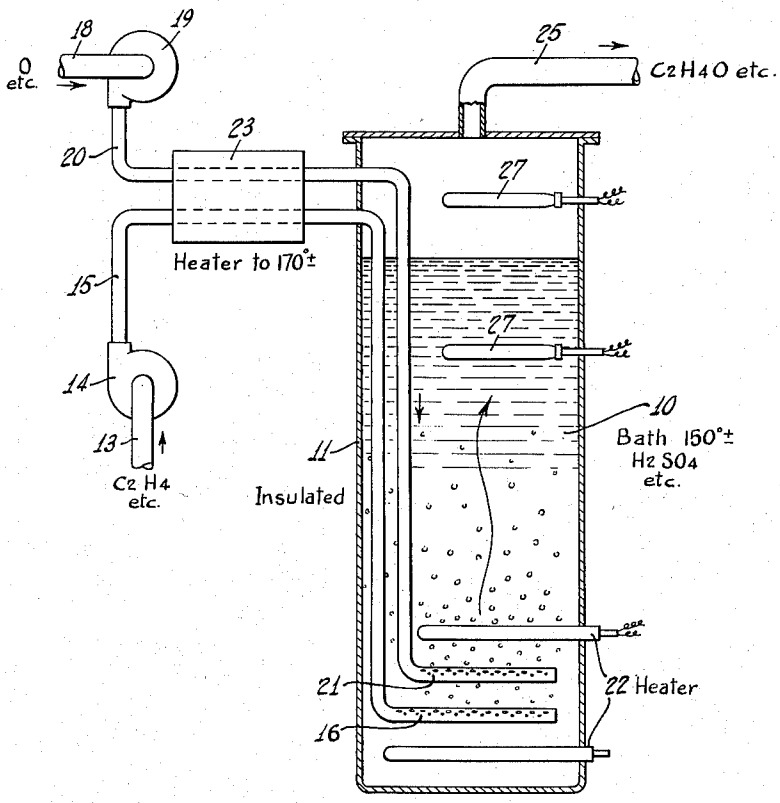
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PROCESS FOR OXIDIZING OLEFINES

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INVENTOR:
Daniel Gardner
BY
Morrison, Kennedy & Campbell
ATTORNEYS.

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PROCESS FOR OXIDIZING OLEFINS

Daniel Gardner, New York, N. Y., assignor to Gardner Thermal Corporation, a corporation of Delaware

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This invention is a novel process for the oxidation of olefins, being the treatment of unsaturated hydrocarbons of the ethylenic series, typically represented by ethylene gas, for the purpose of producing on an industrial scale the ethylenic oxide, preferably in a continuous operation, and the collection of such oxide with or without the further step of conversion othereof to an aqueous or other derivative product such as glycol. While ethylene will be referred to for illustrative purposes, the process hereof is applicable to the treatment of propylene and the higher homologues, by appropriate variations of temperature, duration, selection of catalysts and other factors involved. The olefin gas may be in strong concentration obtained in known ways, or may be very dilute as when accompanied by other gases from cracking operations. The necessary oxygen may be supplied as air or in another gas, for example as nitrous oxide. The ingredient gases however should themselves be in a quite pure condition and free from moisture or other agents which might interfere with or reduce the efficiency of the process.

In a copending application, Serial No. 380,284, filed February 24, 1941, has been disclosed a process for treatment of unsaturated hpdrocarbons, carried out in a non-acid liquid bath, preferably an organic liquid of alkaline reaction.

An object of the present invention is to provide a practical and useful liquid bath system for this subject, wherein the bath is of acid reaction and comprises preferably a plentiful inorganic or mineral acid. A particular object is to permit operations at relatively low temperatures, so as to yield the desired olefinic oxides without danger of disintegration by isomerization or otherwise, while providing for an effective high rate of production in an economic sense. Other objects and advantages of the present process will appear during consideration of the following disclosure.

