The following statement is a full description of this invention, including the best method of performing it known to us:

X837–65–ND–13 P.C.
This invention relates to a process for producing propylene oxide.

The preparation of alkylene oxides by reaction between an olefin and oxygen in the presence of a catalyst based on silver and/or silver oxide is known.

In particular, industrial processes for the production of ethylene oxide from ethylene and oxygen or air have been developed and marketed for a considerable time. Until now, however, the production of higher alkylenic oxides by a similar synthesis, particularly propylene oxide, which is mainly produced indirectly, has not been an attractive commercial proposition.

In French Patent Specification No. 785,149 it was proposed to produce propylene oxide from propylene and oxygen in the presence of a silver-based catalyst by feeding extremely large quantities of inert compounds, in particular carbon dioxide or water vapour, together with the reagents to the catalyst-containing zone. However, the results obtained by such a process are not satisfactory from an industrial point of view.

It is therefore particularly surprising to find that it is possible to obtain propylene oxide in a high selectivity when water vapour in the range from 2 to 25% by volume of the sum of propylene, oxygen and water vapour, is added to the reaction mixture.

Accordingly, the present invention provides a process for producing propylene oxide, which comprises reacting propylene with oxygen or a gaseous mixture including oxygen, in the presence of a silver-based catalyst and in the presence of water vapour in a quantity in the range from
2 to 25% by volume of the sum of the volumes of the propylene, oxygen and water vapour present.

It has been found that if the quantity of water vapour is higher than 30% by volume the selectivity with respect to propylene oxide is not merely not further increased but is significantly reduced.

The term "selectivity" when used herein with respect to propylene oxide is defined as follows:-

\[
\frac{\text{number of moles of propylene oxide produced}}{\text{number of moles of propylene which have reacted}} \times 100
\]

Preferably the process of the present invention is effected by introducing propylene, air (or oxygen) and water vapour in the appropriate relative quantities over a silver-based catalyst in a reactor maintained at a temperature in the range from 110 to 400°C.

Preferably the ratio by volume of propylene to oxygen (or oxygen in air) in the reactor is in the range from 4:96 to 95:5. The quantity of water vapour present is in the range from 2 to 25% with respect to the total of the propylene, oxygen, and water vapour in the feed gas, preferably from 2 to 15%.

In the feed gas, gaseous compounds which do not influence negatively the reaction can be present. Silver-based catalysts which can be used with advantage in the present invention are those based on metallic silver or silver compounds.

This silver-based catalyst can also contain lesser quantities of other elements as activators such as magnesium, calcium, barium, strontium, selenium, tellurium, lead, tin, arsenic, or compounds containing such elements.

The catalyst can be used unsupported or it can be
suitably supported, for example on a silicate of alumina (china clay), carborundum or kieselguhr support.

It is possible to introduce into the reaction zone a suitable inhibitor which regulates the reaction rate, either before or during the reaction of propylene and oxygen. Inhibitors which can be used with advantage can be chosen from organoc or inorganic chlorides.

The following Examples illustrate the present invention.

EXAMPLE 1

Two tests were carried out at a constant temperature without and with 5% H₂O in feeding on a catalyst prepared
in the following way:
100g. of AgNO$_3$, 24g. of calcium nitrate tetrahydrate
and 11 g. of barium nitrate were dissolved in 1500c.c.
of deionized water (ratio Ag:Ca:Ba = 15:2.5:1).
The solution obtained which can be opalescent
due to the presence of a small quantity of silver
chloride formed was filtered with adsorbent media.
42g. of anhydrous sodium carbonate were dissolved
in 500c.c. of distilled water and purified with the
addition of 2g. of silver nitrate.
The solution obtained was filtered.
Before the two solutions were mixed a small
quantity of calcium chloride was added (~ 10mg.).
The coprecipitation of silver, calcium and barium
carbonate was carried out by adding, under rapid agita-
tion the solution of sodium carbonate to the solution
of nitrates.
The carbonate precipitation was obtained in a
finely divided state.
The material obtained was filtered, washed with
deionized water and dried for several hours in an oven
at 110°C. with a weak air flow. About 120g. of catalytic
powder was obtained which was finely ground in a hammer
mill (mullino a martelli). The placing of the catalytic
material on the support was then proceeded with.
A commercial material was chosen as a support, that
is silicate of allumina (china clay) with the following
characteristics (allumina S.A. 5218 of Norton) Shape; as
a sphere, diameter 5/16".
Composition:
Chemical-physical characteristics (R.X.) - $\alpha\text{Al}_2\text{O}_3$

+ Mullite.

Porous structure; porosity in volume
pore radius: 100-700 microns

This support presents a particularly suitable porous structure in that it allowed a complete penetration of the catalytic material to be obtained even in the internal parts of the sphere itself. Logically other types of allumina and supports having the same properties can be used.

Inhibition was carried out by mixing the catalytic powder obtained with 800 g. of a solution of ethylenic glycole and treating the suspension with 550 g. of support maintained under agitation to facilitate inhibition uniformity.

The material obtained was then dried and activated in a controlled airflow around $350^\circ C$ for some hours. This catalyst, in order to carry out the mentioned test, was loaded in a 30 cm. long reactor, diameter 1" thermostatically controlled by dowtherm circulation.

Test conditions were as follows:

pressure = atmospheric
Catalyst volume = 100 cm$^3$
Flow = 5 Nl/h
Ratio $C_3H_6/O_2 = 85/15$
Test results are reported in table 1.
EXAMPLE 2

The same reactor as in example 1 was used; the active part of the catalyst consisted of Ag alone and the 10mg. of CaCl₂ were not added. The test results and the reaction conditions are reported in table 1.

