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PROCESS FOR THE MANUFACTURE OF METHYL KETENE AND PROPIONIC ANHYDRIDE

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FIG. 1.

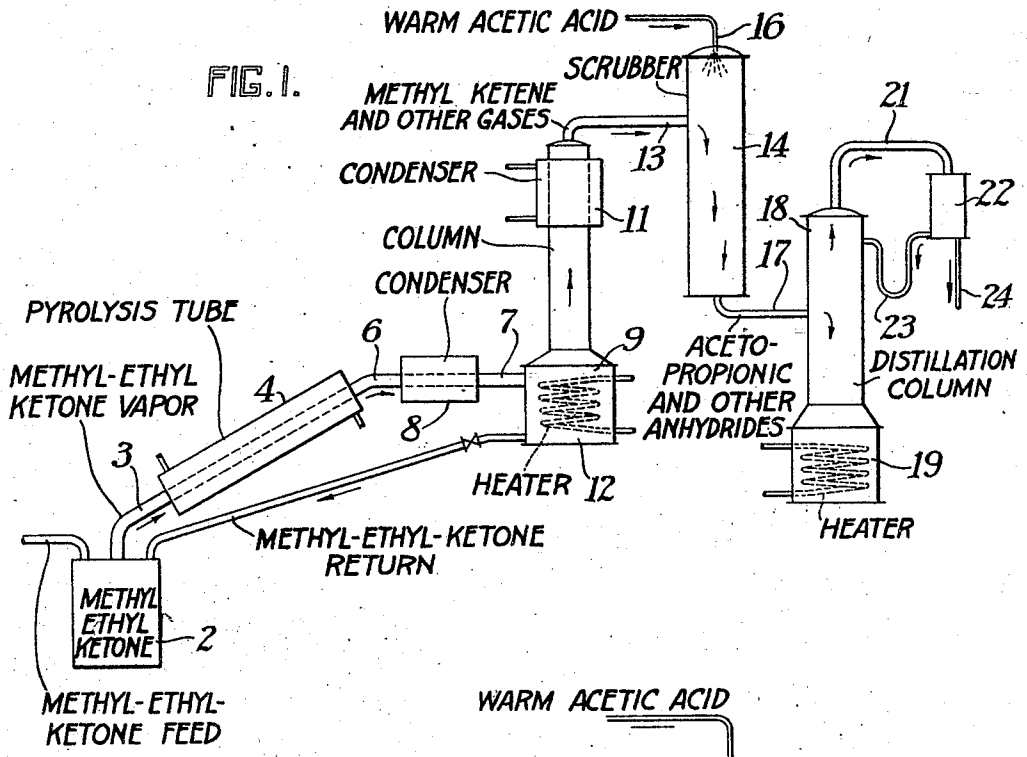
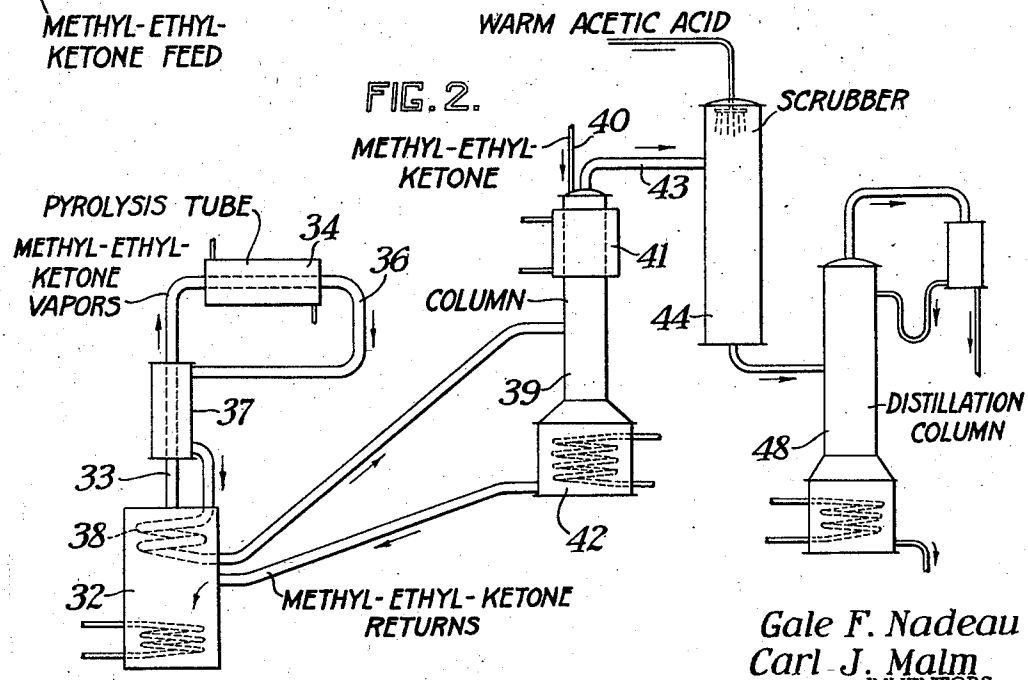