As a first basis of explanation of the present invention the general features herein disclosed may first be recited as follows. The underlying principle may be described as the process, which may be continuous, of oxidizing an olefin, which process comprises conducting streams of gases containing respectively the olefin and the oxygen, supplied in equimolecular proportions i. e. substantially according to their combining weights, and passing each of tnese through a hot bath of a suitable non-aqueous liquid wherein is dispersed or dissolved a catalyst effective to promote the reaction for the combination of the olefin and the oxygen to form the olefinic oxide, carried out at a temperature safely below that at which the olefin or its oxide is liable to disintegrate, as by isomerization or polymerization. By non-aqueous is meant that the bath should contain no appreciable quantity of free water, not referring to the water of combination which is a component of certain acids. The characterizing features include the following. The bath vahicle is of strong acid character, as a concentrated solution of an acid, preferably a mineral acid, and containing no free water. The acid, as sulfuric acid, is adapted to take part in the reaction by first combining with the olefin to form an intermediate product, as ethylsulfuric acid, which next yields the olefin for combination with the oxygen. The ability of such a bath to absorb chemically a given olefin usually ceases within a certain temperature range above which the reaction reverses, so that the bath should be well below such transition temperature. Under these conditions the first reaction step occurs readily, and the catalyzer is for promoting the second step of the described indirect oxidation.

This invention then has to do with the catalytic oxidation of ethylenic hydrocarbons, particularly as taking place when passing a current of air or oxygen through an alkylsulfuric compound, such as said ethylsulfuric acid, present or dissolved in an excess of sulfuric acid, the alkylsulfuric compound being continuously formed by interaction between the ethylenic hydrocarbon and the sulfuric acid, and thereupon continuously giving up its ethylene component to unite with the oxygen.

While sulfuric acid H_2SO_4 was mentioned it is but a preferred representative of acids available for the reaction bath of this invention, such as phosphoric, arsenic, boracic and selenic acids; telluric being operative but too costly. These acids may be classed as examples of the group of mineral acids, but not to the exclusion of other kinds of acids which can first take up the olefin and then yield it to oxidation.

It is advantageous to add auxiliary agents or salts to the bath, for example, to add to sulfuric acid one or more of the acid salts $NaHSO_4$ or $KHSO_4$. These are found to assist the taking up of the olefin, possibly by active or mass action.

Platinum black or sponge is an instance of a suitable catalyzer, and others will be enumerated after reciting an illustrative example of the invention, remembering that any catalyst is subject to fatigue, and that occasional switching of the process from one bath to another is advis-

able to permit refreshing or activating the bath in this and other respects.

Example

The supplied ethylene gas, and as well the oxygen-containing gas, nitrous oxide, may be preheated while being conducted to the furnace or reaction vessel. The bath being maintained between about 145 and 155°, with outside limits of 140 and 160°, the preheating of the supply gases may be for example to 170°. The bath may be in the form of a shower, or preferably a column of the liquid vehicle through which the respective gases may be passed by blowing them into the bottom of the bath to ascend therein in the form of fine bubbles adapted effectively to contact the bath liquid and other agents.

The treatment bath may consist of pure sulfuric acid, and by the joint ascent through the bath of the respective gases there may be some degree of direct combination, or oxidation of the ethylene, but in the main the reaction is a twofold one. In the first step the ethylene makes combination with part of the acid, which loses to the ethylene one atom of hydrogen in the process. Thus is formed the intermediate product ethylsulfuric acid or acid ethyl sulfate, which is an ester and constitutes one of the alkyl sulfur compounds. The temperature is preferably between 145 and 155°, safely below the transition temperature of about 160° above which the first step of the reaction can not occur; and is below the break-up point at which there is a tendency of the ethylene or its oxide to disintegrate by isomerization or otherwise, which in the case of ethyl oxide may be placed in the neighborhood of 200°.

By way of assisting the step of combination of ethylene and sulfuric acid there may be added to the bath an auxiliary agent or salt, for which the acid salts, sodium or potassium bisulfate, or a mixture of them, may be used.

Continuously with the first step may take place the second step, the yielding up by the intermediate product of its ethylene component to combine with the oxygen as ethylene oxide gas, this change operating also to regenerate the sulfuric acid, by the following formula:

$$C_2H_5OSO_3H+O \rightarrow C_2H_4O+H_2SO_4$$

The product gas or ethylene oxide bubbles up and out of the bath, along with the various inert or idle gases with which the ethylene and oxygen supplies were entrained; and the entire stream of outflowing gases may be passed to a suitable point for the collection of the ethylene oxide or for its conversion into derivative products.

