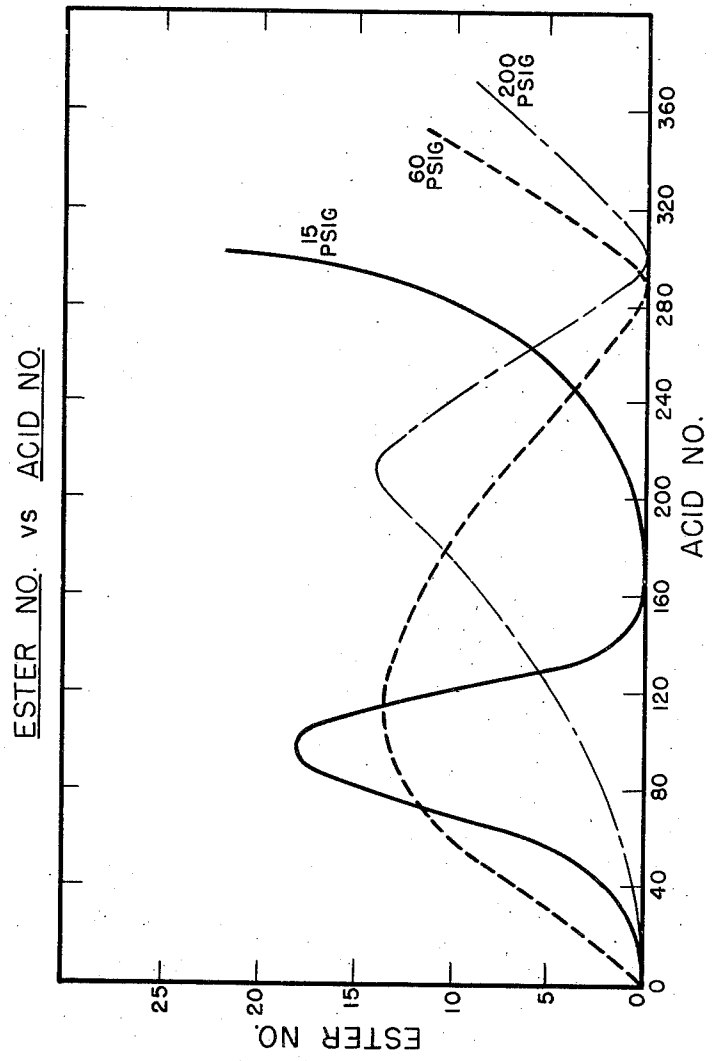
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HYDROCARBON OXIDATION

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HYDROCARBON OXIDATION

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This invention relates to an improved process for the oxidation of aromatic hydrocarbons. In a specific aspect, this invention relates to an improved process for the oxidation of alkylated benzenes. In a more specific aspect, this invention relates to an improved process for the oxidation of p-xylene to p-toluic acid.

In the air oxidation of aromatic hydrocarbons, such as the alkylated benzenes, a variety of undesirable ester intermediates are formed. For example, in the air oxidation of p-xylene to p-toluic acid, esters such as p-methylbenzyl p-toluate and p-carboxybenzyl p-toluate are formed. Such esters are undesirable primarily because they lead to the formation of slimy oxidates with small crystal sizes that are exceedingly difficult to filter. Furthermore, these esters represent a yield loss if they are not converted to p-toluic acid. When the oxidation is carried out at atmospheric pressure, the esters can accumulate to concentrations as high as 40% and 50%. When the oxidation is carried out at superatmospheric pressures, less esters are formed, but sufficient esters are formed at superatmospheric pressures to present problems such as the necessity for disposing of the esters and loss of xylene in the formation of the esters.

In my copending application Serial No. 428,368, filed May 7, 1954, a process is disclosed for reducing the esters formed during the oxidation reaction by maintaining sufficient water in the oxidation medium when the oxidation reaction is effected to reduce substantially the ester number of the reaction mixture, presumably by hydrolysis of the esters formed during the oxidation.

It has been found that the esters formed during the oxidation reaction can be maintained at a minimum by practicing a procedure that involves controlling the conversion level of the aromatic hydrocarbon while carrying out the oxidation reaction at a pressure below that at which sufficient water is retained in the reaction medium to completely hydrolyze the esters formed during the oxidation. The reaction is carried out in a liquid medium and at a temperature sufficiently elevated to effect the desired oxidation. As the oxidation progresses, the acid number and ester number of the oxidate increase until a maximum ester number is obtained. When the oxidation is carried beyond this point, the acid number of the oxidate continues to increase, but the ester number of the oxidate is reduced until it reaches zero or very nearly zero. Further oxidation results in an increase of the ester number and a further increase in the acid number. Thus, in practicing this invention, it is possible to carry out the oxidation in such a manner that undesirable ester formation and the attendant problems are either minimized or completely eliminated. In accordance with this invention, the oxidation is effected to a point where the acid number of the oxidation medium is at least 100 and until the ester number of the oxidation medium has reached a level above 10 and then is decreased to a level below 10.

