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PROVISIONAL SPECIFICATION.



Improvements in or relating to the Manufacture of Aliphatic Acids.

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 aliphatic acids from aliphatic alcohols and especially to the manufacture of acetic acid from ethyl alcohol.

According to the invention I have now found that aliphatic acids (and especially acetic acid) can be produced by passing the vapours of aliphatic alcohols (and especially ethyl alcohol vapour) in admixture with oxygen or a gas containing the same, such for instance as air, over or otherwise in contact with one or more of the following catalysts, at temperatures insufficiently high to produce ketones (such as acetone) or substantial quantities of acetone or other ketones, namely:—

(a) One or more metallic oxides (including the various oxides of metals which have oxides of various degrees of oxidation)—and particularly oxides of metals the acetates of which yield acetic acid on heating or by reaction with water or steam under the action of heat (e.g. oxides of manganese, Cobalt, Nickel, Iron, Zinc, Lead, Uranium)—including mixtures of two or several of such oxides whether of similar or dissimilar metals but excluding the use of one or more alkali or earth alkali oxides alone, or,

(b) one or more of the metallic oxides of (a) above in admixture with:—one or more alkali, or, preferably earth alkali oxides, hydroxides or carbonates, or,

(c) instead of the metallic oxides of (a) above there may be used, alone or in admixture with the alkali or earth alkali oxides, hydroxides or carbonates of (b) above, and/or in admixture with the metallic oxides of (a) above, other compounds of the metals, e.g. carbonates.

In performing the invention I preferably employ one or more of the oxides of (a) above, and especially one or more oxides of metals the acetates of which yield acetic acid on heating or by reaction with steam or water under the action of heat, as the catalyst. For instance, I may employ a catalyst composed of one or more

of the following oxides:—Copper oxide, one or more Iron oxides (e.g. Ferric oxide), Cobalt oxide, one or more oxides of manganese (e.g. manganese dioxide), one or more oxides of lead or uranium. Aluminium oxide is another instance of a metallic oxide which may be employed for the purposes of the invention.

The catalysts may, if desired, be employed spread upon, or deposited upon or mixed with filling or contact materials such for instance as pumice, kieselguhr or the like.

The temperature at which the reaction is to be performed varies to some extent with the catalyst or catalysts and conditions employed. Generally the reaction may be performed at temperatures between about 150° C. and 400° C. and especially between about 200° and 350° C. When the catalyst comprises one or more earth alkali or alkali compounds it is advisable to use somewhat lower temperatures in order to avoid formation of ketones, for instance in such cases it is advisable to use temperatures not exceeding about 300° C., e.g. temperatures between about 150° and 300° C. As above stated the temperature must always be insufficiently high to cause the formation of substantial quantities of acetone or other ketones.

The reaction may be performed under any desired pressure, whether higher or lower than normal atmospheric, for instance under normal atmospheric pressure, or under reduced pressure or "vacuum", or under increased pressure such for example as under 3 to 10 atmospheres or more.

For the purposes of the invention I preferably employ mixtures of alcohol vapour and oxygen (or air or other gaseous mixture containing oxygen) containing more than one molecule of oxygen relatively to each molecule of the alcohol, whether or not water vapour or humidity is present in the mixture, or even containing substantially large proportions of oxygen e.g. from 2 to 10 or more parts by volume of oxygen relatively to each volume of alcohol.

I preferably perform the reaction in

[Price 1/-]

presence of water vapour or steam, as such water vapour or steam facilitates the decomposition to free acid of aliphatic acid salts (e.g. acetates) which may be formed intermediately. Further, by varying the quantity of water vapour or steam employed the concentration of the aliphatic acid produced may be varied at will.

I preferably add the water vapour or steam to the mixture of alcohol vapour and oxygen (or gas containing the same) prior to passing the said mixture over or otherwise in contact with the catalyst, and I preferably add relatively large amounts of steam or water vapour to said mixture, e.g. amounts such as 2 to 10 or more times the volume of the alcohol vapour present in the mixture. If desired, vapours of the aliphatic acid to be produced may be added to the mixture of alcohol vapour and oxygen (or gas containing the same) prior to passing said mixture over or otherwise in contact with the catalysts, whether or not said mixture contains water vapour or steam. By varying the

quantity of aliphatic acid vapour and/or water vapour or steam added to the mixture of alcohol vapour and oxygen (or gas containing the same), the concentration of the aliphatic acid produced by the process may be varied at will.

