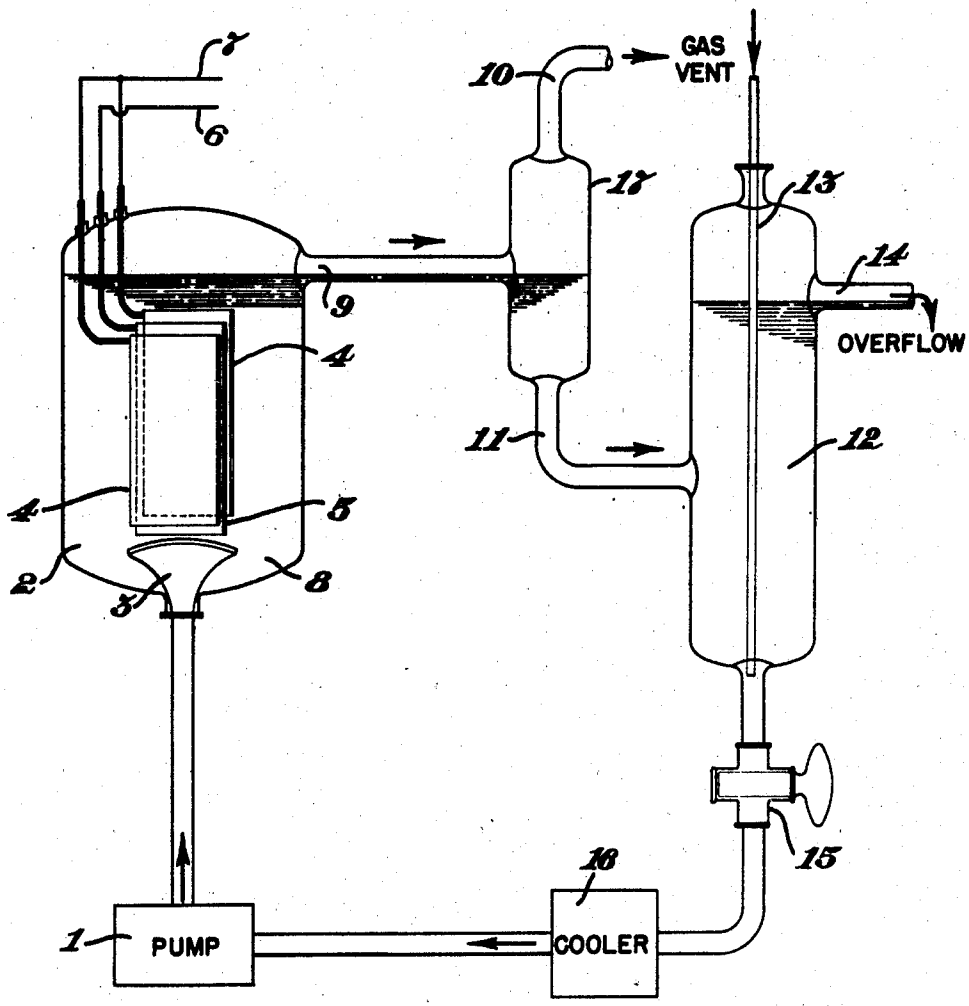
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PROCESS FOR PREPARING DIALKYL ESTERS OF DICARBOXYLIC ACIDS

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## PROCESS FOR PREPARING DIALKYL ESTERS OF DICARBOXYLIC ACIDS

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This invention pertains to the synthesis of diesters and more particularly to the synthesis of diesters of dibasic acids by electrolysis of monoesters of dibasic acids. In a specific embodiment the invention is directed to the synthesis of dialkyl esters of sebacic acid by the electrolysis of monoalkyl adipates.

It has been known for many years that alkali metal salts of monoesters of dibasic acids, upon electrolysis, yield diesters of higher dibasic acids (Ann., 261, 111 (1891); Bull. Soc. Chem. [3], 29, 1038 (1903); Transactions of Electrochemical Society 69, 287, (1936), 77, 459, (1940)). More recently it has been observed that certain amines such as pyridine and diethylamine may be present during the electrolysis of certain monocarboxylic acids, whereby a complex mixture of products is generally obtained. All of the aforesaid prior art processes for the preparation of esters by electrolysis of monoesters of dibasic acids have had numerous disadvantages. For example, when an aqueous medium was employed, yields of dialkyl esters having less than about 14 carbon atoms in the chain were generally not greater than about 30%. If a methanolic medium was employed, the alkali metal salt of the monoalkyl ester of the dibasic acid had a relatively low solubility in the mixture, especially after substantial quantities of the diester had been formed, which gave rise to operating difficulties.

