PROCESS FOR THE PRODUCTION OF 2-PARADIOXANONE

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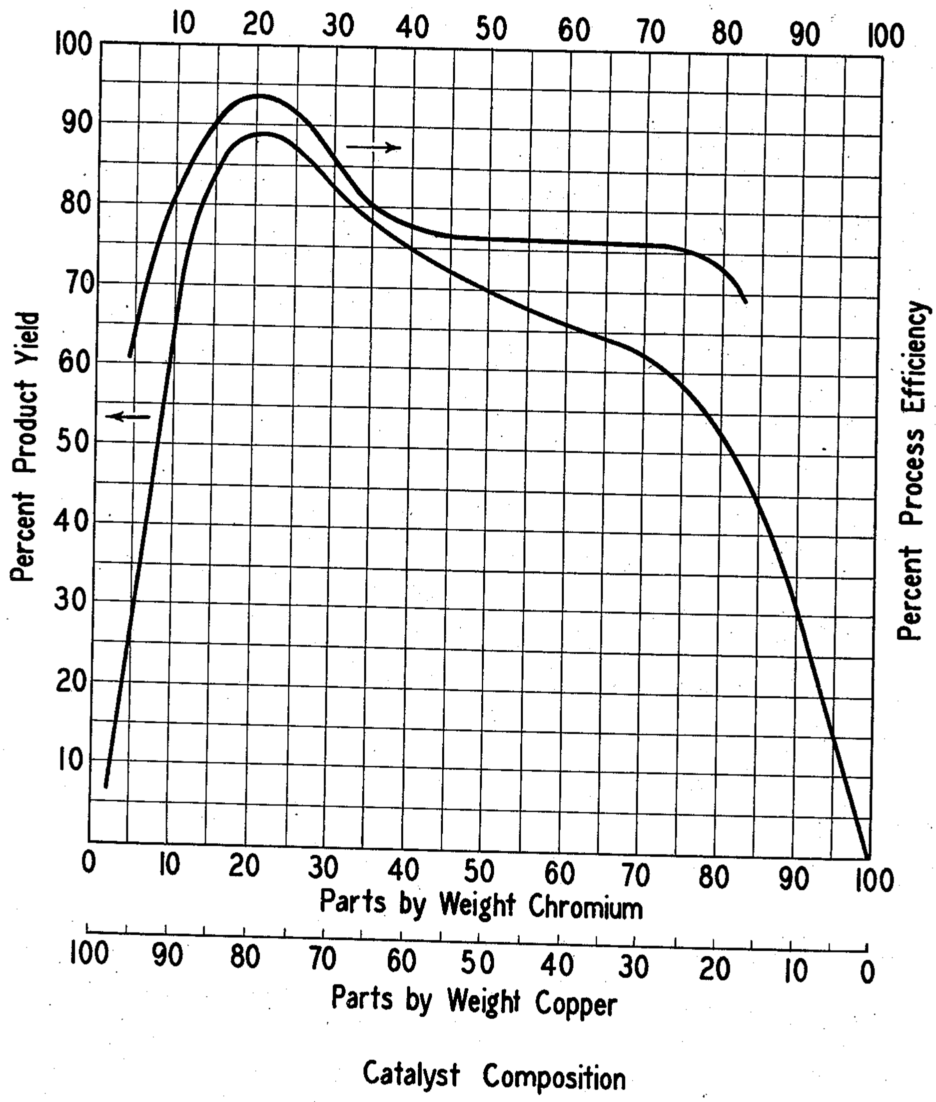

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PROCESS FOR THE PRODUCTION OF 2-PARADIOXANONE

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This invention relates to an improved process for the production of 2-paradioxanone.

One of the processes proposed for the production of 2-paradioxanone is the vapor-phase dehydrogenation of diethylene glycol. This process is disclosed in U.S. Patent No. 2,142,033, issued on December 27, 1938, to Raymond W. McNamee and Charles M. Blair. According to the aforementioned U.S. patent, vapors of diethylene glycol are brought in contact with a catalyst, composed essentially of reduced copper and about 5.0 percent by weight or less of chromium to produce the lactone, 2-paradioxanone. The commercial utility of the aforementioned process of producing 2-paradioxanone is somewhat limited due to its overall efficiency, which is only about 75.0 percent, and it is also made somewhat less attractive due to its comparatively low yield which is about 25.0 percent.