The example recited is illustrated by the single diagrammatic figure of drawings with legends indicating suitable materials and temperatures. The liquid bath **10** represents either a spray or a column as shown, through which the supply gases must flow. The furnace or vessel **11**, of non-corrosive material, contains the reaction chamber or space within which is maintained the bath. The olefin is shown fed by supply pipe **13**, blower **14** and passage or flue **15** to a discharger **16** shown as a perforated extension of the pipe. The oxygen, as air or nitrous oxide, is supplied by pipe **18** and driven by blower **19** through passage or flue **20** to perforated discharger **21**. The dischargers are placed low to deliver the gas streams as bubbles ascending in intimate mixture through the height of the bath. As a conventional heating means is shown a pair of electrical resistance devices **22**; and any known means may be employed for preheating the gases between blowers and dischargers, such as the heater **23** shown conventionally as a box through which the flues extend. The product gases are conducted from the furnace or vessel by an outtake pipe **25** leading to a suitable collection or conversion point. If the reactions are to be fostered by chemically active rays such as ultraviolet light, affording better activity at lower temperatures, suitable sources of such rays may be provided, as conventionally shown in the form of ultraviolet tubes **27** positioned within the reaction space.

Manifestly the gases outgoing at pipe **25** could be recirculated back through intake pipe **15** or **20** for more exhaustive reactions; and in such way the process could be discontinuous if desired, or batch by batch.

Supplemental explanations

The different catalysts to be enumerated all have in common that, when dispersed in hot sulfuric acid or another suitable acid solution, such as molten bisulfate of sodium or potassium, they act catalytically within a definite temperature range and thereby contribute to the oxidation of any of the ethylenic hydrocarbons. By this process, and these catalysts, either pure ethylenic hydrocarbons can be submitted to oxidation, or the same hydrocarbons mixed with other hydrocarbons; as with gases obtained by modern oil cracking processes or those resulting from coke-oven or similar operations.

For the most part the indicated catalysts have already been made use of in various chemical processes; but it is believed to be novel to apply said catalysts in the process or system herein disclosed or in the conditions as already stated or summarized; the matters of novelty being of practical value since they afford an economic advantage, without need of discarding the prevailing types of industrial installations that are not only costly but often complicated. The various catalysts will now be discussed separately.

(1) Platinum black or platinum sponge has long been industrially applied for the actual manufacture of sulfuric acid. In the practice of the present invention it is advantageous to use platinum black in form of a suspension in concentrated sulfuric acid, of density 1.84. Since the metal does not dissolve in the acid, it is essential to have the metal in very fine state for suspension or colloidal dispersion therein. The oxidation of ethylene is carried out at a temperature below about 160° C., and goes as follows:

$$2SO_4.C_2H_5.H+O_2 \rightarrow 2OH.CH_2.CH_2.HSO_4$$

By treatment with potassium hydrate the so obtained product gives ethylene oxide, in the same bath, thus:

$$OH.CH_2.CH_2.HSO_4+2KHO \rightarrow CH_2.CH_2.O+K_2SO_4+2H_2O$$

If desired, the ethylene oxide can be introduced into water in order to obtain ethylene glycol.

(2) Palladium black in very finely divided state dissolves in concentrated sulfuric acid, thus giving a certain advantage over platinum black. Otherwise the action is a very much similar one.

(3) Silver sulfate. The use of silver salts, more particularly of silver sulfate, is well established for catalysis, for instance for the production of esters, as by action upon halogen alkyls. Silver sulfate is soluble in concentrated sulfuric

acid, affording good results of oxidation, even at a temperature of up to 250°.

(4) Copper sulfate works in similar manner to silver sulfate; but it has a lower melting point.

(5) Thallous sulfate. This salt functions also like silver sulfate. However, it is well soluble only in dilute sulfuric acid, and besides has the drawback of going over into thallic sulfate.

