



# PATENT SPECIFICATION

DRAWINGS ATTACHED

877,662

Date of Application and filing Complete Specification: Dec. 22, 1959.

No. 43520/59.

Application made in United States of America on Dec. 24, 1958.

Complete Specification Published: Sept. 20, 1961.

Index at acceptance:—Class 2(3), C3A15.

International Classification:—C07c.

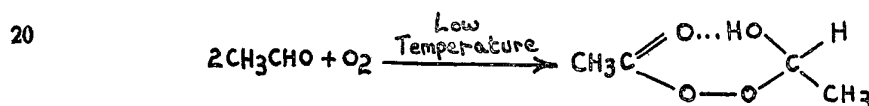
## COMPLETE SPECIFICATION

### Preparation of Acetaldehyde Monoperacetate

We, UNION CARBIDE CORPORATION, of 270, Park Avenue, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America, (Assignee of LLOYD ELLIS HILBERT), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the low temperature catalytic oxidation of acetaldehyde under turbulent flow conditions to produce acetaldehyde monoperacetate.

Patent No. 795,927 describes a method for the oxidation of lower aliphatic aldehydes to obtain the corresponding peroxide product. The reaction is illustrated by the following equation:—



Preferably, this low temperature reaction employs catalysts such as ozone. The peroxide product, acetaldehyde monoperacetate, can be regarded as a hemiacetal of acetaldehyde and peracetic acid. This complex of a reducing and oxidizing agent is very unstable and if a solution thereof is heated above 20° C. a vigorous reaction ensues with the formation of two equivalents of acetic acid. Similarly if the reaction is carried out at temperatures about 20° C., or if catalysts such as manganese ion or water, are present, the peroxide, as it forms, decomposes with the formation of acetic acid. Acetaldehyde monoperacetate can be used itself as an oxidizing agent or can be converted to peracetic acid. This process thus provides a valuable route for the synthesis of a strong oxidizing agent which finds wide utility in the oxidation of unsaturated compounds to their corresponding alkylene oxide derivatives.

Without wishing to be bound by any particular theory, it appears that the oxidation of acetaldehyde with oxygen, as illustrated in Equation I is a reaction of the free radical type in which the catalyst, e.g., ozone, is absorbed into the liquid acetaldehyde and reacts therewith to produce free radicals which in turn initiate a type of chain reaction between acetaldehyde and oxygen to form acetaldehyde monoperacetate and additional free radicals. Both oxygen and ozone, are sparingly soluble in liquid acetaldehyde and the driving force for

their absorption thus depends upon the rate at which their concentrations can be reduced by reaction with acetaldehyde. Ozone, being a highly reactive compound, reacts immediately, resulting in a rapid rate of absorption. Oxygen, however, reacts only as rapidly as it can contact acetaldehyde in the presence of the free radicals created by the absorption of ozone. The oxidation reaction continues until the ozone absorption is complete and the relatively short-lived free radicals have disappeared. Regardless of the actual locus of the oxidation reaction, the reaction rate is apparently determined to a large extent by the diffusional resistance of the liquid film at the oxygen-acetaldehyde interface. Thus if the reaction occurs in the liquid film at the gas liquid interface, acetaldehyde must diffuse into this film from the main body of liquid and the oxidation product, acetaldehyde monoperacetate, must diffuse in the reverse direction. If, however, the reaction occurs in the main body of the liquid, oxygen and ozone must diffuse through the liquid film at the gas-liquid interface from the vapor phase. In either instance the diffusional resistance of the liquid film controls both the rate and completeness of oxygen absorption. Since the life of free radicals created by the absorption of ozone into acetaldehyde is relatively very short, the efficiency of ozone utilization in the preparation of acetaldehyde monoperacetate therefore

depends upon a high rate of absorption of oxygen per unit of ozone absorbed.