It has been found that by the utilization of the present improvement the yield of 2-paradioxanone, produced by the vapor phase dehydrogenation of diethylene glycol, may be substantially increased with a corresponding increase in efficiency. The present invention is based upon the discovery that if the active composition of the catalyst, utilized in the dehydrogenation process, is varied by increasing its chromium content the efficiency and yield of the process may be increased to values as high as about 94.0 percent and 84.0 percent, respectively.

Broadly stated, this invention comprises an improved process for the production of 2-paradioxanone by the catalytic vapor phase dehydrogenation of diethylene glycol, utilizing an improved copper-chromium catalyst.

One embodiment of the process of the present invention comprises passing vapors of diethylene glycol into a heated reaction chamber containing a dehydrogenation catalyst supported on a suitable inert carrier. This catalyst comprises chromium oxide and copper, nominally as cuprous oxide, with the chromium being present in a ratio to copper greater than about 5 parts by weight chromium to 95 parts by weight copper, and less than about 85 parts by weight chromium to 15 parts copper, on the basis of metal content above. The vapors issuing from the reaction zone are recovered and the product 2-paradioxanone may be separated in yields as high as about 84 percent.

The active ingredients of the dehydrogenation catalyst are chromium and copper. It has been found that to achieve improved yields the chromium content must be higher than about 5 parts by weight chromium to 95 parts by weight copper, but less than about 85 parts by weight chromium to 15 parts by weight copper. Good yields are achieved with chromium contents between about 10 parts by weight chromium to 90 parts copper and about 75 parts by weight chromium to 25 parts copper. The most preferred range is between about 15 parts by weight chromium to 85 parts copper and about 40 parts by weight chromium to 60 parts copper. The optimum catalyst contains about 20 parts by weight chromium to about 80 parts by weight copper.

The improved catalyst utilized in the present process may be supported on any suitable inert carrier for instance a carrier made of either aluminum oxide, silica, asbestos, kieselguhr, or pumice. It has been found that a catalyst as afore-described may be successfully utilized in the process of the present invention, but it is preferred to subject the catalyst to hydrogen, at a temperature of between about 275° C. and 300° C. before use.

It has also been found that the product, 2-paradioxanone, will be effectively produced when vapors of diethylene glycol are contacted with the present improved catalyst at a temperature above about 200° C., but it is preferred if the temperature of the reaction system is maintained between about 275° C. and 300° C. during the contact period.

The vapors issuing from the reaction zone consist of unreacted diethylene glycol together with 2-paradioxanone which is the product of the reaction. These vapors may be condensed and refined by any convenient method to recover pure 2-paradioxanone, as for instance by distillation.

The single figure drawing relates to the catalytic vapor phase dehydrogenation of diethylene glycol to produce 2-paradioxanone. The drawing comprises two curves respectively showing process efficiency and product-yield of the aforesaid process when the proportions of the metallic components of the dehydrogenation catalyst are varied. The data upon which these curves are based was obtained experimentally and is tabulated in Table I. The table sets forth the proportions of the metallic components (expressed in parts by weight) of each of the dehydrogenation catalysts utilized in the present process and the corresponding percent process efficiency and percent yield of the product when each of said individual catalyst in the form of its oxide, which is the preferred form of the catalyst, was utilized in the process of dehydrogenating diethylene glycol.

TABLE I

Active Components of the Catalyst, Expressed in Parts by Weight of Metal		Percent Product Yield	Percent Process Efficienty
Chromium	Copper		
19.3	80.7	88.6	94.0
38.9	61.1	67.6	75.8
40.9	59.1	73.4	76.2
43.9	56.1	75.0	77.0
66.0	34.0	63.7	78.5
100.0	----	Nil	Nil

As may be seen from the graph when the chromium content present in the active ingredients of the catalyst, which is utilized in the vapor-phase dehydrogenation of diethylene glycol, is increased in its ratio to the copper which is also present the product-yield of 2-paradioxanone will be increased. For example, at the ratio level of about 5 parts by weight chromium to about 95 parts by weight copper the product-yield is only about 25 percent, while at the ratio level of about 10 parts by weight chromium to about 90 parts by weight copper the product-yield is about 49 percent and at the ratio level of about 20 parts by weight chromium to about 80 parts by weight copper the product-yield will be at an optimum of about 88.6 percent. Yields above about 50 percent are obtained with increasing proportions of chromium up to a ratio of about 75 parts by weight chromium to 25 parts by weight copper. This outstanding increase in product-yield, as illustrated in the graph, is the direct result of utilizing a dehydrogenation catalyst in the process which possesses a ratio level of chromium to copper of greater than about 5 parts by weight chromium to about 95 parts by weight copper. This increase in product-yield, which at its optimum represents greater than about three times the product-yield that has heretofore been obtainable from such process, is quite surprising and unexpected because heretofore the chromium content of the catalyst was thought to be limited to the ratio level of about 5 parts by weight or less of chromium to about 95 parts by weight copper which would limit the process to a product-yield of about 25 percent or less.

