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PRODUCTION OF ACETOPHENONE

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The present invention relates to the production of acetophenone by the catalytic, liquid phase oxidation of ethylbenzene and deals more particularly with a method for preventing the accumulation of by-product methylphenylcarbinol.

In the catalytic, liquid phase oxidation of ethylbenzene, for example, as described in the Binapff Patent No. 1,813,606, or in the copending application of William S. Emerson, Serial No. 496,078, filed July 24, 1943, which issued as Patent No. 2,376,674 on May 22, 1945, there is usually formed a certain amount of methylphenylcarbinol. When the desired product is acetophenone, the problem of disposing of the constantly increasing quantities of the carbinol thus arises. In order to achieve an economy of the starting material it is desired to convert the carbinol to acetophenone by further oxidation. However, in spite of the fact that the catalytic, liquid phase oxidation of such materials as cymene is accelerated by the presence in the starting material of a small quantity of the crude oxidation reaction mass from a previous run, in the present reaction the presence of methylphenylcarbinol in such material is seriously detrimental. We have discovered that the presence of methylphenylcarbinol in ethylbenzene, even in small amounts at the start of the oxidation, seriously retards the oxidation reaction; in amounts of 5% by weight or more, based on the ethylbenzene, it almost completely inhibited the oxidation. Hence, in the production of acetophenone, it was hitherto impossible to recycle by addition to the starting reaction mixture any unreacted ethylbenzene which contained any appreciable amounts of methylphenylcarbinol.

The adverse effect of methylphenylcarbinol, when present in an ethylbenzene which is to be oxidized may be illustrated by results obtained in a series of experiments on the oxidation of ethylbenzene containing varying proportions of methylphenylcarbinol. The conversion is expressed in mole per cent of ethylbenzene converted to acetophenone and methylphenylcarbinol.

Table 1

Experiment No.	Per cent Carbinol Present	Conversion, Mole Per cent
1	0.0	32.0
2	2.0	22.0
3	2.5	20.2
4	5.0	0.3
5	5.0	1.6

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All of the above experiments were made under the same conditions. These were as follows:

Charge	1800 g. ethylbenzene
Time	6.5 hours
5 Temperature	140° C.
Pressure	100 p. s. i. gauge
Air flow	15 cu. ft./hour
Catalyst concentration	1% by weight of charge
10 Stirring speed	750 R. P. M.

In experiments 1 to 4, inclusive, in Table 1, the carbinol was added to the ethylbenzene in the cold at the beginning of the experiment. The air was then bubbled through the ethylbenzene, 15 heat applied to the container in amount so as to raise the temperature of the contents to 140° C., and the test continued at this temperature for 6.5 hours.

In experiment 5, the procedure was the same as that used for experiments 1 to 4, except that the carbinol was added after the contents of the container had reached 140° C.

The catalyst employed in all of the above experiments was chromium oxide; however, similar results with respect to decreasing conversion in the presence of increasing amounts of carbinol in the initial reactant have been obtained when using other known catalysts for the liquid phase oxidation of ethylbenzene or by employing other 30 conditions than those shown above.

We have now found that the adverse effect exhibited by the presence of methylphenylcarbinol at the start of the reaction, is not experienced if the normal oxidation of the ethylbenzene in the absence of the carbinol is carried to the point where the refractive index thereof shows an increase over that of pure ethylbenzene. When this point is reached, the addition of methylphenylcarbinol may be made, and the oxidation 40 continued to completion. We have found that the conversion of the carbinol to acetophenone proceeds at a high rate and that actually less carbinol is produced with this method of operation than is normally formed when no carbinol 45 is added.