(6) Manganous sulfate is soluble in concentrated sulfuric acid; and can be easily incorporated in the acid in a suitable quantity. It gives lower yields when used as a catalyst.

(7) Ferrous sulfate is a well known catalyst in certain organic reactions. This is a cheap catalyst and, contrary to ferric sulfate, it dissolves in concentrated sulfuric acid. Although the yield with ferrous sulfate is lower than with silver sulfate, this catalyst becomes less "fatigued" and gives a more steady operation and output of the olefinic oxide desired, at about the same temperature.

(8) Nickel sulfate is of great interest, since its use assists in obtaining constant results. It otherwise resembles ferrous sulfate in catalytic operation.

(9) Thallous selenate much resembles in its action thallous sulfate. It is the salt of selenic acid, H_2SeO_4, which corresponds to sulfuric acid; and is particularly appropriate in an oxidizing bath of selenic acid, and dissolves also in sulfuric acid. The catalytic action is marked, but it is necessary to work at the lowest practical temperature, below 260°, to avoid decomposition and carrying away of the salt.

(10) Silver nitrate. Like silver sulfate, the nitrate has already been frequently used in organic processes. Its great advantage consists in its low melting point of 212°. It is easily incorporated in concentrated sulfuric acid.

(11) Lead nitrate has given satisfactory results as a catalyst. When incorporated in concentrated sulfuric acid, it partly goes over into lead sulfate, which precipitates in the form of a fine powder, since it is only slightly soluble.

(12) Thallous nitrate is an excellent catalyst and has a relatively low melting point, but is poisonous. The salt otherwise acts like thallous sulfate, but permits working at lower temperatures, which is always an advantage when working with ethylenic hydrocarbons and their derivatives.

The above twelve catalysts were among a long series of salts, including other sulfates, nitrates and selenates that were tested, others of which were not satisfactory. The twelve have been especially mentioned as illustrative catalysts because they all gave satisfactory results, but their mention is not to exclude others that trial may show to be useful.

Since at the bath temperatures designated saturated hydrocarbons are not attacked or converted in passing through the reaction zone, and since at the speed and short duration of passage they are not subject to sulfuration, gases issuing from modern cracking processes or from coke-ovens can be passed directly through the above described system, in their diluted condition, without fear of impairing the reactions or contaminating the products desired. In other words, under the described process conditions, only the ethylenic or other unsaturated hydrocarbons are attacked, these taking part in the chemical changes and becoming rapidly transformed into the respective oxides or glycols. The entire content of the ethylenic compounds is thereby practically extracted from the supply gases and rendered available for industrial purposes.

Under the principles of this invention the bath must be acid; and while strong acidity is preferable, this may be weakened so long as it remains liquid up to the hot reaction temperatures used, such as about 160° or 200°; and as instances within this suggested equivalent may be mentioned molten salts, as Na_2SO_4 or K_2SO_4, or a stable hydrocarbon, liquid and acid, operated under hot temperature and with the catalyst incorporated.

What is claimed is:

1. The process of oxidizing ethylene or other olefin comprising conducting supply streams of gases containing respectively the ethylene and the oxygen supplied in substantially equimolecular proportions, passing the ethylene and the oxygen gases into and through a substantially non-aqueous liquid bath of a concentrated mineral acid of the group consisting of sulfuric, phosphoric, arsenic, boracic and selenic acids, in which bath is dispersed a catalyzer which is stable in the acid bath, the oxidation being in two reaction steps, the ethylene first combining with the acid to form ethylsulfuric acid as an intermediate product, and the intermediate product then yielding the ethylene to combine with the oxygen as ethylene oxide while the acid is regenerated, the catalyzer being a substance other than the bath acid acting to promote the second step, and the temperature being maintained at a reaction temperature well below that of liability of the ethylene or its oxide to disintegrate, and within a temperature range in which the first step can occur, between about 145° and 155°.

2. The process of oxidizing an olefin comprising conducting streams of gases containing respectively the olefin and the oxygen supplied in substantially equimolecular proportions and substantially at atmospheric pressure, passing the olefin and the oxygen through a heated bath of substantially non-aqueous concentrated acid liquid wherein is dispersed a catalyzer other than the bath acid which is stable in the bath and acts to promote therein the combination of the olefin and the oxygen to form the olefin oxide, and maintaining said bath at a reaction temperature between about 140° and 160° C.

