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TSUTOMU KUWATA ETAL

3,313,717

ELECTROLYTIC METHOD FOR PREPARING DIALKYL DICARBOXYLATES

Filed Dec. 11, 1962

Fig. 1

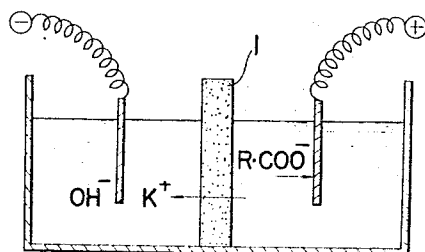


Fig. 2

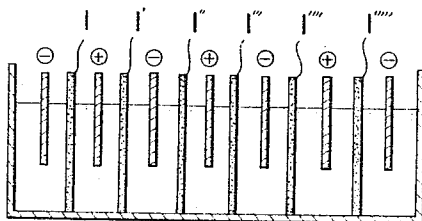
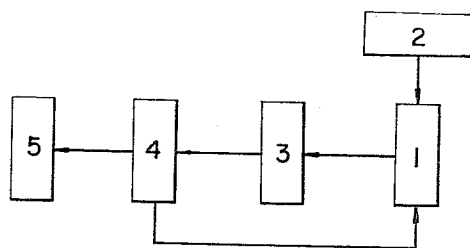


Fig. 3



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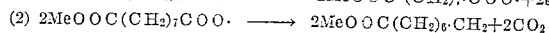
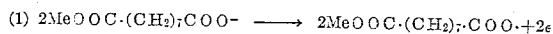
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6 Claims. (Cl. 204—79)

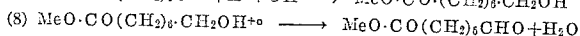
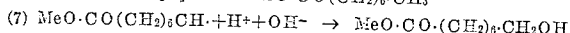
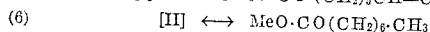
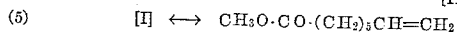
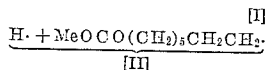
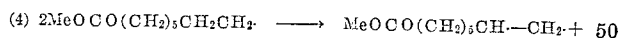
The present invention relates to a method of preparing dialkyl dicarboxylates and more particularly, to a method of synthesizing dialkyl dicarboxylates by means of electrolytic oxidation in which there has been utilized an anodic reaction.

More specifically, this invention relates to a method of preparing dialkyl dicarboxylates which comprises forming diesters (dialkyl dicarboxylates) by the electrolytic oxidation of an alkali salt solution of an alkyl hydrogen dicarboxylate, effecting the electrolytic oxidation in a cell consisting of at least one cathodic compartment and one anodic compartment, feeding to said anodic compartment a neutral or slightly acidic solution containing the aforesaid alkali salt, and passing a current of electricity while maintaining said cathodic compartment in an alkaline state.

Prior to the present invention it was known that dialkyl dicarboxylates, e.g., dimethylthapsiate could be prepared by electrolytic oxidation of the alkali salts of alkyl hydrogen dicarboxylate, for example, the sodium salt of methyl hydrogen azelate, using a platinum wire as the anode in accordance with the following Equations 1, 2 and 3, namely:



However, in accompaniment with the principal reactions in accordance with the foregoing Equations 1, 2 and 3, there occur side reactions in accordance with the following Equations 4, 5, 6, 7 and 8, namely:



As a result, the by-products such as methyl octenate [Equation 5], methyl caprylate [Equation 6], methyl oxycaprylate [Equation 7] and methyl- $\omega$ -oxocaprylate [Equation 8] are formed.

