Note.—The application for a Patent has become void.

This print shows the Specification as it became open to public inspection on Dec. 23, 1933, under Section 91 (4) (a) of the Patents and Designs Acts, 1907 to 1932.

PATENT SPECIFICATION

Application Date: June 22, 1933. No. 17799/33. **425,973**

Complete Specification not Accepted

COMPLETE SPECIFICATION

Improvements in or relating to the Manufacture of Keten

We, E. I. Du Pont de Nemours and Co., of Wilmington, Delaware, United States of America, a corporation organised and existing under the laws of the State of Delaware, United States of America, 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 methods of manufacturing keten from vapours of organic compounds which are decomposed by heat into substances including keten, and more particularly, relates to a method of manufacturing keten from acetone at elevated temperatures.

Heretofore keten has been prepared by passing acetone vapours through a hot reaction chamber at temperatures up to about 700° C. and usually in the presence of so-called "preventive catalysts." In these processes the yield of keton has rarely approached 80% of the theoretical, while the conversion of acetone vapours to keten in one run has been exceedingly low, usually around 10%. It is known that keten may be prepared without the use of preventive catalysts by employing a network of copper in the reaction chamber to insure proper heat distribution. In this process if the conditions of heating are properly controlled, yields up to 80% may be obtained from acetone, the temperatures being in the neighbourhood of 675° C. and the only requirement as to time of contact of the gases in the heated zone being less than 5 seconds.

An object of the present invention is to provide a method of manufacturing keten from acetone and other organic compounds which are decomposed by heat into substances including keten, with higher yields and higher conversions than have heretofore been obtained. Another object is to provide a method for the large scale production of keten in which relatively small empty reaction chambers can be used, thus avoiding the use of the metallic network packing and preventive catalysts heretofore considered necessary. A further object is to avoid local overheating of the vapours of acetone and also to control the contact time of the vapours in the high temperature zone in order that decomposition of keten may be reduced to a minimum.

The above objects are accomplished by the present invention according to which vapours of organic compounds which are decomposed by heat into substances including keten, are passed through a chamber heated to at least 675° C., the contact time of the gases derived from said vapours in the zone of high temperatures being limited to less than one second. More specifically, the above objects are accomplished by passing the vapours of acetone through an empty tube, preferably of copper, heated to a temperature of 750—850° C., the contact time of the gases derived from said vapours in the zone of high temperatures being between 0.015—0.3 seconds, and immediately thereafter cooling said gases to below 600° C. by bringing them into contact with liquid acetone.

The method of manufacture may be conveniently carried out by pumping liquid acetone at a suitable rate through a copper tube heated by gas burners, or by an electric furnace, or any other desirable method. Initial heating of the acetone may be accomplished by heat exchange with the reaction products emerging from the reaction chamber, if desired. The maximum temperature attained within the reaction chamber is very carefully controlled and the rate of flow of acetone is adjusted so as to give the desired time of contact at the temperature used. Since the temperature to be employed, although highly favourable for the decomposition of acetone to keten, also has a strong tendency to decompose keten, it is important that the contact time of the gases at such high temperatures be carefully controlled and it has

[*Price* 1/-]

been found that this can be done advantageously by spraying liquid acetone into the gases emerging from the reaction chamber at a rate sufficient to cool said gases below 600° C., whereby further decomposition of keten is avoided. It will be apparent that the same object may also be accomplished by passing the gases from the reaction chamber immediately into a water-cooled condenser of the usual type.

The gases leaving the reaction chamber will consist of keten and the methane equivalent to it, together with unchanged acetone and any carbon monoxide and ethylene which may have resulted from decomposition of the keten. The acetone can be condensed by suitable cooling of the vapour mixture. The non-condensable gases, including keten, are then used in any desired manner. For example, they may be washed with glacial acetic acid which combines readily with the keten to form acetic anhydride.

The reaction chamber may be made of a wide variety of materials, including copper, bronze, silver, quartz, Sillimanite, and the like, but the use of materials including nickel and iron, as well as nickel chromium alloys, should be avoided. The use of a copper tube $\frac{1}{8}$" internal diameter as the reaction chamber is preferred. Copper has been found to be the most practical material for the reaction chamber, unless temperatures above 1000° C. are to be used, in which event some higher melting point material naturally must be employed. Due to the short time of contact of the gases in the reaction chamber, a tube of relatively small diameter may be employed for large scale production. The time of contact of the gases according to the present method is far shorter than the time of contact used by prior investigators, and in all cases should be less than one second, and preferably should not exceed 0.3 seconds. The best results have been obtained by employing a contact time of 0.015—0.05 seconds. Within the limits disclosed, the time of contact should be increased for a constant temperature as the diameter of the reaction tube is increased, but should be materially decreased where excessively high temperatures, such as 1000° C. and upwards are employed.