Various methods and means have been heretofore suggested for carrying out the oxidation of acetaldehyde to obtain acetaldehyde monoperoacetate. A common procedure, for example, involves sparging oxygen, containing catalytic amounts of ozone, into a liquid solution of acetaldehyde in acetone or other suitable solvent, the exothermic heat of reaction being removed by either an external heat exchanger or internal cooling coil. While various modifications in reactor design, diffusing techniques, and heat transfer arrangement, etc., have been proposed, such systems have been found unsuitable for providing high productivity and good production rate.

This invention comprises a method for producing acetaldehyde monoperoacetate by oxidizing acetaldehyde with molecular oxygen in the presence of ozone or ultra-violet light at a temperature between  $-15^{\circ}\text{C}$ . and  $+30^{\circ}\text{C}$ . characterized in that a liquid stream comprising acetaldehyde is contacted with molecular oxygen in a reaction zone under conditions producing a Reynolds number of at least 2100. Under preferred conditions, the oxidation of acetaldehyde to acetaldehyde monoperoacetate is carried out continuously under atmospheric or superatmospheric pressure at temperatures within the range between  $-5^{\circ}$  to  $5^{\circ}\text{C}$ ., and in the presence of ozone as catalyst. By intimately contacting oxygen and acetaldehyde under conditions of substantial turbulence in the liquid phase and simultaneously maintaining a low reaction temperature, acetaldehyde monoperoacetate is obtained at high productivity and increased production rates. As compared to prior art methods wherein oxygen and acetaldehyde are dispersed without turbulence in the liquid phase, the method of the present invention provides increased production rates yielding up to thirty times the amount of acetaldehyde monoperoacetate obtained by conventional techniques and with a productivity, as measured by the pounds of acetaldehyde monoperoacetate obtained per pound of ozone used, amounting to a tenfold increase.

It is of the essence of the invention that the liquid acetaldehyde and oxygen-containing gas be contracted under conditions of substantial turbulence in the liquid phase. The expression "substantial turbulence" as employed herein refers to that degree of turbulence in the liquid phase equivalent to a Reynolds number of at least 2100 in consistent units. Accordingly, and for the reasons above described, if the oxidation is occurring in the liquid film at the gas-liquid interface, the turbulence provides rapid transfer of fresh acetaldehyde molecules to the interface and of acetaldehyde monoperoacetate back into the main body of the liquid. Similarly, if the reaction is occurring in the main body of acetaldehyde, the turbulence provides

rapid distribution of oxygen throughout the liquid as fast as it dissolves and thereby prevents the oxidation reaction from being retarded by the inability of oxygen to diffuse past a saturated surface layer. In this respect the turbulence created in the liquid phase is critical to the method of the invention.

The preparation of acetaldehyde monoperoacetate in a preferred embodiment is effected by supplying ozonized oxygen, solvent, and acetaldehyde to an elongated reaction vessel. The effluent from the reaction vessel, although containing some acetaldehyde monoperoacetate, is circulated through a heat exchanger for heat removal and back through the reaction vessel under highly turbulent flow conditions. Ozonized oxygen and acetaldehyde are continuously fed to the reaction vessel for contact with the circulating liquid under conditions of substantial turbulence in the liquid phase. The flow of reactants is concurrent and oxidation occurs downstream from the point of contact. Substantially all the oxygen in the fluids issuing from the reaction vessel is absorbed. Any unabsorbed oxygen is removed in an entrainment separator along with inert gases, etc. The liquid material is then circulated through a heat exchanger, as above described, and recycled to the reaction vessel. A constant content of material is maintained in the system by withdrawing a liquid product comprising acetaldehyde monoperoacetate, acetaldehyde, and solvent. The solution of acetaldehyde monoperoacetate may be stored or converted to peracetic acid.

While the Reynolds number must be above 2100 to insure liquid turbulence in the reaction vessel, we prefer that the Reynolds number be above 250,000, and desirably above 300,000. The particular reaction vessel employed is not critical to the method of the invention and may comprise any suitable type of reactor, e.g., a tubular reactor placed horizontally or vertically or at an angle to the horizontal. We prefer to limit the concentration of acetaldehyde monoperoacetate in the reaction mixture to about 30% by weight in view of the explosion hazard existing with concentrated solutions of this material.