FIG. 2.



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PROCESS FOR THE MANUFACTURE OF METHYL KETENE AND PROPIONIC ANHYDRIDE

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9 Claims. (Cl. 260—546)

This invention relates to the manufacture of methyl ketene, propionic acid and propionic anhydride.

The production of propionic acid and anhydride is of considerable importance inasmuch as there are a number of industrial uses therefor, such as, for example, the manufacture of cellulosic compounds as described in U. S. Clarke and Malm Patent 1,800,860. Such acids are at the present time produced from propyl alcohol, pyroligneous liquor or synthetically and the acids may be subsequently converted to the anhydrides.

We have found a novel method for the manufacture of propionic acid and anhydride which is highly desirable because of its adaptation to the treatment of readily available commercial materials.

This invention has for an object to provide a process for producing organic acids and organic acid anhydrides. A still further object is to provide a process for producing propionic acid and propionic anhydride. A still further object is to provide a process for producing propionic acid and anhydrides involving simple pyrolysis. A still further object is to provide a process for the production of organic acids and organic acid anhydrides utilizing ketonic starting materials. Still another object is to provide a process for converting unstable pyrolysis products into acids and anhydrides. A still further object is to provide a process for the pyrolysis of the higher ketones such as methyl ethyl ketone. Still another object is to provide a method for separating acids and anhydrides by means of ketenes. Other objects will appear hereinafter.

There is available commercially as a solvent an organic chemical material comprising methyl ethyl ketone. We have found that this compound, by means of our novel process, constitutes a source of propionic acid and anhydride. Some work has been done on the pyrolysis of simple ketones such as the pyrolysis of acetone to ketene. Schmidlin, Berglin, Hurd, Cochrane, Nightingale, Clarke and Waring (see U. S. 1,723,724), Rice, Law and others describe the pyrolysis of acetone to ketene. Some mention is made in the art relative to the pyrolysis of methyl ethyl ketone but one investigator states to the effct that when methyl ethyl ketone is pyrolized at 600° C., only ketene is formed in small yields; hence, it was concluded that methyl ethyl ketone is not superior to acetone. Also, the aforementioned investigators and others have described various procedures for treating acetone pyrolysis products. Some condense the products directly, others indicate that condensation should be omitted.

We have found after considerable investigation relative to the treatment of higher ketonic materials, that by our process, methyl ethyl ketone, may be passed through a reaction chamber heated to a temperature of 500–800° C., and under other proper conditions, where it is decomposed to a mixture containing methyl ketene and certain other gaseous products. When the products of the reaction are passed into warm acetic acid, any ketene forms acetic anhydride with the acetic acid and the methyl ketene forms with the acid, a mixture of propionic anhydride and aceto-propionic anhydride. Upon distillation of the mixture, one obtains first, acetic acid, then acetic anhydride and finally the propionic anhydride, the aceto-propionic anhydride having re-arranged during the distillation to form acetic anhydride and propionic anhydride. The propionic anhydride may be then converted to propionic acid.

Our novel process may be carried out without the use of catalysts and is, as described, a simple pyrolysis. One feature of the process is to obtain as high a yield of propionic anhydride as possible, but the fact that ketene itself may be formed in the reaction does not represent a loss because it is converted into acetic anhydride as soon as it passes into the acetic acid.

For a more complete understanding of our novel processes, reference is made to the attached drawing forming a part of the present application. Fig. 1 is a semi-diagrammatic side elevation showing one form of apparatus arrangement for carrying out our process. Fig. 2 is a similar type view of another apparatus arrangement for carrying out our process.

