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PREPARATION OF TEREPHTHALIC ACID

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This invention relates to a method of preparing aromatic dicarboxylic acids and particularly to a method of oxidizing an alkylated benzoic acid to produce a terephthalic acid.

The aromatic dibasic acids other than phthalic acid have, in the past, been limited in their industrial application by virtue of the fact that their known methods of preparation were only suited to small-scale laboratory equipment. The preparation of these acids, and particularly terephthalic acid, has previously been accomplished by chemical reagent methods which require costly reagent materials and invariably result in low yields of desired product along with difficultly extractable intermediate and by-products.

It has now been discovered that a terephthalic acid may be prepared in economic yields and high purity by a method of preparation which involves a minimum of reaction variables and is well suited to commercial production. According to the process of the invention, a terephthalic acid is produced by the oxidation of a benzene monocarboxylic acid possessing an alkyl group para to the carboxyl group in the liquid phase with an oxygen-containing gas at temperatures of at least about 370° F. The dibasic acids, or terephthalic acids, thus produced possess two carboxyl groups para to one another and may contain further substituents in the remaining positions of the benzene nucleus corresponding to the original substituents in the monocarboxylic acid charge stock.

The charge stock to the oxidation process may be any benzene monocarboxylic acid possessing an alkyl group para to the carboxyl group. The alkyl group is not restricted in chain length, but from the practical standpoint, the lower alkyl groups such as methyl, ethyl, and isopropyl are to be desired. These para alkyl benzoic acids may also contain additional substituents in one or more of the remaining positions of the nucleus, provided such substituents remain substantially inert to the oxidation reaction. This description of the charge stock is predicated upon the charging of a single compound, but it is to be understood that mixtures of compounds falling within the general class of charge compounds or technical mixtures in which the para alkyl benzoic acids predominate may be used in the reaction. In addition, partial oxidation products of the para alkyl benzoic acids such as p-acetyl benzoic acid, etc., are suitable charge compounds for the process.

In the preferred form of the invention, p-toluic acid and mixtures of isomeric toluic acids in which p-toluic acid predominates are used as the oxidation charge. Accordingly, p-toluic acid will be used as illustrative of a representative charge stock in the subsequent description of the subject process. Any modifications of the specific reaction conditions required when using charge stocks

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other than p-toluic acid will be obvious to those skilled in the art in view of the present teachings.

As hereinbefore mentioned, this charge stock is contacted with an oxygen-containing gas while maintained in the liquid phase and at temperatures of at least about 370° F. Any of the conventional oxidizing gases may be used as the source of oxygen, but when operating at atmospheric pressure and charging p-toluic acid, it is preferable to use oxygen itself in order to avoid excessive sublimation and carry-over of the p-toluic acid. If the reaction is carried out under pressure, the sublimation problem is minimized and air can satisfactorily be used as the oxidizing gas. Proper design of the oxidation reactor and recovery system will also minimize the losses of p-toluic acid by sublimation and carry-over.

It has been found that the oxidation of the para alkyl benzoic acids to the desired dibasic acids proceeds at temperatures above 370° F. The optimum oxidation temperatures vary with the composition of the charge stock and generally lie within the range of from 370° F. to about 550° F. Selection of the desired operating temperatures is dependent upon a balance of economic factors. Higher purity acids are produced at the lower operating temperatures, whereas the oxidation rate is increased at the higher temperatures. Additional factors which bear on the selection of the operating temperatures will become apparent from the further discussion of the operation of the process. In the oxidation of p-toluic acid to terephthalic acid, the optimum temperature range is between 400° and 500° F., with the preferable range at atmospheric pressure between 440° and 460° F.

One of the important factors affecting the efficiency of the oxidation reaction is the solubility of the oxygen of the oxidizing gas in the liquid charge under the reaction conditions. For optimum conversion, a high solubility of oxygen is required. The greater the solubility, the faster the rate of reaction and the higher the yields of dibasic acids. For a given charge compound and constant pressure, the degree of solubility is a function of the reaction temperature. As the temperature is increased, the oxygen solubility is decreased. However, on application of pressure such as 2 to 10 atmospheres, the oxygen solubility is increased. Accordingly, for effective oxidation in the upper range of the operating temperatures, it may be desirable to conduct the reaction under pressure. An additional advantage of a pressure reaction is the fact that less volatilization of charge compound is obtained and, consequently, oxidizing gases containing inert constituents such as air may be used satisfactorily.