The advantages and utility of this invention are apparent by referring to the accompanying drawing and the following runs which exemplify this invention. A series of runs was made at three different pressures, namely, 15, 60, and 200 p. s. i. g. In each run, 2000 parts by weight of p-xylene were charged to a stainless steel autoclave along with 4.0 parts of cobaltous toluate as a catalyst. The temperature in the reactor was 140° C., and an air rate of about 25 s. c. f. per hour per kilogram of p-xylene was used in all the oxidations. At various time intervals the acid number and ester number of the oxidate were determined, and these data are plotted in the accompanying drawing at the various pressures employed. It is apparent from this drawing that at each pressure employed the acid number and ester number of the oxidate increased to a point of maximum ester number. As the oxidation continued beyond this point, the acid number of the oxidate continued to increase, while the ester number of the oxidate decreased to zero. After reaching this optimum condition, the ester number then began to increase again along with increasing acid number. The curves in the accompanying drawing demonstrate that at a given pressure the oxidation can be carried to a point at which the oxidation has produced an oxidate having an ester number which has increased to a level well above 10 and then decreased to a level below 10. In fact, the oxidation can be effected to maintain the ester number of the oxidate below 5 and at optimum conditions an ester number of zero can be obtained and maintained. When oxidizing p-xylene to p-toluic acid in accordance with this invention, the problems encountered by the formation of organic esters can be reduced to the point where the esters create very little, if any, difficulty in the operation.

In practicing this invention, the oxidation of the alkylated benzene is carried out at a temperature and pressure such that the oxidation reaction medium is in the liquid phase. The temperature can vary from about 80° C. to about 250° C. with a preferable temperature range being about 125° C. to 175° C. The pressure is suitably adjusted to maintain the oxidation medium in the liquid phase. At low pressures the formation of undesired esters presents a greater problem in such an oxidation than at the higher pressures, and this invention is particularly useful at low pressures in minimizing the problems caused by ester formation. However, the invention can be practiced at the higher pressures, and when that is done the problems encountered by undesirable ester formation are also reduced. It is preferred to carry out the oxidation at a superatmospheric pressure of about 15 to 400 p. s. i. g. and preferably from 125 to 175 p. s. i. g., since superatmospheric pressures tend to reduce the amount of undesirable esters that are formed during the oxidation.

In carrying out the oxidation, a cobalt salt of an organic acid is preferably employed. Such cobalt salts as cobalt toluate, cobalt naphthenate, cobalt acetate, and cobalt salts of saturated aliphatic acids containing from about 6 to 12 carbon atoms can be used. The amount of catalyst that is employed to effect the oxidation is variable, and generally from 10 to 400 parts per million of cobalt are present in the oxidation reaction medium. However, it will be realized that catalyst concentrations outside this range can be used when desired, and that other metal catalysts than cobalt can be used. Suitable catalysts for the oxidation reaction are those that are known for use in oxidation with gaseous oxygen. Salts of metals having more than one valence and selected from the group consisting of cobalt, manganese, iron and mercury can be used.

The hydrocarbons that are oxidized in accordance with this invention are the alkylated benzenes, such as toluene,

the xylenes, ethylbenzene, propylbenzene, and the like. The preferred hydrocarbons are of the dialkyl type and each alkyl group usually contains no more than about 4 carbon atoms. Any of the xylenes can be oxidized in accordance with this invention, and it is preferred to oxidize p-xylene to p-toluic acid. This acid is quite useful in the production of dimethyl terephthalate since it can be esterified to the monoester which, after another oxidation, can be esterified to the diester.

To effect the oxidation, an oxygen-containing gas is passed through the liquid reaction medium. Air is the preferred oxygen-containing gas. However, if desired, substantially pure oxygen as well as oxygen-enriched or oxygen-depleted air can be employed. However, in most instances, air will be used as the oxidizing agent. It is usually desirable to employ the oxygen-containing gas at a rate such that the off-gas from the reactor contains from about 0 to 10% oxygen by volume.