An object of this invention is to provide an improved process for the preparation of dialkyl esters, especially dialkyl esters of dicarboxylic acids of the empirical formula

$$(CH_2)_{2n}(COOH)_2$$

in which $n$ is an integer, preferably from 2 to 7. A further object is to provide a process for the preparation of dialkyl sebacates in high yield from readily available starting materials. A more specific object is to provide a commercially feasible process for the manufacture of dimethyl sebacate by the electrolysis of monomethyl adipate. Other objects of the invention will appear hereinafter.

These objects are accomplished in accordance with the invention by the electrolysis of monoesters of dibasic acids, preferably in methanol solution, in the presence of controlled amounts of the trimethylamine salt of the said monoester, as set forth in greater detail hereinafter. The invention contemplates subjecting a monoalkyl ester of a dibasic acid of the empirical formula $(CH_2)_n(COOH)_2$, $n$ being any integer, and the

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trimethylamine salt of the said ester, to electrolysis, and thereafter separating the resultant dialkyl ester of a dicarboxylic acid of the empirical formula $(CH_2)_{2n}(COOH)_2$ from the electrolysis product. In a preferred embodiment the present invention contemplates the electrolysis of a monomethyl adipate solution, obtained by treating monomethyl adipate with trimethylamine in a methanol solvent, in a plate-type cell whereby dimethyl sebacate is produced in high yield; and the trimethylamine initially introduced into the electrolysis mixture is recoverable almost quantitatively in unchanged form.

One of the surprising features of the present invention is the discovery of the highly specific action of trimethlyamine when employed in methanol solution. This is more readily appreciated upon consideration of the fact that other organic solvents, such as ethanol, etc., are completely inoperative, or nearly so, in the practice of the invention. Moreover, it is not possible to substitute for trimethylamine other organic compounds having salt-forming properties; for example, pyridine is inoperative and is attacked very rapidly under the conditions necessary for the formation of the diesters; ammonia, dimethylamine, and the like also have been found by the applicant to be of no value in the process. In general, such compounds give rise to tarry materials, and virtually none of the desired diester is obtained. A few amines, such as ethylene diamine, behave like trimethylamine, and may be employed in an equivalent manner. In general, however, trimethylamine gives outstanding results, and appears to be highly specific in the practice of the invention. This may be due to the stability of trimethylamine towards electrolytic oxidation, for it is noted that methyl groups survive reaction conditions which tend to destroy ethyl groups, etc. This is further supported by the fact that monomethyl esters give better yields than monoethyl esters in the practice of the invention. Whatever the explanation, trimethylamine may be employed with the monoesters of dibasic acids in place of the alkali metal salts heretofore employed, thus avoiding the above-mentioned disadvantages which are encountered in processes employing the said alkali metal salts. Moreover, the use of trimethylamine facilitates recovery of the dialkyl ester, for it has been discovered, in accordance with the invention, that the solution withdrawn from the electrolytic cell, as herein described, is of such nature that, upon cooling, a separation of dimethyl sebacate in crystalline

form takes place. This, of course, could not be accomplished in processes in which the alkali metal salts are electrolyzed, for the unconverted salts, being relatively insoluble, are precipitated with, or in preference to, the dimethyl sebacate, upon cooling the electrolysis products. The applicant has discovered that, even if lithium salts are employed, the process does not operate satisfactorily, partly due to an excessive formation of tarry by-products.