In Fig. 1, 2 is a pre-evaporator or still pot. This device is connected by conduit 3 through the reaction or pyrolysis chamber 4.

The pyrolysis chamber may be of the type such as described in U. S. 1,723,724 and if desired, contain a metal network, corebuster or other means for heat distribution. Or, a tube having a con-

tinuous passage therethrough may be employed, but as described in the aforementioned patent, it should be constructed of proper metals. Copper and silver are suitable metals but for commercial installation, high grade stainless steels containing from about 15–40% chromium may be utilized for the construction of some of the parts.

The pyrolysis chamber is connected by conduits 6, 7 through condenser 8 to a reflux apparatus 9, which may comprise a column. This apparatus will include a condenser or dephlegmator 11 for furnishing reflux. A base heater having heating means may be provided at 12. The upper portion of this apparatus is connected by conduit 13 to a scrubber 14 or other equivalent device into which reaction medium such as acetic acid may be introduced at 16.

The scrubbing device 14 is provided with a draw-off conduit 17 which leads to distillation column 18 of conventional construction, hence extensive description thereof is unnecessary. This distillation column will include a base heater 19, vapor draw-off 21 which leads to condenser 22. A reflux line is provided at 23 and a conduit for drawing off distilled components at 24.

In Fig. 2, the apparatus disclosed is in some respects similar to Fig. 1 and includes the vaporizer 32, and the conduit 33 which leads to pyrolysis tube 34. In this apparatus arrangement the materials from the pyrolysis chamber are conducted through conduit 36 to the condenser-heat exchange arrangement 37, 38. As will be more apparent hereinafter, this arrangement has a number of advantages. The conduit 38 is connected to a reflux column 39, provided with a condenser or dephlegmator 41 and a base heater 42. In addition, this column includes a feed conduit 40 for raw material. By this means the raw materials may be caused to exert a reflux action.

The reflux unit 39 is connected by conduit 43 to a scrubber 44 and distillation column 48 of a construction such as already described with respect to Fig. 1.

The following example is set forth with particular reference to Fig. 1. This example is described primarily for the purposes of illustrating our invention and is not to be construed as a limitation thereof.

Methyl ethyl ketone of commercial quality such as sold industrially for solvent purposes was placed in vaporizer 2 from which the liberated vapors may be passed to pyrolysis tube 4. If desired, these vapors may be substantially preheated either by interposing a preheater or by construction of a long pyrolysis tube in which instance a portion of the pyrolysis tube would act as a preheater.

The construction and operation of either pyrolysis tube 4 or 34 is in many respects the same as described in Clarke and Waring Patent 1,723,724. The tubes may be constructed of metals principally or entirely of copper or silver, or chrome steels containing from about 15% to 40% chrome may be employed. However, the presence of free iron or nickel is to be avoided. The methyl ethyl ketone vapors are subjected to a short time of contact in the pyrolysis chamber at a temperature of from about between 400° C. to 1000° C. dependent upon speed of passage and tube construction. As pointed out in the Clarke and Waring patent, the tube may contain metal network, corebuster or other type of construction for better heat distribution or a narrow diameter tube may be employed. The time of contact would generally be less than 10 seconds and in many instances may be reduced to considerably less than 1 second. The employment of reduced pressure will also reduce the time of pyrolysis contact.

The pyrolysis products leaving the pyrolysis tube 4, at 6 contained considerable amounts of unstable material such as ketene and methyl ketene. However, we have found that methyl ketene is actually produced by pyrolysis treatment. These pyrolysis products containing methyl ketene, which also contain ketene as well as various hydrocarbons and unreacted methyl ethyl ketone, were subjected to a substantial cooling in condenser 8. From condenser 8 the materials were passed into reflux column 9 where by means of condenser 11 the methyl ethyl ketone is caused to fully condense out. In condensing out, this methyl ethyl ketone washes the methyl ketene gases, thereby condensing out methyl ethyl ketone contained therein. The condensed methyl ethyl ketone collects in the column base 12 where it may be subjected to a certain amount of heating for liberating any ketenic components. The unreacted methyl ethyl ketone may be subsequently returned to the vaporizer 2.