The subject process is applicable to either batch or continuous operation, and the design of the equipment may be analogous to the con-

ventional liquid phase oxidation processes. The oxidizing gas should be introduced into the liquid charge in a finely-dispersed condition, such as attained through a turbo-mixer, fritted glass injector, etc., so as to approach complete physical saturation. The rate at which the oxidizing gas is introduced into the reactor should be controlled to correspond with the rate of solution or utilization of the oxygen in order to provide a short contact time and minimize overoxidation and thermal decomposition.

The degree of conversion in the oxidation reaction is dependent upon the type of equipment used and the nature of the resulting products obtained. In the batch oxidation of p-toluic acid to terephthalic acid, the reaction is preferably controlled to not more than about a 50% conversion, since terephthalic acid is a substantially insoluble in the reaction medium, and at high concentrations forms a thick slurry which is difficult to handle. Furthermore, operating to high conversions results in decreased yields due to decarboxylation and overoxidation of the terephthalic acid. In the preferable batch operations, the reaction is conducted to a conversion of from 30 to 40%.

The separation and extraction of the desired dibasic acids may be carried out in any of the conventional and obvious manners. Due to the insolubility of terephthalic acid in p-toluic acid, the separation may easily be accomplished by filtration. Representative data show that all but about 1-2% of the terephthalic acid may be removed from the oxidation mixture by a simple filtration. The filter cake may contain about 5-10% p-toluic acid adsorbed by the terephthalic crystals, which may be removed by solvent extraction with solvents such as ethyl alcohol, xylenes, etc. During the course of the oxidation, color bodies are generally formed and are carried through by the terephthalic crystals. These in turn may be removed by sublimation.

The following examples are presented as an illustration of the practice of the process of the invention.

Example I

453 grams of 90% pure p-toluic acid were heated to 475° F. in a glass vessel with violent agitation. Oxygen was admitted at the base of the vessel at such a rate as to maintain complete saturation in the p-toluic acid. A total of 33 cc. of water distilled from the reaction vessel was condensed along with some p-toluic acid which was carried over. After a period of 8½ hours, which was calculated to correspond to approximately a 30% conversion, the reaction products were cooled, ground to a powder, and extracted with 95% ethanol. The insoluble material was filtered off and dried to give 193 grams of a light tan powder. This was washed with an additional 600 cc. of ethanol, and, upon drying, 123 grams of insoluble material remained with a molecular weight of 174 by neutral equivalent (molecular weight of terephthalic acid is 166). The yield of 95.5% pure terephthalic acid was found to be 97.7% by weight.

Example II

453 grams of 98+ % pure p-toluic acid was heated to 440° F. in a glass vessel with violent agitation. Oxygen was admitted through the bottom of the vessel at a rate equivalent to its chemical utilization in the reactant liquid. At the initial temperature of 440° F., the rate of utilization of the oxygen was very slow, but as the tempera-

ture was increased, the rate of chemical saturation was increased to a maximum at 460° F. After 20 minutes, a granular precipitate of terephthalic acid began to appear, and would settle to the bottom of the reactor when agitation was discontinued. After 5½ hours of reaction at 460° F., a heavy slurry of terephthalic acid in the p-toluic acid had formed. The reaction was discontinued in order to facilitate handling, and the hot mixture poured through a heated fritted disk filter at 400° F. The filter cake of 80% terephthalic acid was then washed with p-xylene to dissolve out unconverted p-toluic acid. After drying, the washed cake analyzed 94% pure terephthalic acid.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process for the product of a benzene para dicarboxylic acid which comprises non-catalytically oxidizing a benzene monocarboxylic acid possessing an alkyl group para to the carboxyl group by intimate contact with an oxygen-containing gas in the liquid phase at the temperature within the range of about 370 to 550° F.

2. A process for the production of a benzene para dicarboxylic acid which comprises non-catalytically oxidizing a benzene monocarboxylic acid possessing a methyl group para to the carboxyl group by intimate contact with an oxygen-containing gas in the liquid phase at a temperature within the range of about 370 to 550° F.

3. A process for the production of terephthalic acid which comprises noncatalytically oxidizing para-toluic acid by intimate contact with an oxygen-containing gas in the liquid phase at a temperature within the range of about 370 to 550° F.

4. A process for the production of terephthalic acid which comprises noncatalytically oxidizing para-toluic acid by intimate contact with an oxygen-containing gas in the liquid phase at atmospheric pressure and a temperature within the range of about 370° to 500° F.

5. A process for the production of a benzene para dicarboxylic acid which comprises non-catalytically oxidizing a benzene monocarboxylic acid possessing an alkyl group para to the carboxyl group by intimate contact with oxygen in the liquid phase at a temperature within the range of about 370 to 550° F.

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