Into a closed vessel containing ethylbenzene and from, say, 1% to 5% by weight of any metal oxide oxidation catalyst, air in finely divided form is introduced. Observations of the refractive index of the reaction mass are made from 50 time to time. After a period of time, which may vary depending upon the temperature, rate of air influx and catalyst activity, a sudden, sharp increase in the refractive index of the reaction mixture will be observed. At this point, or at

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any time thereafter during the oxidation, there may be added methylphenylcarbinol in amounts of, say, up to 25% by weight of the ethylbenzene originally present without in any way affecting the progress of the oxidation. Thenceforth, the reaction proceeds normally, the oxidation of the ethylbenzene and the added carbinol being converted to acetophenone in excellent yields. While there is formed some carbinol during such oxidation, there is no accumulation thereof, because when operating according to our invention the capacity for converting carbinol to acetophenone greatly exceeds the rate of carbinol production. When working with a chromium sesquioxide catalyst, for example, we recover from the oxidation product a mixture consisting of about 85% by weight of acetophenone and 15% by weight of methylphenylcarbinol, this mixture representing approximately 33% conversion of the initial ethylbenzene. We separate the acetophenone from the methylphenylcarbinol and then add all of the latter to a subsequent reaction mixture after the refractive index of such mixture has increased, as described above. There is obtained in this subsequent run a product consisting of 85% by weight of acetophenone and 15% by weight of methylphenylcarbinol, the total amount of these two compounds being at least as great as that obtained in the first run, and in many cases being substantially greater.

The length of the induction period, during which no apparent oxidation occurs, varies from, say, 15 minutes to an hour, or even two hours, depending upon the quantities of reactants employed, the speed of stirring, catalyst temperature, pressure, etc. When oxidation begins there is noted a sharp increase in the refractive index of the reaction mixture, which increase is due to the presence of oxidation products. This is also generally accompanied by a rise in temperature. For many purposes, especially when running a series of reactions under the same conditions, it is sufficient only to note this temperature rise and then to add the carbinol or the carbinol-containing material to the reaction mixture. However, it is somewhat more satisfactory to determine the point at which addition of the carbinol may be safely made by noting the change of refractive index of the reaction mixture. This may be readily effected by removing samples of the reaction mixture at regular intervals, say, at intervals of from 5 to 10 minutes, and noting the refractive index of each sample. Addition of the carbinol to the reaction mixture may be safely made immediately after an increase in refractive index of as little as 0.0002 or 0.0003 has been noted.

The present invention is further illustrated, but not limited, by the following examples:

EXAMPLE 1

This example illustrates the change in temperature and refractive index which accompanies the oxidation of ethylbenzene in the liquid phase and in the presence of chromium sesquioxide catalyst.

Oxidation was carried out in an autoclave under an air pressure of 100 p. s. i. gauge and at an initial temperature of 133° C., 2500 g. of ethylbenzene and 25 g. of chromium sesquioxide was charged into the autoclave, and air was passed through continuously with stirring at the rate of 15 cubic feet per hour. Over a period of about 2 hours the temperature and the refractive index of the reaction mixture were observed at ten

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minute intervals. Table 2 shows the results obtained:

Table 2

Time, Minutes	Temperature, °C.	n_D^{20}
10.....	133	1.4932
20.....	133	1.4932
30.....	134	1.4932
40.....	139	1.4931
50.....	143	1.4934
60.....	146	1.4943
70.....	146	1.4952
80.....	150	1.4961
90.....	150	1.4971
100.....	146	1.4961
110.....	142	1.4969

From the above table it is readily apparent that after a time of from 50 to 60 minutes there is a sudden and sharp increase in the refractive index of the reaction mixture. Since the change in refractive index indicates a change in the composition of the reaction mixture it may be used to denote a point at which oxidation is actually taking place. Rise in temperature also indicates reaction, but since no apparent change in the refractive index of the mixture appears until several minutes after the initial rise in temperature, when employing the change in a temperature as a criterion by which is judged the advantageous time for addition of carbinol, it is desirable to wait for a time before adding carbinol to the reaction mixture.