The invention will be better understood by reference to the accompanying drawing. The drawing represents diagrammatically an apparatus which consists essentially of 1 a centrifugal pump which introduces the solution of monomethyl adipate, trimethylamine, and methanol into the plate-type cell 2, through a fish-tail nozzle 3, which directs the flow of liquid between the cathode 4, and the anode 5. The current is passed to and from the electrodes by means of the glass-enclosed wires 6 and 7. Thus the electrolytic cell contains the cathode and anode immersed in a bath of the methanol solution 8 of monomethyl adipate and trimethylamine, which solution is rapidly circulated between the plates by reason of the flow from the nozzle 3. The solution is thereafter continuously withdrawn through the outlet 9, into a separator 17, for release of carbon dioxide and hydrogen through the vent 10, and the withdrawal of liquid through the outlet 11, to the vessel 12. The vessel 12 is equipped with a means for introducing make-up monomethyl adipate and trimethylamine through the inlet 13. It is also equipped with an overflow 14, whereby a portion of the reaction product can be continuously purged, or removed to suitable devices for recovery of trimethylamine and dimethyl sebacate. The mixture which accumulates in the vessel 12 is in part continuously withdrawn through the valve 15, to the cooler 16 and thence to the pump 1, which returns recovered solution to the electrode cell 2. Alternatively the cooler 16, may be operated at a sufficiently low temperature (e. g., —50° to 0° C.), to cause a continuous separation of dimethyl sebacate therein. The supernatant liquor may be recirculated to the electrolytic cell. In such embodiments, it is preferable to add the make-up monomethyl adipate to the supernatant liquor after the cooling and separating of diester.

In the practice of the invention it is generally desirable to employ as the initial reaction mixture a solution of partially neutralized monoester in methanol, said solution containing about 0.1 to 0.9 preferably 0.3 to 0.8 mol of trimethylamine, in the form of monoester salt, per mol of monoester, i. e., per mol of monoester in the neutralized plus the unneutralized form. In a preferred embodiment the reaction mixture is a solution of monomethyl adipate in methanol obtained by dissolving about 2 mols of monomethyl adipate per liter of methanol and introducing also sufficient trimethylamine to neutralize about 50% of the acidic hydrogen present in the said monomethyl adipate. Alternatively, a solution of monomethyl adipate in water containing about 2 mols of monomethyl adipate per liter, 75% neutralized with trimethylamine, may be employed but as stated above water has a highly deleterious effect upon the yield of desired products.

The electrolysis is generally conducted at a temperature of about 0° to 55° C., preferably about 20° to 45° C. The anode current density should be at least about 0.1, and preferably about 0.2 to 1.0, ampere per square centimeter. The best yields are obtained at the highest controllable current densities.



The apparatus employed in the practice of the invention may be made of or lined with suitable inert materials such as inert metals or Pyrex glass. Since the anode tends to oxidize very rapidly during the electrolysis, it is essential that the anode be constructed of materials which are very resistant to oxidation, such as metallic platinum, platinum on Carborundum, or the like. The cathodes should also be constructed of inert materials such as, platinum, other noble metals, copper, carbon or the like. Since the electrochemical reaction, and the resistance of the cell (especially after a substantial amount of diester has accumulated), causes the development of heat, it is generally desirable to employ a means for removal of heat. This may be done as shown in the diagrammatic drawing by cooling the recirculated solution. Alternative methods, such as internally cooled electrodes and the like may be employed if desired.

It is highly desirable that there be a very rapid flow of the solution between the electrodes. This may be achieved by means of a nozzle which directs the flow of the solution rapidly between the plates. Moreover, it is preferred that the electrodes be placed closely together, with a spacing of about 2 millimeters or less, since the cell resistance, at least in part, is a function of the distance between the electrodes.

The invention is illustrated further by means of the following example.

*Example 1.*—A solution (850 cc. total volume, containing 1.7 mols of monomethyl adipate and 0.721 mol of trimethylamine, the remainder of the solution being methanol) was circulated through a plate-type cell of the type illustrated in the drawing, containing two platinum cathodes (2 x 4 centimeters) and a platinum anode having an area of 16 square centimeters. The circulation was continued for 1.5 hours at a current density of 0.875 ampere per square centimeter at a temperature of 30° C. The voltage gradient was 32.0 to 51.5, an increase in voltage being caused by the building up of dimethyl sebacate in the system during the electrolysis. The resulting product was removed from the apparatus and was found to contain 1.192 mols of monomethyl adipate and 0.225 mol of dimethyl sebacate. The current efficiency was 57.6%. When monoethyl adipate is used in place of monomethyl adipate a considerably lower yield of diethyl sebacate is obtained.