The mixture of alcohol vapour and oxygen (or gas containing the same), whether or not containing steam or water vapour, or aliphatic acid vapour, may be submitted to the reaction in any convenient way. As for instance the mixture may be passed in a rapid stream through a tube or other form of apparatus (e.g. a tube or other form of apparatus of copper, iron, Staybrite, earthenware or the like) filled or provided with the catalyst and heated to the desired temperature.

Dated this 6th day of September, 1929.
WHITEHEAD & STEPHENS,
Chartered Patent Agents,
Celanese House, 22 & 23, Hanover Square,
London, W. 1.

COMPLETE SPECIFICATION.

Improvements in or relating to the Manufacture of Aliphatic Acids.

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 aliphatic acids from aliphatic alcohols and especially to the manufacture of acetic acid from ethyl alcohol.

According to this invention I produce aliphatic acids (and especially acetic acid) by passing the vapours of aliphatic alcohols (and especially ethyl alcohol vapour) in admixture with oxygen or a gas containing the same, such for instance as air, over or otherwise in contact with one or more of the hereinafter specified catalysts, at elevated temperatures such as are insufficiently high to produce acetone or other ketones in substantial quantity.

The catalysts I employ are the following:—

(a) One or more metallic oxides, hydroxides or carbonates, other than alkali or earth alkali oxides, hydroxides or carbonates, and particularly oxides, hydroxides or carbonates of metals, the acetates of which yield acetic acid on heating or by reaction with water or steam

under the action of heat (e.g. oxides of manganese, cobalt, nickel, iron, zinc, lead, uranium), or

(b) one or more of the metallic compounds of (a) above in admixture with:— one or more alkali, or, preferably earth alkali oxides, hydroxides or carbonates.

In regard to the metallic oxides of (a) above the various oxides of metals having oxides of various degrees of oxidation or mixtures of two or several of such oxides can of course be present in the catalysts of the invention. I wish it, however, to be understood clearly that whenever the catalyst of the invention is to comprise a plurality of the compounds the said compounds are employed in the form of mixtures of said compounds and not in the form of metallic metallates formed by interaction between the said compounds, whether in the reaction of the invention or otherwise.

I am of course aware that a number of the catalysts are well known for promoting the oxidation of organic compounds but so far as I am aware their use as catalysts for the reaction of the invention is novel.

In performing the invention I preferably employ one or more of the oxides of (a) above, and especially one or more oxides of metals the acetates of which yield acetic acid on heating or by reaction

with steam or water under the action of heat, as the catalyst. For instance, I may employ a catalyst composed of one or more of the following oxides:—Copper oxide, 5 one or more iron oxides (e.g. ferric oxide), cobalt oxide, one or more oxides of manganese (e.g. manganese dioxide), one or more oxides of lead or uranium, 10 Aluminium oxide is another instance of a metallic oxide which may be employed for the purposes of the invention.

The catalysts may, if desired, be employed spread upon, or deposited upon or mixed with filling or contact materials 15 such for instance as pumice, kieselguhr or the like.

The temperature at which the reaction is to be performed varies to some extent with the catalyst or catalysts and conditions employed. Generally the reaction 20 may be performed at temperatures between about 150° C. and 400° C. and especially between about 200° and 350° C. When the catalyst comprises one or more 25 earth alkali or alkali oxides, hydroxides or carbonates it is advisable to use somewhat lower temperatures in order to avoid formation of ketones, for instance in such cases it is advisable to use temperatures 30 not exceeding about 300° C., e.g. temperatures between about 150° and 300° C. As above stated the temperature must always be insufficiently high to cause the 35 formation of substantial quantities of acetone or other ketones.

The reaction may be performed under any desired pressure, whether higher or lower than normal atmospheric, for instance under normal atmospheric pressure, 40 or under reduced pressure or "vacuum", or under increased pressure such for example as under 3 to 10 atmospheres or more.

For the purposes of the invention I preferably employ mixtures of alcohol vapour and oxygen (or air or other gaseous mixture containing oxygen) containing more than one molecule of oxygen 45 relatively to each molecule of the alcohol, whether or not water vapour or humidity is present in the mixture, or even containing substantially large proportions of oxygen e.g. from 2 to 10 or more parts by 50 volume of oxygen relatively to each volume of alcohol.