EXAMPLE 2

This example shows the extent to which methylphenylcarbinol may be consumed when the latter is added to ethylbenzene after oxidation has started. The following conditions were employed in all of the experiments reported below:

A mixture consisting of 1800 g. of ethylbenzene and 18 g. of chromium oxide catalyst was charged to an autoclave and the oxidation was conducted at an initial temperature of 140° C., a pressure of 100 p. s. i., an air flow of 15 cubic feet per hour and a stirring speed of 750 R. P. M. In each case the methylphenylcarbinol or the mixture containing the same was added to the reaction mass after the refractive index had increased by at least 0.0002. The data obtained in the several experiments are summarized in the following Table 3:

Table 3

Run No.	Time, Hrs.	Added Material	Conversion, ¹ percent	g. Carbinol at Start	g. Carbinol at End
1.....	6.5	290 g. of mixture	32.8	36	19
2.....	6.5	36 g. each of acetophenone and methylphenylcarbinol.	33.0	36	28.5
3.....	6.5	90 g. each of acetophenone and methylphenylcarbinol.	33.2	90	20
4.....	5.5	36 g. each of acetophenone and methylphenylcarbinol.	31.0	36	18
5.....	6.5	90 g. methylphenylcarbinol.	44.3	90	trace

¹ Mixture of ethylbenzene, acetophenone and methylphenylcarbinol containing 68.5 mole per cent acetophenone.

² Mole percent based on ethylbenzene charged.

From the above table, it is obvious that addition of more methylphenylcarbinol to the reaction mixture than is normally formed by the reaction always resulted in the production of a smaller amount of carbinol than that which was introduced and without substantial effect on

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conversion of the ethylbenzene to acetophenone.

While the above runs were made in the presence of a chromium sesquioxide catalyst, other catalysts which are known to induce oxidation of ethylbenzene to a mixture of acetophenone and carbinol may be employed, for example, the oxides or hydroxides of copper, calcium, manganese, iron, lead, cobalt, vanadium or mercury. Organic or inorganic salts containing these metals may be employed, for example, cobalt oxalate, lead benzoate, etc. Mixtures of such catalytic materials may be employed.

Instead of employing air as the oxidation agent, oxygen, either alone or in admixture with inert gases, may be used. The oxidation may be effected at ordinary or added pressures. An inert liquid diluent may be used in the reaction mixture.

Instead of employing an autoclave or other pressure device for the reaction, other means of contacting air or oxygen with the material to be oxidized may be employed. For example, air and the liquid material may be passed in counter-current through reaction towers.

Reaction temperatures may be widely varied, these being regulated by the nature of the catalyst used as well as by other reaction conditions as may be apparent to those skilled in the art.

What we claim is:

1. The process for producing acetophenone which comprises passing an oxygen containing gas through liquid ethylbenzene containing an oxidation catalyst, whereby oxidation products of ethylbenzene are formed, thereupon adding to said ethylbenzene, methylphenyl carbinol and then further oxidizing said ethylbenzene to form acetophenone.

2. The process for producing acetophenone which comprises passing an oxygen containing gas through liquid ethylbenzene containing an oxidation catalyst, whereby oxidation products are formed therein and the refractive index thereof has been increased by at least 0.0002,

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thereupon adding methylphenylcarbinol to said ethylbenzene and further oxidizing said ethylbenzene to acetophenone.

3. The process for producing acetophenone which comprises passing an oxygen containing gas through liquid ethylbenzene containing an oxidation catalyst, whereby oxidation products are formed therein and the refractive index thereof has been increased by at least 0.0003, thereupon adding methylphenylcarbinol to said ethylbenzene and further oxidizing said ethylbenzene to acetophenone.

4. The process for producing acetophenone which comprises passing an oxygen containing gas through liquid ethylbenzene containing an oxidation catalyst, whereby oxidation products are formed therein and the refractive index thereof has been increased by at least 0.0002, thereupon adding methylphenylcarbinol to said ethylbenzene and further oxidizing said ethylbenzene and methylphenylcarbinol to acetophenone.

5. The process for producing acetophenone which comprises passing an oxygen containing gas through liquid ethylbenzene containing an oxidation catalyst, whereby oxidation products are formed therein and the refractive index thereof has been increased by at least 0.0003, thereupon adding methylphenylcarbinol to said ethylbenzene and further oxidizing said ethylbenzene and methylphenylcarbinol to acetophenone.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

40 Number	Name	Date
1,813,606	Binapfl	July 7, 1931
2,223,383	Moyer	Dec. 3, 1940
2,376,674	Emerson	May 22, 1945