Although the oxidizing medium is maintained in the liquid form, there is insufficient water present to completely hydrolyze the esters formed during the oxidation and to prevent the possible accumulation of those esters in the oxidizer. At low pressures the reaction medium is substantially anhydrous. Higher pressures tend to cause an increase in the amount of water that is retained in the oxidizer. However, at the conditions employed, there is an accumulation of esters in the reaction medium in spite of the presence of the water. To practice this invention, substantial amounts of water are removed from the reaction medium, since water, when present, tends to hydrolyze the undesirable esters, and water itself, when present in a sufficient amount, can prevent the build-up or accumulation of these esters. A suitable method of effecting water removal is to permit water of reaction to become separated from the reaction mixture in the off-gas. This off-gas can be condensed and any organic phase thus obtained can be recycled to the reaction medium if desired. However, the water that is obtained during this condensation is not returned to the oxidation reactor. It will be understood that completely anhydrous conditions are ordinarily not obtained by this procedure, particularly at superatmospheric pressures, since all of the water will not distill off with the off-gas from the oxidation medium. However, most of the water of reaction will be removed in this manner, and any water that may remain in the reaction medium is not sufficient to hydrolyze the esters formed during the oxidation and to prevent the possible build-up of those esters, although any water that is present can hydrolyze some of the esters formed during the oxidation.

This invention can be employed to carry out the oxidation procedure in either a batch process or a continuous operation. In a batch process the oxidation is carried out until the oxidate has the desired low ester number, and in a continuous operation the rate of addition of reactants to the reactor and the rate of withdrawal of reaction products from the reactor are such that at the reaction conditions employed the ester number of the oxidate is maintained at the desired level.

The conversion level at which the oxidation reaction is effected to maintain the ester number of the oxidate at the desired low level can be determined either from the ester number of the oxidate or the acid number of the oxidate. For example, at any selected pressure for operation, the oxidation reaction can be carried out in such a manner that the ester number of the oxidate has increased to a level above 10 and then decreased to a level below 10. Preferably, after the ester number of the oxidate has

reached its maximum level above 10, it is maintained at a level not above 5. On the other hand, at any given operating pressure, the acid number of the oxidate can be suitably selected and maintained so that the ester number of the oxidate is at the desired low level. For example, when the oxidation pressure is 15 p. s. i. g., the acid number of the oxidate should be within the range of about 120 to about 260, preferably from about 130 to about 245, and more preferably about 165. When the oxidation pressure is 60 p. s. i. g., the acid number of the oxidate should be within the range of about 180 to about 350, preferably from about 240 to about 320, and more preferably about 285. Similarly, at a pressure of 200 p. s. i. g., the acid number of the oxidate should be within the range of about 250 to about 380, preferably from about 270 to about 350, and more preferably about 300.

The following procedure was used to determine acid number. A 4 to 5 g. oxidate sample was dissolved in 50 ml. methanol or ethanol, and the solution was titrated to neutrality using 0.1 N NaOH and phenolphthalein indicator. The acid number of the sample was calculated from the formula:

$$\text{Acid No.} = \frac{\text{Ml. alkali} \times N \times 56.1}{\text{Grams sample}}$$

The saponification number was determined by refluxing a separate sample of the oxidate with a known amount of 0.8–0.9 N aqueous KOH in a 1:1 aqueous alcohol solution and determining the amount of alkali consumed by titrating the amount remaining with 0.5 N HCl. The saponification number was calculated from the formula:

$$\text{Sapon. No.} = \frac{(B-S) \times N \times 56.1}{\text{Grams sample}}$$

where S is the ml. HCl required to titrate the sample and B is the ml. HCl required to titrate a blank to which no sample was added. The ester number is the saponification number minus the acid number.

Modifications and advantages of this invention will be readily apparent to those skilled in the art from the above disclosure.

What I claim and desire to protect by Letters Patent is:

1. In the oxidation of a methylated benzene having not more than two methyl groups to an aromatic carboxylic acid wherein said methylated benzene is oxidized in the liquid phase in the presence of an oxidation catalyst comprising a salt of a metal selected from the group consisting of cobalt, manganese, iron, and mercury with an oxygen-containing gas at a temperature from 80–250° C. and at a pressure of from 15–400 p. s. i. but below that at which sufficient water is retained in the oxidate to completely hydrolyze esters formed during the oxidation, the improvement which comprises periodically determining the ester number of the oxidate and terminating the oxidation when the ester number has reached a maximum level and then decreased to a level substantially below said maximum.

2. The process of claim 1 in which the reaction is terminated when the ester number has risen above 10 and then has decreased to not above 5.

3. The process of claim 1 in which the reaction is terminated by the withdrawal of product from and the introduction of methylated benzene to the oxidate.

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