3. The continuous process of oxidizing an olefin comprising passing preheated streams of gases containing respectively the olefin and the oxygen through a heated bath of substantially non-aqueous concentrated acid liquid wherein is dispersed a catalyzer other than the bath acid which is stable in the bath and acts to promote therein the combination of the olefin and the oxygen to form the olefin oxide, and maintaining said bath at a reaction temperature well below the disintegration temperature of the olefin oxide.

4. The process of oxidizing an olefin comprising conducting streams of gases containing respectively the olefin and the oxygen, passing the olefin and the oxygen through a heated bath of substantially non-aqueous concentrated acid liquid wherein is dispersed a catalyzer which is stable in the acid bath, thereby to cause a two-stage reaction, the olefin first forming an intermediate compound with the bath acid which compound thereupon yields the olefin for combination with the oxygen; and maintaining said bath at a reaction temperature well below the

temperature of reversal of the first reaction stage; the catalyzer being an added substance other than the bath acid adapted to promote the second reaction stage with the olefin oxide as a product, and such second stage acting to regenerate the acid of the bath.

5. A process as in claim 2 and wherein the reaction bath is of an acid liquid containing an acid of the group consisting of the mineral acids, sulphuric, phosphoric, arsenic, selenic.

6. A process as in claim 2 and wherein the non-aqueous reaction bath consists of sulfuric acid.

7. A process as in claim 2 and wherein the non-aqueous reaction bath is of an acid liquid containing selenic acid.

8. A process as in claim 2 and wherein the non-aqueous reaction bath is of an acid liquid comprising molten acid salts of the group consisting of sodium sulfate and potassium sulfate.

9. A process as in claim 4 and wherein the non-aqueous acid bath is fortified with an auxiliary agent or acid salt adapted to promote the first reaction stage, selected from the group consisting of sodium bisulfate, potassium bisulfate and a mixture of the two.

10. The process as in claim 4 carried out with a catalyzer which is a metal salt soluble in the non-aqueous bath and selected from the group consisting of the sulfates of silver, copper, iron, thallium, manganese, tellurium and nickel.

11. The process as in claim 4 carried out with a catalyzer which is a metal salt soluble in the non-aqueous bath and selected from the group consisting of the nitrates of silver, lead and thallium.

12. The process as in claim 4 and wherein the catalyzer is palladium black.

13. The process as in claim 1 and wherein the catalyzer is of the group consisting of the sulfates of silver, copper, iron, thallium, manganese, tellurium and nickel.

14. The process of oxidizing an olefin comprising conducting streams of gases containing respectively the olefin and the oxygen passing the olefin and the oxygen jointly through a bath of a substantially non-aqueous acid liquid wherein is dispersed a catalyzer which is stable in the acid bath and acts to promote the oxidation hot reaction, and maintaining said bath at a reaction temperature well below the temperature of disintegration of such oxide, such catalyst being selected from the group consisting of the sulfates of silver, copper, iron, thallium, manganese, tellurium and nickel.

15. The process of oxidizing an olefin comprising conducting streams of gases containing respectively the olefin and the oxygen supplied in equimolecular proportions, passing the olefin and the oxygen jointly through a bath of a substantially non-aqueous acid liquid wherein is dispersed a catalyzer which is stable in the acid bath and acts to promote the oxidation hot reaction, and maintaining said bath at a reaction temperature well below the temperature of disintegration of such oxide, such catalyst being selected from the group consisting of the nitrates of silver, lead and thallium.

16. The process of oxidizing an olefin comprising conducting streams of gases containing respectively the olefin and the oxygen, passing the olefin and the oxygen jointly through a bath of a substantially non-aqueous acid liquid wherein is dispersed a catalyzer which is stable in the acid bath and acts to promote the oxidation reaction, and maintaining said bath at a hot reaction temperature well below the temperature of disintegration of such oxide, and below about 160 to 170° C.; such catalyst being palladium black.

DANIEL GARDNER.