.

I, HENRY DREYFUS, of 8, Waterloo Place, London, S.W. 1, a citizen of the Swiss Republic, do hereby declare the nature of this invention to be as follows:—

This invention relates to the production of acetic acid from mixtures of or containing hydrogen and carbon monoxide.

It has been known since 1913—1914 (Badische Anilin & Soda Fabrik's Specification No. 20,488 of 1913) that when mixtures of carbon monoxide and hydrogen, usually mixtures in which the carbon monoxide is preponderant or largely preponderant, are submitted to high temperature and high pressure, hydrocarbons together with a series of oxygenated aliphatic products are obtained. In this process a large number of products are produced together, each in relatively small amounts, and the industrial recovery and separation of these products is a matter of extreme difficulty and even impossibility. A number of processes have since been proposed, according to which, by the selection of particular proportions of carbon monoxide and hydrogen, particular classes of catalysts, and particular conditions of working, it has been attempted to modify the reaction so as to produce larger quantities of particular organic compounds.

My Specification No. 15,392/25 (262,494) concerns especially the production of methyl alcohol from mixtures of or containing hydrogen and carbon monoxide in certain relative proportions under the action of heat and pressure, with the aid of zinc oxide as catalyst, the formation of methyl alcohol taking place, as is believed, via intermediate formation of formaldehyde which is converted into methyl alcohol by splitting off carbon monoxide.

Now I have found that by employing the catalysts hereinafter referred to, while employing the hydrogen and carbon monoxide in suitable relative proportions in the gas or gaseous mixture taken, namely in a proportion of about one molecule of hydrogen to one molecule of carbon monoxide, it is possible to obtain acetic acid under the action of heat and pressure.

The catalysts employed for this purpose comprise as essential element substances which are, or are capable of forming, acetates which decompose with the formation of acetic acid at temperatures under about 400—450° C. and preferably between about 200 and 300° C. These substances may be used alone or in combination with other catalysts or contact materials such as are capable of initiating or effecting the combination of the said gases. If the substances are themselves capable of effecting the combination of carbon monoxide and hydrogen, they may be used alone: If, however, they are not capable of combining carbon monoxide and hydrogen, they must be combined or be associated with catalysts or contact materials capable of effecting the combination of these gases. By employing such catalysts or catalyst mixtures the gases can be combined and acetic acid be split off or evolved continuously, with regeneration of the catalysts.

It is possible that formaldehyde may be formed intermediately which is transformed into acetic acid.

Catalysts which favour the production of methane or more than traces of methane are to be avoided.

Some of the catalysts which may be employed are copper oxide, tin oxide, lead oxide, copper acetate, aluminium methylate, tin methylate and like methylates, or mixtures of two or more

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of any of the foregoing with each other, or mixtures of any of them with more basic materials such as potassium acetate or sodium acetate. Especially useful are mixtures of or containing one or more of the foregoing—and especially the said metal methylates—with one or more alkali methylate such as potassium methylate or sodium methylate.

In carrying out the process one may employ similar conditions of temperature and pressure to those indicated for the production of methyl alcohol in my said other specification, for example temperatures below about 350° to 400° or 450° C. and preferably between about 200° and 300° C., and pressures which may be up to 200 atmospheres or more, variable according to the catalysts used, but generally pressures of about 50 to 150 atmospheres.

Dated this 13th day of June, 1925.

T. L. WHITEHEAD,
Chartered Patent Agent,
Patent Department, British Celanese Ltd.,
8, Waterloo Place, London, S.W. 1.

COMPLETE SPECIFICATION.

Improvements in or relating to the Manufacture of Acetic Acid.

I, HENRY DREYFUS, of 8, Waterloo Place, London, S.W. 1, a citizen of the Swiss Republic, 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 production of acetic acid from mixtures of or containing hydrogen and carbon monoxide.

It has been known since 1913—1914 (Badische Anilin & Soda Fabrik's Specification No. 20,488 of 1913) that when mixtures of carbon monoxide and hydrogen, usually mixtures in which the carbon monoxide is preponderant or largely preponderant, are submitted to high temperature and high pressure, hydrocarbons together with a series of oxygenated aliphatic products are obtained. In this process a large number of products, including acetic acid, are produced together, each in relatively small amounts, and the industrial recovery and separation of these products is a matter of extreme difficulty and even impossibility. A number of processes have since been proposed, according to which, by the selection of particular proportions of carbon monoxide and hydrogen, particular classes of catalysts, and particular conditions of working, it has been attempted to modify the reaction so as to produce larger quantities of particular organic compounds.