The methyl ketene containing vapors issuing from above the condenser 11 were passed into a contact device 14 such as a packed column or scrubber, where the gases were washed with warm acetic acid. This acetic acid may be of temperatures between about room temperature and 90° or 95° C. This acetic acid is preferably glacial acetic acid but a hydrous acid may be employed as will be set forth in further detail hereinafter.

The acetic acid may contain catalysts such as an inorganic acid (hydrochloric or sulphuric acid) or some organic compound containing either a sulphate or chloride group. Such a catalyst may be employed to facilitate the reaction between the methyl ketene and the acetic acid in which event either higher or lower temperatures than the above specified may be employed. The washing of the methyl ketene containing gases with warm acetic acid causes the formation of aceto-propionic anhydride as well as acetic anhydride. Acetic anhydride is formed due to the presence of ketene along with the methyl ketene.

This anhydride mixture was conducted to a fractional distillation column and subjected to a fractional distillation treatment. The distillation treatment caused the aceto-propionic anhydride to re-arrange, forming acetic anhydride and propionic anhydride. The acetic and propionic anhydride was then fractionally distilled in accordance with conventional procedure. Acetic anhydride may be distilled off first and then a relatively pure high-grade propionic anhydride distilled off and recovered at 24 or if desired, after the distillation of the acetic anhydride, water or dilute acid may be added which will convert propionic anhydride to propionic acid or the propionic acid may be distilled from the column and recovered from the propionic acid-water azeotrope or propionic acid may be withdrawn from the base heater 19. Any acetic anhydride formed, if desired, may be converted to acetic acid and employed for scrubbing in either column 14 or 44.

The mechanism of our reaction probably may be described by the following series of equations.

However, we do not wish to be bound thereby as these equations are set forth merely for the purpose of technical explanation and for a better understanding of the theory of operation of our process.

Decomposition of methyl ethyl ketone takes place probably in accordance with both of the following reactions:

(a) $CH_3CH_2COCH_3 \rightarrow CH_3CH{=}CO + CH_4$
Methyl ethyl ketone — Methyl ketene + methane

(b) $CH_3CH_2COCH_3 \rightarrow CH_2{=}C{=}O + C_2H_6$
Methyl ethyl ketone — Ketene + ethane

Part of the methyl ketene ($CH_3CH{=}CO$) decomposes to ketene as:

(c) $2CH_3CH{=}CO \rightarrow 2CH_2{=}C{=}O + C_2H_4$
Methyl ketene — Ketene — Ethylene

(d) The methyl ketene reacts with warm acetic acid as follows:

$$CH_3CH{=}CO + CH_3COOH \longrightarrow CH_3CH_2CO(\text{-O-})CH_3CO$$

Methyl ketene — Acetic acid — Aceto-propionic anhydride

The product produced, on distillation, rearranges:

(e) $$2CH_3CH_2CO(\text{-O-})CH_3CO \longrightarrow (CH_3CO)_2O + (CH_3CH_2CO)_2O$$

(f) Any ketene present reacts in accordance with:

$$CH_2{=}CO + CH_3COOH \rightarrow (CH_3CO)_2O$$
Ketene — Acetic acid — Acetic anhydride

The propionic anhydride may then be converted to propionic acid by reaction with water or methyl ketene may be converted directly:

(g) $CH_3CH_2{=}CO + H_2O \rightarrow CH_3CH_2COOH$
Methyl ketene — Propionic acid

A similar process to that described may be carried out in the apparatus of Fig. 2, in which event more efficient results may be expected. The passage containing methyl ketene pyrolysis vapors in contact with methyl ethyl ketone as shown in Fig. 2 produces a substantial cooling but at the same time prevents too great a cooling with the attendant condensation of methyl ethyl ketone. By this arrangement the removal of methyl ethyl ketone may be delayed and the materials are washed with the incoming methyl ethyl ketone in the reflux column 39. By this arrangement an improved separation of components is obtained as well as considerable heat recovery.

In place of pyrolyzing methyl ethyl ketone, we may also include the pyrolysis of diethyl ketone, which is decomposed in our apparatus in accordance with the following equations:

$$CH_3CH_2COCH_2CH_3 \rightarrow CH_3CH{=}CO + C_2H_6$$
Diethyl ketone — Methyl ketene — Ethane

The methyl ketene formed would be converted to propionic acid and anhydride as already described.