The oxidation of acetaldehyde to acetaldehyde monoperoacetate is carried out in the presence of a catalyst which preferentially excludes the formation of acetic acid. Suitable methods of catalyzing the reaction are irradiating the acetaldehyde with ultraviolet light or including a small amount of ozone in the oxygen-containing gas. Both of these methods have the advantage of not introducing impurities. When ozone is employed, the oxygen-containing gas, e.g. air or molecular oxygen, can be passed through an ozonator in which it is subjected to an electrical discharge causing a part of the oxygen to be converted to ozone.

The amount of ozone required preferably ranges from 0.0001 to 5% by weight based on

the acetaldehyde, more preferably from 0.5 to 2.0% by weight.

When the oxidation of acetaldehyde to acetaldehyde monoperacetate is conducted to a high degree of conversion, the product crystallizes from unoxidized acetaldehyde in the form of colorless needles. As with other crystalline peroxides, these needles are sensitive to shock and merely the stirring of a slurry of the crystals can result in an explosion. By the use of an organic liquid solvent which keeps the peroxide crystals in solution, the possibility of an explosion is avoided. Suitable solvents which are non-reactive with the peroxide include acetone, methyl ethyl ketone, ethyl acetate, and butyl acetate. Acetaldehyde can also be used as the solvent provided the oxidation is not conducted to a degree of conversion so high that the acetaldehyde monoperacetate crystallizes out of solution. The unreacted aldehyde serving as solvent can subsequently be replaced by another solvent. The amount of solvent is not critical and can range from 0 to 85% by weight based on the acetaldehyde.

The accompanying flow sheet illustrates one of the preferred procedures adapted for carrying out the method of the invention as applied to the continuous preparation of acetaldehyde monoperacetate.

As shown in the drawing, a preferred form of the reaction vessel comprises a tubular reactor 10 having a length of at least four times its diameter. The vertical sides of reactor 10 may be surrounded by a temperature control means consisting of a reactor jacket 13 provided with one or more conduits 14 through which a coolant or heat exchange medium can be circulated. In the absence of reactor jacket 13, adequate heat exchange must be provided somewhere in the system to remove the exothermic heat of reaction while holding the temperature of the liquid between  $-15^{\circ}\text{C.}$  and  $30^{\circ}\text{C.}$  The temperature rise within the reaction zone of reactor 10 is preferably less than  $1^{\circ}\text{C.}$  regardless of whether or not the reaction vessel is jacketed.

A mixing jet 16 is mounted at the bottom of reactor 10 and serves to provide intimate contact between the gas stream introduced through conduit 18 and the acetaldehyde and recycle liquid streams introduced to the reactor through conduits 20 to 21 respectively.

The effluent issuing from reactor 10, containing solvent, acetaldehyde, and acetaldehyde monoperacetate passes to liquid level controller 24 by way of conduit 17. From controller 24 the liquid stream is recycled through heat exchanger 40 and conduit 21 to reactor 10 by means of circulating pump 35. The heat exchanger 40 is provided with conduits 15, and 15<sup>1</sup> through which a coolant is circulated for removing the exothermic heat of reaction.

The quantity of liquid in the reaction system is controlled by means of the liquid level controller 24. While continuous feeds of gas and

liquid are maintained to reactor 10 through conduits 18, 20, and 21, the liquid level controller is operated so that when a predetermined level of liquid is reached, a liquid product comprising acetaldehyde, solvent, and acetaldehyde monoperacetate is withdrawn from the reaction system through conduit 39. Removal of liquid product through conduit 39 is effected by conventional valve means (not shown) directly operated by the liquid level controller.

The advantages and utility of the invention will be apparent from the description of the following examples which illustrate the best mode now contemplated for practicing the invention.