It should also be noted that if the chromium content present in the active ingredients of the catalyst is increased in its ratio to copper to a ratio level of about 20 parts by weight chromium to about 80 parts by weight copper the efficiency of the process may be increased to as high as about 94 percent. It may also be seen from the graph that the product-yield of 2-paradioxanone will decrease from the optimum of about 83.6 percent, when the chromium present in the active ingredients of the catalyst is increased or decreased in its ratio to copper from the ratio level of about 20 parts by weight chromium to about 80 parts by weight copper. Although the percentage product-yield of the process decreases from the optimum when the chromium content of the active ingredients is increased beyond the ratio level of about 20 parts by weight chromium to about 80 parts by weight copper, it has been found as indicated by the graph that the chromium content may be maintained at ratio levels up to about 40 parts by weight chromium to 60 parts by weight copper, with excellent yields and efficiency. Even with as high a ratio level as about 85 parts by weight chromium to 15 parts by weight copper the product-yield obtained from the process will still be greater than about 25 percent. It can also be seen from the graph that no reaction takes place if the only active ingredients in the catalyst is chromium, therefore the presence of copper is essential to the process of dehydrogenating diethylene glycol to produce 2-paradioxanone.

Example I

A total of about 4731 grams of diethylene glycol vapor, in a continuous flow of about 160 grams per hour, was passed into a reaction chamber which contained about 275 grams of a catalyst comprising reduced copper oxide, chromium and an aluminum oxide carrier. The active composition of the catalyst contained these metals in the proportions of about 80.0 parts by weight of cuprous oxide and about 20.0 parts by weight of chromium oxide (which is the equivalent on the basis of metal content alone of about 80.7 parts by weight of copper and 19.3 parts by weight of chromium). A temperature of between about 283° C. and 287° C. was maintained throughout the reaction. The vapors passing from the reaction chamber were condensed and the resulting effluent condensate was distilled and found to contain about 3814 grams of 2-paradioxanone and about 513 grams of unreacted diethylene glycol. The product was obtained at an efficiency of about 94.6 percent, with a corresponding yield of about 83.6 percent.

Example II

A total of about 1102 grams of diethylene vapor, in a continuous flow of about 147 grams per hour, was passed into a chamber which contained about 300 grams of a catalyst comprising reduced copper oxide, chromium and a silica carrier. The active composition of the catalyst contained these metals in the proportions of about 60.0 parts by weight of cuprous oxide and about 40.0 parts by weight of chromium oxide (which is the equivalent on the basis of metal content alone of about 61.1 parts by weight of copper and about 38.9 parts by weight of chromium). A temperature between about 296° C. and 302° C. was maintained throughout the reaction. The vapors passing from the reaction chamber were condensed and the resulting effluent condensate was distilled and found to contain about 718 grams of 2-paradioxanone and about 118 grams of unreacted diethylene glycol. The product was obtained at an efficiency of about 75.8 percent, with a corresponding yield of about 67.6 percent.

Example III

A total of about 790 grams of diethylene glycol vapor, in a continuous flow of about 158 grams per hour, was passed into a chamber which contained about 300 grams of a catalyst composed of reduced copper oxide, chromium and a silica carrier. The active composition of the catalyst contained these metals in the proportions of about 58.0 parts by weight of cuprous oxide and about 42.0 parts by weight of chromium oxide (which is the equivalent on the basis of metal content alone of about 59.1 parts by weight of copper and about 40.9 parts by weight of chromium). A temperature of about 297° C. was maintained throughout the reaction. The vapors passing from the reaction chamber were condensed and the resulting condensate was distilled and found to contain about 558 grams of 2-paradioxanone and about 30.0 grams of unreacted diethylene glycol. The product was obtained at an efficiency of about 67.2 percent, with a corresponding yield of about 73.4 percent.