I preferably perform the reaction in presence of water vapour or steam, as such water vapour or steam facilitates the decomposition to free acid of aliphatic acid 60 salts (e.g. acetates) which may be formed intermediately. Further, by varying the quantity of water vapour or steam employed the concentration of the aliphatic acid produced may be varied at will.

65 I preferably add the water vapour or

steam to the mixture of alcohol vapour and oxygen (or gas containing the same) prior to passing the said mixture over or otherwise in contact with the catalyst, and I preferably add relatively large amounts 70 of steam or water vapour to said mixture, e.g. amounts such as 2 to 10 or more times the volume of the alcohol vapour present in the mixture. If desired, vapours of 75 the aliphatic acid to be produced may be added to the mixture of alcohol vapour and oxygen (or gas containing the same) prior to passing said mixture over or otherwise in contact with the catalysts, 80 whether or not said mixture contains water vapour or steam. By varying the quantity of aliphatic acid vapour and/or water vapour or steam added to the mixture of alcohol vapour and oxygen (or gas containing the same), the concentration of 85 the aliphatic acid produced by the process may be varied at will.

The mixture of alcohol vapour and oxygen (or gas containing the same), whether or not containing steam or water 90 vapour, or aliphatic acid vapour, may be submitted to the reaction in any convenient way. As for instance the mixture may be passed in a rapid stream through a tube or other form of apparatus (e.g. a 95 tube or other form of apparatus of copper, iron, nickel chromium steels such as staybrite, silicaware earthenware or the like) filled or provided with the catalyst and heated to the desired temperature. 100-

The following Example illustrates a convenient form of execution of the invention, but it is to be understood that it is in no way limitative.

EXAMPLE.

A mixture of ethyl alcohol, oxygen and steam, in about the proportions of 1:3:5 by volume, is passed through a tube (e.g. of copper) or other form of apparatus 105 filled or provided with the catalyst, for example ferric oxide, and maintained at a temperature of about 280—320° C. There results a copious yield of acetic acid which can be separated by fractional distillation, if desired, from unchanged 115 ethyl alcohol, water, or any by-products formed in the reaction.

If a catalyst is employed which contains alkali or earth alkali oxides, hydroxides or carbonates, such for example as a catalyst comprising a mixture 120 of ferric oxide and calcium carbonate (e.g. a mixture containing two molecular equivalents of ferric oxide to one of calcium carbonate), lower temperatures 125 e.g. about 230°—280° C. should be maintained.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to 130

be performed, I declare that what I claim is:—

- 5 1. Process for the manufacture of aliphatic acids which comprises subjecting the vapours of aliphatic alcohols to the action of oxygen or a gas containing the same in the presence of a catalyst comprising one or more metallic oxides, hydroxides or carbonates other than 10 oxides, hydroxides or carbonates of the alkali or earth alkali metals, at elevated temperatures such as are insufficiently high to produce substantial quantities of ketones.
- 15 2. Process for the manufacture of acetic acid which comprises subjecting ethyl alcohol vapour to the action of oxygen or a gas containing the same in the presence of a catalyst comprising one 20 or more metallic oxides, hydroxides or carbonates other than oxides, hydroxides or carbonates of the alkali or earth alkali metals, at elevated temperatures such as are insufficiently high to produce substantial 25 quantities of acetone.
3. Process according to Claim 1 or 2, and wherein the catalyst employed also contains one or more alkali and/or earth

alkali oxides, hydroxides or carbonates.

4. Process according to Claim 1 or 2, 30 and wherein the operation is performed at temperatures of between about 150 and 400° C. and especially between about 200 and 350° C.

5. Process according to Claim 3 and 35 wherein the operation is performed at temperatures not exceeding about 300° C.

6. Process according to any of the preceding claims, and characterised in that 40 the operation is performed in the presence of water vapour.

7. Process for the manufacture of aliphatic acids substantially as described with reference to the Example.

8. Process for the manufacture of aliphatic acids substantially as hereinbefore 45 described.

9. Aliphatic acids whenever produced by the process claimed in any of the preceding claims. 50

Dated this 6th day of June, 1930.
 WHITEHEAD & STEPHENS,
 Chartered Patent Agents,
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 London, W. 1.