EXAMPLE 3

The same reactor as in example 1 was used; the active part of the catalyst was prepared starting from 100g. AgNO₃ and 32.4g. of Ca(NO₃)₂.4H₂O.

CaCl₂ was not used. The test results and reaction conditions are reported in table 1.

EXAMPLE 4

The same reactor of example 1 was used; the active part of the catalyst was prepared starting from 100g. of AgNO₃ and 35.9g. of Ba(NO₃)₂. CaCl₂ was not used. Test results and operative conditions are reported in table 1.

EXAMPLE 5

Another catalyst was prepared by a method which involved impregnation of a support with solutions of the active components. It consisted in the preparation of solutions of organic silver salts and promoters, and then the impregnation of the support with such solutions.

A general procedure is to maintain the temperature around 90 to 95°C. during the operation for a variable duration depending on the type of support; however, not more than an hour later, the solution is removed and the impregnated material maintained at 90 to 95°C for a further 15 minutes.

The material was then placed in the oven at 70-80°C.
in a weak air flow for about 12 hours; a calcination at 320°C for about 5 hours in a controlled air flow followed. The test was carried out in the same reactor as example 1. The catalyst was prepared starting from 100g. of Ag(lattate) and 0.8g. of Ba.(lattate). The support consisted of allumina in spheres of a diameter equal to 3/16". Test results and operative conditions are reported in table 1.

EXAMPLE 6

40g. of the powder making up the active part of the catalyst described in example 1 were loaded in a glass reactor of 13 diameter which was heated by means of a dowtherm circulation. Some tests were carried out on this catalyst with constant temperature and different H₂O content. The conditions in which the tests were carried out were as follows:

- Pressure = atmospheric
- Temperature = 184°C.
- Reagent mixture flow = 5NL/h
- Ratio C₃H₆/O₂ = 85/15

The results obtained are reported in table 2.

EXAMPLE 7

Tests of propylene oxide synthesis from propylene and oxygen were carried out using a catalyst made up of silver powder, with different water contents in the gas feed.

The reactor used was the same as in previous examples and the reaction conditions were as follows:

- Pressure = atmospheric
- Reagent mixture flow = 5NL/h
$\text{TOC} = 181$

Molar ratio $C_3H_6O_2 = 85/15$

The test results are summarized in table 3.
<table>
<thead>
<tr>
<th>Example n.,</th>
<th>Atomic ratio (Ag/Ca/Ba)</th>
<th>Feed (C₂H₆/O₂ (% mols))</th>
<th>T°C.</th>
<th>S % mol. (selectivity)</th>
<th>without H₂O</th>
<th>with H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15/2.5/1</td>
<td>85/15</td>
<td>195</td>
<td>24.4</td>
<td>50.0</td>
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<tr>
<td>2</td>
<td>15/0/0</td>
<td>85/15</td>
<td>215</td>
<td>6.0</td>
<td>21.0</td>
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<tr>
<td>3</td>
<td>15/3.5/0</td>
<td>85/15</td>
<td>193</td>
<td>8.9</td>
<td>24.5</td>
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<tr>
<td>4</td>
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<td>85/15</td>
<td>195</td>
<td>12.0</td>
<td>23.5</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1400/0/7.9</td>
<td>85/15</td>
<td>210</td>
<td>3.5</td>
<td>7.0</td>
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### Table 2

<table>
<thead>
<tr>
<th>% H₂O</th>
<th>Selectivity % mol</th>
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<tr>
<td>0</td>
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<td>4</td>
<td>52</td>
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<td>5</td>
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<td>14</td>
<td>45</td>
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<td>33</td>
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</table>

### Table 3

<table>
<thead>
<tr>
<th>% H₂O</th>
<th>Selectivity % mol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<tr>
<td>6.5</td>
<td>41.6</td>
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<td>17.5</td>
<td>34.4</td>
</tr>
<tr>
<td>48.5</td>
<td>10</td>
</tr>
</tbody>
</table>
The claims defining the invention are as follows:

1. A process for producing propylene oxide, which comprises readting propylene with oxygen or a gaseous mixture including oxygen, in the presence of a silver-based catalyst, and in the presence of water vapour in a quantity in the range from 2 to 25% by volume of the sum of the volumes of the propylene, oxygen and water vapour present.

2. A process according to Claim 1, wherein the quantity of water vapour introduced is in the range from 2 to 15% by volume of the sum of the volumes of the propylene, oxygen and water vapour present.

3. A process according to Claim 1 or 2, wherein the reaction is carried out at a temperature in the range from 110 to 400°C.

4. A process according to Claim 1, 2 or 3, wherein the molar ratio of propylene to oxygen is in the range from 4:96 to 95:5.

5. A process according to any preceding claim, wherein the gaseous mixture including oxygen is air.

6. A process according to any preceding claim, wherein a mixture of propylene, oxygen or gaseous mixture including oxygen and water vapour is passed over the silver-based catalyst in a heated reaction zone.

7. A process according to any preceding claim, wherein the silver-based catalyst includes one or more of magnesium, calcium, barium, strontium, selenium, tellurium, lead, tin and arsenic.

8. A process according to Claim 1, substantially as described in any one of the foregoing Examples.

9. Propylene oxide whenever produced by a process accord-
ing to any preceding claim.


PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:
SNAM PROGETTI S.p.A.