My Specification No. 15,392/1925 (262,494) concerns especially the production of methyl alcohol from mixtures of or containing hydrogen and carbon monoxide in certain relative proportions under the action of heat and pressure, with the aid of zinc oxide as catalyst, the formation of methyl alcohol taking place, as is believed via intermediate formation of formaldehyde which is converted into methyl alcohol by splitting off carbon monoxide.

Now I have found that by employing the catalysts hereinafter referred to, while employing the hydrogen and carbon monoxide in suitable relative proportions in the gas or gaseous mixture taken, namely in a proportion of about one molecule of hydrogen to one molecule of carbon monoxide, it is possible to obtain acetic acid under the action of heat and pressure.

The catalysts or catalyst mixtures employed for this purpose comprise as essential element substances which are, or are capable of forming, acetates which decompose with the formation of acetic acid at temperatures under about 400—450° C. and preferably between about 200 and 300° C. These substances may be used alone or in combination with other catalysts or contact materials. If the substances are themselves capable of effecting combination of carbon monoxide and hydrogen, they may be used alone. If, however, they are not capable of combining carbon monoxide and hydrogen, they must be combined or associated with catalysts or contact materials of the kind employed for combining these gases to produce methyl alcohol or other oxygenated organic compounds. By employing such catalysts or catalyst mixtures the gases can be combined and acetic acid be split off or evolved continuously, with regeneration of the catalysts.

It is possible that formaldehyde may be formed intermediately which is transformed into acetic acid.

Catalysts which favour the production

of methane or more than traces of methane are to be avoided.

Some of the catalysts which may be employed for the manufacture of acetic acid are copper oxide, tin oxide, lead oxide, copper acetate, aluminium methylate, tin methylate and like methylates, or mixtures of two or more of any of the foregoing with each other, or mixtures of any of them with more basic materials such as potassium acetate or sodium acetate. Mixtures of or containing one or more of the foregoing, for instance, the said metal methylates, with one or more alkali methylates such as potassium methylate or sodium methylate, may also be used.

Zinc oxide however is not used as catalyst for the production of acetic acid in accordance with this invention, since in the presence of zinc oxide methyl alcohol is formed as main or sole product as explained in my Specification No. 15,392/25 (262,494).

In carrying out the process one may employ temperatures below about 350° to 400° or 450° C. and preferably between about 200° and 300° C., and pressures which may be up to 200 atmospheres or more, variable according to the catalysts used, but generally pressures of about 50 to 150 atmospheres.

The following example is given by way of illustration but as will be understood the invention is capable of being performed in many other ways.

EXAMPLE.

A mixture containing approximately equal volumes of carbon monoxide and hydrogen is passed under a pressure of about 80—120 atmospheres through a chamber filled with granules of tin oxide, and maintained at a temperature of about 250—300° C. The products are separated by condensation and the acetic acid is purified by distillation if necessary. The uncondensed gases are recirculated through the system for further reaction.

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 production of acetic acid characterised in that gaseous mixtures containing about one molecule of hydrogen to one molecule of carbon monoxide, are subjected to the action of heat and pressure in presence of certain catalysts, namely substances (other than zinc oxide and catalysts which favour the production of methane or more than traces of methane) which are, or are capable of forming, acetates which decompose with the formation of acetic acid at temperatures under about 400° to 450° C. and preferably between 200° and 300° C., and which either are at the same time themselves capable of combining said gases or contain or are associated with additional catalytic or contact substances of the kind employed for combining said gases to produce methyl alcohol or other oxygenated organic compounds.

2. Process according to Claim 1, characterised by the employment of the following as catalysts:—Copper oxide, tin oxide, lead oxide, copper acetate, aluminium methylate, tin methylate and like methylates, or mixtures of two or more of any of the foregoing with each other, or mixtures of any two of them with more basic materials such as potassium acetate or sodium acetate.

3. Process according to Claim 1 or 2, characterised in that the reaction is performed at temperatures below about 350° to 400° or 450° C. and preferably between about 200° and 300° C.

4. Process according to Claim 1, 2 or 3, characterised in that the reaction is performed under pressures of up to 200 atmospheres or more and especially under pressures of from 50 to 150 atmospheres.

5. Process for the production of acetic acid from gases containing carbon monoxide and hydrogen substantially as described.

6. Acetic acid when prepared and produced by the processes herein described and claimed.

Dated this 12th day of April, 1926.

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