It is to be understood that the foregoing example is illustrative only and that numerous embodiments of the invention will occur to those who are skilled in the art. For example, when water is employed in place of methanol as the reaction medium the diester may be withdrawn from the reaction products as an oily layer. Moreover, it is to be understood that, in the embodiments of the invention illustrated herein, the trimethylamine is converted to a salt by reaction with the monoester of the dibasic acid, hence the trimethylamine may be introduced in the form of such a salt, or in any other form which, by simple interchange or otherwise, yields such a salt. Furthermore, it is to be recognized that the rate of separation of diester from the electrolysis product obtained in the practice of the invention is primarily an economic factor, since the current efficiency decreases with increased conversion and increased resistance of the electroly-

sis mixture. The dialkyl sebacates which are obtainable in accordance with the present invention are widely useful as plasticizers and are especially valuable as intermediates for the preparation of sebacic acid and nylon intermediates which may be obtained therefrom.

Since many embodiments of the invention may be made without departing from the spirit and scope thereof I do not limit myself except as set forth in the following claims.

I claim:

1. A process for preparing dialkyl esters of dicarboxylic acids of the empirical formula

$$(CH_2)_{2n}(COOH)_2$$

in which $n$ is any integer; which comprises subjecting a methanol solution of a monoalkyl ester of a dibasic acid of the empirical formula $(CH_2)_n(COOH)_2$, and a trimethylamine salt of the said ester, to electrolysis and thereafter separating the resultant dialkyl ester of a dicarboxylic acid of the empirical formula

$$(CH_2)_{2n}(COOH)_2$$

from the electrolysis product.

2. A process for preparing dialkyl esters of dicarboxylic acids of the empirical formula

$$(CH_2)_{2n}(COOH)_2$$

in which $n$ is any integer, which comprises subjecting to electrolysis a methanol solution of monoalkyl ester of a dicarboxylic acid of the empirical formula $(CH_2)_n(COOH)_2$, said monoalkyl ester being partially neutralized with trimethylamine whereby it contains 0.1 to 0.9 mol of trimethylamine monoester salt per mol of monoester in the neutralized plus unneutralized form, and thereafter separating the resultant dialkyl ester of a dicarboxylic acid of the empirical formula $(CH_2)_{2n}(COOH)_2$ from the electrolysis product.

3. A process for preparing dialkyl esters of dicarboxylic acids of the empirical formula $(CH_2)_{2n}(COOH)_2$, in which $n$ is any integer, which comprises subjecting to electrolysis a methanol solution of monoalkyl ester of a dicarboxylic acid of the empirical formula $(CH_2)_n(COOH)_2$, said monoalkyl ester being partially neutralized with trimethylamine whereby it contains 0.3 to 0.8 mol of trimethylamine monoester salt per mol of monoester in the neutralized plus unneutralized form, at an



anode current density of about 0.2 to 1.0 ampere per square centimeter.

4. A process for preparing dialkyl esters of dicarboxylic acids of the empirical formula $(CH_2)_{2n}(COOH)_2$, in which $n$ is any integer, which comprises subjecting to electrolysis a methanol solution of monoalkyl ester of a dicarboxylic acid of the empirical formula $(CH_2)_n(COOH)_2$, said monoalkyl ester being partially neutralized with trimethylamine whereby it contains 0.3 to 0.8 mol of trimethylamine monoester salt per mol of monoester in the neutralized plus unneutralized form, at an anode current density of about 0.2 to 1.0 ampere per square centimeter and a temperature of 0° to 55° C., and thereafter separating the resultant dialkyl ester of a dicarboxylic acid of the empirical formula $(CH_2)_{2n}(COOH)_2$ from the electrolysis product.

5. A process for preparing dialkyl esters of dicarboxylic acids of the empirical formula $(CH_2)_{2n}(COOH)_2$, in which $n$ is any integer, which comprises subjecting to electrolysis a methanol solution of monoalkyl ester of a dicarboxylic acid of the empirical formula $(CH_2)_n(COOH)_2$, said monoalkyl ester being partially neutralized with trimethylamine whereby it contains 0.3 to 0.8 mol of trimethylamine monoester salt per mol of monoester in the neutralized plus unneutralized form, at an anode current density of about 0.2 to 1.0 ampere per square centimeter and a temperature of 20° to 45° C. and thereafter separating the resultant dialkyl ester of a dicarboxylic acid of the empirical formula $(CH_2)_{2n}(COOH)_2$ from the electrolysis product.

6. The process of claim 5 in which the said monoalkyl ester is a monomethyl ester.

7. The process of claim 5 in which the said monoalkyl ester is monomethyl adipate.

8. The process of claim 5, in which the said monoalkyl ester is monoethyl adipate.

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