Example IV

A total of about 1110 grams of diethylene glycol vapor, in a continuous flow of about 148 grams per hour, was passed into a chamber which contained about 300 grams of a catalyst comprising reduced copper oxide, chromium and a silica carrier. The active composition of the catalyst contained these metals in the proportions of about 55.0 parts by weight of cuprous oxide and about 45.0 parts by weight of chromium oxide (which is the equivalent on the basis of metal content alone of about 56.1 parts by weight copper and about 43.9 parts by weight of chromium). A temperature between about 302° C. and 310° C. was maintained throughout the reaction. The vapors passing from the reaction chamber were condensed and the resulting condensate was distilled and found to contain about 802 grams of 2-paradioxanone and about 31.0 grams of unreacted diethylene glycol. The product was obtained at an efficiency of about 77.0 percent with a corresponding yield of about 75.0 percent.

Example V

A total of about 1095 grams of diethylene glycol vapor, in a continuous flow of about 146 grams per hour, was passed into a chamber which contained about 300 grams of a catalyst comprising reduced copper oxide, chromium and a silica carrier. The active composition of the catalyst contained these metals in the proportions of about 33.0 parts by weight of cuprous oxide and about 67.0 parts by weight of chromium oxide (which is the equivalent on the basis of metal content alone of about 34.0 parts by weight copper and about 66.0 parts by weight of chromium). A temperature between about 301° C. and 310° C. was maintained throughout the reaction. The vapors passing from the reaction chamber were condensed and the resulting condensate was distilled and found to contain about 672 grams of 2-paradioxanone and 200 grams of unreacted diethylene glycol. The product was obtained at an efficiency of about 78.0 percent, with a corresponding yield of about 63.7 percent.

By way of comparison, a continuous flow of diethylene vapor, at the rate of about 160 grams per hour, was passed into a chamber which contained 300 grams of a catalyst comprising chromium and a silica carrier. The active composition of the catalyst consisted of chromium oxide. The vapors passing from the reaction chamber were condensed and the resulting condensate was distilled but found not to contain any 2-paradioxanone.

It is emphasized that the results obtained by increasing the chromium content in the active ingredients of the catalyst were unpredictable and unexpected. Before the present discovery it was felt that the chromium content could vary considerably but should not exceed the ratio level of about 5 parts by weight chromium to about 95 parts by weight copper. It has now been found that the chromium content of the active ingredients of the catalyst may not only be varied over a wider range but also the product-yields of the process may be increased tremendously thereby making the process commercially more attractive from an economic point of view.

What is claimed is:

1. An improvement in the production of 2-paradioxanone by the catalytic dehydrogenation of vapors of diethylene glycol at temperatures of at least 200° C., said improvement comprising conducting the process in the presence of a copper-chromium catalyst wherein the proportion of chromium to copper is between about 12 parts by weight chromium to 90 parts by weight copper and about 75 parts by weight chromium to 25 parts by weight copper.

2. An improvement in the production of 2-paradioxanone by the catalytic dehydrogenation of vapors of diethylene glycol at temperatures of at least 200° C., said improvement comprising conducting the process in the presence of a copper-chromium catalyst wherein the proportion of chromium to copper is between about 12 parts by weight chromium to 75 parts by weight copper and about 40 parts by weight chromium to 60 parts by weight copper.

3. An improvement in the production of 2-paradioxanone by the catalytic dehydrogenation of vapors of diethylene glycol at temperatures of at least 200° C., said improvement comprising conducting the process in the presence of a copper-chromium catalyst wherein the proportion of chromium to copper is about 20 parts by weight chromium to about 80 parts by weight copper.

4. An improved process for the production of 2-paradioxanone by the catalytic dehydrogenation of vapors of diethylene glycol which comprises contacting said vapors at a temperature of at least 200° C. with a copper-chromium catalyst wherein the proportion of chromium to copper is between about 12 parts by weight chromium to 90 parts by weight copper and about 75 parts by weight chromium to 25 parts by weight copper.

5. An improved process for the production of 2-paradioxanone by the catalytic dehydrogenation of vapors of diethylene glycol which comprises contacting said vapors at a temperature of at least 200° C. with a copper-chromium catalyst wherein the proportion of chromium to copper is between about 12 parts by weight chromium to 85 parts by weight copper and about 40 parts by weight chromium to 60 parts by weight copper.

6. An improved process for the production of 2-paradioxanone by the catalytic dehydrogenation of vapors of diethylene glycol which comprises contacting said vapors at a temperature of from 275° C. to 300° C. with a copper-chromium catalyst wherein the proportion of chromium to copper is about 20 parts by weight chromium to about 80 parts by weight copper.

References Cited in the file of this patent

UNITED STATES PATENTS

2,142,033 McNamee et al. -------- Dec. 27, 1938