It is therefore apparent that we have provided a novel method for the manufacture of propionic acid and anhydride from readily available raw material. The quality of propionic acid and anhydride is entirely satisfactory. Our process is also advantageous inasmuch as it employs acetic acid which is more readily available than many other organic acids.

While the above examples represent our preferred embodiment, our invention has wider applications. For example, we have found that the ketene materials produced at 13 instead of being contacted in 14 or 44 as already described may be contacted with the acid sludge obtained from the fibrous esterification of cellulose to cause a separation thereof.

The aforementioned sludge comprises acetic and propionic acids and anhydrides mixed with Stoddard solvent or other type hydrocarbon or hydrocarbon solvent. This mixture presents considerable difficulty of separation. Such sludge mixtures cannot be separated by direct distillation inasmuch as the acetic and propionic acids form constant boiling mixtures with the hydrocarbon solvent. Analysis of a sludge sample, for example, shows the following components:

	Grams
Acetic acid	550
Propionic acid	179
Acetic anhydride	226
Propionic anhydride	276
Stoddard solvent	420

By passing ketene-containing materials produced in accordance with the aforementioned processes into sludge mixtures the acids may be converted to anhydrides as above described. This will cause the sludge mixtures to separate into layers. These layers may be then treated for separation purification by conventional fractional distillation processes. We have also found that ketene such as produced from the pyrolysis of acetone, acetic acid and the like will also produce a layer separation in sludge mixtures.

From the foregoing description of this invention, it is apparent that various changes might be made without departing from the spirit or scope thereof, hence, we do not wish to be restricted except in so far as necessitated by the prior art and the spirit of the appended claims.

What we claim and desire to secure by Letters Patent of the United States is:

1. A process for the preparation of propionic anhydride, which comprises preparing a gas containing methyl ketene and ketene, contacting the methyl ketene and ketene with acetic acid to form an aceto-propionic anhydride and acetic anhydride mixture and subjecting anhydride mixture to fractional distillation whereby propionic anhydride is obtained.

2. A process for the manufacture of propionic anhydride and acid, which comprises preparing vapors containing substantial amounts of methyl ketene, and contacting said vapors with acetic acid containing a catalyst and thereafter subjecting the reaction mixture to distillation.

3. A process for the preparation of propionic anhydride, which comprises preparing a gas containing methyl ketene and ketene from a 4-[illegible] atom ketone, contacting the methyl ketene and ketene with undecomposed ketone and then with acetic acid to form aceto-propionic anhydride and acetic anhydride, and subjecting the anhydride mixture to distillation whereby propionic anhydride is obtained.

4. The process for the manufacture of propionic anhydride and acid which comprises preparing vapors containing substantial amounts of methyl ketene and contacting said vapors with acetic acid containing an acetylation catalyst.

5. A process for producing propionic anhydride, which comprises preparing ketene-containing vapors, passing the ketene-containing vapors into contact with a sludge mixture obtained from cellulose ester manufacture containing propionic acid mixed with hydrocarbons whereby separa-

tion into layers is obtained, and recovering propionic anhydride from the layers.

6. In a process for the manufacture of methyl ketene, the step which comprises passing methyl ethyl ketene through a stainless steel pyrolysis tube maintained at a temperature between 500° C. and 800° C. in less than 3 seconds.

7. In a process wherein methyl ketene is produced, the steps which comprise passing a 4–5 carbon atom lower dialkyl ketone through a stainless steel pyrolysis tube maintained at a temperature between 500° C. and 800° C. in less than 3 seconds, and subjecting the resultant methyl ketene containing vapors to a wash with incoming ketone.

8. In a process wherein the methyl ketene is produced, the steps which comprise pyrolysing 4–5 carbon atom lower dialkyl ketone in less tha 3 seconds and at a temperature between 500° and 550° C. in contact with a stainless ste pyrolysis tube and under reduced pressure.

9. In a process wherein methyl ketene is pr duced, the steps which comprise passing meth ethyl ketone through a stainless steel pyrolys tube maintained at a temperature between 50 C. and 800° C. in less than 3 seconds, contactin the products of pyrolysis which contain meth ketene with a lower fatty acid and distilling th reaction products resulting from said conta with the lower fatty acid.

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CERTIFICATE OF CORRECTION.

Patent No. 2,235,561. March 18, 1941.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 4, first column, line 5, for "ketene" read --ketone--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 29th day of April, A. D. 1941.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)