#### EXAMPLE I

A 2.5 cm. diameter jacketed tubular reactor 3.05 meters long was employed to prepare acetaldehyde monoperacetate continuously at a temperature of  $-5^{\circ}\text{C.} \pm 2^{\circ}\text{C.}$  Separate feed streams of liquid and gas were introduced to the reactor inlet through a liquid aspirating jet. The liquid feed, comprising a 69.7% by weight solution of acetaldehyde in acetone, was introduced at a rate of 12.5 kg. per hour; ozonized oxygen, containing 0.60% ozone was introduced at a rate of 0.908 cu. meter per hour.

The effluent from the reactor, containing 27.0% acetaldehyde monoperacetate, 5% acetic acid, solvent and unreacted acetaldehyde was continuously discharged to a liquid level controller. Vapor overhead materials were vented and the liquid stream circulated through a heat exchanger to the reactor at a rate of 5560 liters per hour. The Reynolds number maintained in the reactor was approximately 292,800. While continuous feeds of gas and liquid were maintained to the reactor, a portion of the circulating liquid stream was withdrawn to maintain a constant liquid level in the system. Under these conditions the production rate of acetaldehyde monoperacetate amounted to 3.73 kg. per liter of reactor volume per hour. The productivity amounted to 335 grams of acetaldehyde monoperacetate per gram of ozone employed.

#### EXAMPLE II

The preparation of acetaldehyde monoperacetate was carried out in a conventional system in which ozonized oxygen was sparged through a diffuser into a tank filled with acetaldehyde and ethyl acetate solvent. The reaction temperature was maintained at  $0^{\circ}\text{C.} \pm 3^{\circ}\text{C.}$  by means of cooling coil mounted in the tank. The production rate achieved ranged from 0.036 to 0.12 kg. of acetaldehyde monoperacetate per liter of reactor volume per hour. The productivity amounted to 30 to 70 grams of acetaldehyde monoperacetate per gram of ozone employed.

As readily seen from the results obtained in Example II, the method of the invention as illustrated in Example I provides an increase

of more than thirty fold in the production rate of acetaldehyde monoperacetate. The productivity of acetaldehyde monoperacetate achieved per pound of ozone used amounted to a five or ten fold increase.

- 5 Although the method of the invention is directed to the preparation of acetaldehyde monoperacetate by circulating a liquid stream comprising acetaldehyde under highly turbulent flow conditions and oxidizing the acetaldehyde under conditions of substantial turbulence in the liquid phase, it is within the purview of the instant method to effect certain variations without departing from the scope of the invention as defined by the appended claims. For example, the turbulence may be effected by causing the liquid and gas streams to simultaneously impinge upon one another at high velocities and thereby cause substantial turbulence after the impact of the streams.

20 WHAT WE CLAIM IS:—

- 25 1. A method for producing acetaldehyde monoperacetate by oxidizing acetaldehyde with molecular oxygen in the presence of ozone or ultra violet light at temperatures between  $-15^{\circ}\text{C}$ . and  $+30^{\circ}\text{C}$ . characterized in that a liquid stream comprising acetaldehyde is contacted with molecular oxygen in a reaction zone under conditions producing a Reynolds

number of at least 2100.

2. A method as claimed in claim 1 in which the ozone is present in an amount ranging from 0.5 to 2.0 per cent by weight.

3. A method as claimed in claim 1 or 2 in which the oxygen contains ozone.

4. A method as claimed in any of the preceding in which the liquid stream comprises acetaldehyde and a liquid solvent for acetaldehyde monoperacetate.

5. A method as claimed in claim 4 in which the solvent is acetone.

6. A method as claimed in any of the preceding claims in which the temperature is between  $-5^{\circ}$  and  $+5^{\circ}\text{C}$ .

7. A method as claimed in any of the preceding claims in which the Reynolds number is at least 250,000.

8. A method for producing acetaldehyde monoperacetate substantially as described herein with reference to Example I and/or the accompanying drawing.

9. Acetaldehyde monoperacetate when produced by the method as claimed in any of the preceding claims.

W. P. THOMPSON & CO.,  
12, Church Street, Liverpool, 1.  
Chartered Patent Agents.

This drawing is a reproduction of  
the Original on a reduced scale.