It will be apparent to those skilled in the art that the temperature within the reaction tube will increase along the tube in the direction of flow of the reacting gases. The temperatures herein disclosed are those obtained at the hottest point along the tube. Since the rate of decomposition of the acetone increases so rapidly with temperature, it can be safely assumed that the decomposition takes place substantially entirely within that portion of the tube which is within 50° of the maximum temperature. The contact time of the gases, as disclosed herein, has been calculated as the number of seconds during which the vapours of acetone, at the reaction temperature, are permitted to remain within that portion of the tube which is within the 50° temperature range mentioned.

As an example of the calculation of the contact time of the gases, the following run is cited:

Rate of acetone feed, 12.7 g. per min. = 12.7/58 = 0.219 mol./min.
Maximum temperature, 810° C.
Length of tube within range 760—810° C., 39 in.
Inside diameter of tube, $\frac{1}{8}$" in.
Vol. of reaction zone = $39/16^2 = 0.0476$ cu. in. = 7.8 cc.
Vol. of 1 mol. at 810° C. = $22.4 \times 1083/273 = 88.7$ l.
Rate of flow in cc. of vapour at 810° per sec. =

$$\frac{88.7 \times 0.219 \times 1000}{60} = 323$$

Time of contact = 7.8/323 = 0.024 sec.

The yields given herein are calculated as the percentages of the acetone decomposed which recovered as keten and the conversion is the percentage of the total acetone fed to the reaction tube which is recovered as keten.

In the following table are given the results of runs made according to the present method employing acetone. In all cases a copper tube was employed as the reaction chamber. Inspection of the table will reveal that, with the same tubes, slightly better conversions are obtained for a given yield as the temperature is increased, but that to obtain the given yield the time of contact must be shortened materially at the higher temperatures. The table also shows that with a reaction tube of $\frac{1}{4}$" internal diameter a longer time of contact is necessary than with a reaction tube of $\frac{1}{8}$" internal diameter to obtain the same results:

Diameter of Tube In Inches	Temperature °C.	Time of Contact in Seconds	% Yield	Conversion
1/8	810	0.021	98	20.5
1/8	785	0.048	98	20
1/8	725	0.18	98	18
1/8	675	0.305	98	5.0
1/8	810	0.027	90	25
1/8	785	0.060	90	23
1/8	725	0.159	90	17
1/8	675	0.690	90	17.8
1/8	810	0.024	95	20.2
1/4	810	0.040	95	19
1/4	810	0.055	90	23
1/8	675	0.414	95	10

It will be seen from the above table that in every run a yield of at least 90% was obtained with a conversion of around 20% in most instances. In carrying out the present invention it is more practical to employ a temperature of 725° C., or greater, with a contact time of less than 0.5 seconds due to the increased conversion of acetone to keten. However, temperatures as low as 675° C. with a contact time of less than one second show higher yields than those obtained by any prior investigators, and also a fair per cent. of conversion. Where temperatures materially above 850° C. are to be employed, the contact time must be reduced to a few thousands of a second in order to obtain high yields due to the fact that decomposition of the products at such temperatures is very rapid.

An advantage of the present invention is that it gives yields hitherto unobtainable, together with exceptionally high conversion percentages. A further advantage lies in the fact that the method of the present invention may be carried out employing empty tubes which naturally simplifies large scale operation materially. It will be understood that catalysts and metal network may be employed in the method but have little practical advantage. A most unexpected advantage of the present invention is the high yield obtained. As shown by the table given herein, hitherto unobtainable yields and conversion percentages result by employing relatively small reaction chambers, high reaction chambers, high reaction temperatures, and short contact times.

The temperatures given herein are the temperatures of the walls of the reaction chambers and not of the gases within the reaction chambers, whose temperature may be slightly below that of the walls of the chambers inasmuch as the reaction is endothermic.

The term "contact time of said vapours" as used in the claims means the time during which the vapours are in that portion of the reaction chamber which has a temperature within 50° C. of the temperature at the hottest point of the reaction chamber.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for the manufacture of keten, which comprises passing the vapour of an organic compound which on thermal decomposition yields keten, through a chamber heated to at least 675° C., the contact time of the said vapour being less than 1 second, and thereafter immediately cooling the gaseous products of the reaction.

2. Process for the manufacture of keten, which comprises passing acetone vapour through a chamber heated to at least 675° C. and preferable to 750—850° C., the contact time of the vapour being less than 0.3 second, and preferably being between 0.015—0.05 second, and thereafter immediately cooling the gaseous products of the reaction to below 600° C. by any suitable means, e.g. by bringing them into contact with liquid acetone or by passing them into a water-cooled condenser.

3. Process according to Claim 1 or Claim 2 in which the reaction chamber is an empty copper tube, the internal diameter of which substantially does not exceed $\frac{1}{2}$ inch, and which is preferably about $\frac{1}{8}$ inch.

4. Keten whenever prepared by a process claimed in any of the preceding claims or by the obvious chemical equivalent of such process.

Dated the 22nd day of June, 1933.

E. A. BINGEN,
Imperial Chemical House,
Millbank, London, S.W.1,
Solicitor for the Applicants.

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