Therefore, in the preparation of diesters in accordance with Equations 1, 2 and 3, diesters cannot be obtained in good yield unless the side reactions of Equations 4, 5, 6, 7 and 8 are restrained. When restraining such side reactions, it was known in the prior art to raise the concentration of the material alkyl hydrogen dicarboxylate, to operate at a high current density, and when restraining the reaction of Equation 7 to lower the pH of the solution of the material alkali salt of alkyl hydrogen dicarboxylate.

However, what becomes a problem with respect to the pH of the liquid is that in this reaction the alkali is formed at the cathode, and unless some means or other could be adopted, the pH of the liquid raises high as the reaction proceeds and the rate of formation of oxy acids becomes high. In addition, the saponification of the material alkyl hydrogen dicarboxylate occurs so as to bring about a fall in the yield of the main reaction product.

20 As for methods that have been known hitherto for  
restraining said side reactions, one such method involves  
the use of an alkali salt of alkyl hydrogen dicarboxylate  
in a methyl alcohol solution as illustrated in the Journal  
of Chemical Soc., 1679 (1938) and 3326 (1950). Still  
25 another method utilized an aqueous solution of a potas-  
sium salt prepared by using, based on the alkyl hydrogen  
dicarboxylate, potassium hydroxide in about its stoichi-  
ometric quantity, neutralizing the potassium hydroxide  
that forms at the cathode, as the reaction proceeds, to  
30 prevent the pH of the reaction liquid to move to the  
alkaline side by replenishing the starting material alkyl  
hydrogen dicarboxylate monoester, while separating the  
diesters formed.

35 However, results that will give complete satisfaction commercially cannot be obtained even by these methods. More particularly, the preparation selectively and advantageously in good yield continuously over a long period of time is impossible.

In accordance with these conventional methods, as there are provided a cathode and an anode in a single electrolytic cell not partitioned by a bulkhead, the material monoester (alkyl hydrogen dicarboxylate), and the esters which are formed as the product oil, being hydrolyzed by the alkali forming in the vicinity of the cathode form alkali salts of acids. The surface activity of the material liquid containing these alkali salts becomes intense to a marked degree so as to accelerate the solubilization of the neutral oil product whereby said oil accumulates in the reaction liquid. The quantity that accumulates increases with the passage of time, and if the reaction is continued this brings about an increase in the electrical resistance. On the other hand, as a result of secondary reactions between the alkali salts of acids formed by the hydrolysis of the thus formed esters and particularly between these salts and the alkali salt of the material monoester, various troublesome by-products besides those by the aforementioned Equations 4-8 are formed, which bring about the degradation of the intended diester compositions that are formed. Considerable quantities of high boiling fractions and resinous substances are formed so as to greatly impede the continuance of the reaction and in extreme cases render operations impossible.

Moreover, in the case when methyl alcohol is used as the reaction solvent in accordance with the conventional method, since the reaction is started with a liquid of high concentration from a zone of low pH and ends with a liquid of low concentration and a higher pH (slightly alkaline) than at the start and in a state in which the product formed is accumulated in the material liquid, the carrying out of the reaction under constant conditions is not possible. In other words, in order to maintain the electric current at a level necessary for proceeding with the reaction, concomitant with the increase in resistance due to the accumulation of the product formed the voltage must be gradually increased. Furthermore, even if the voltage is so regulated, the reaction must still be discontinued because of the rise in the pH and the increase in the resistance. In addition, the accumulation of the formed product in the liquid inevitably makes its separation operation difficult of performing. Hence, it is of great disadvantage from a commercial standpoint.

Also, in the case of the conventional method in which the pH is maintained at the desired pH by replenishing the alkyl hydrogen dicarboxylate as the reaction proceeds, if continuous operation over an extended period is attempted, the formation of the intended diesters gradually falls. Therefore, when attempting to obtain diesters in amounts equaling that obtained at the start of the reaction, it becomes necessary to continue the reaction for an exceedingly long period of time, which would make it impractical. Consequently, the intended diesters cannot be obtained regularly by such a method.

Again, since a very high voltage is required in these conventional methods, the electric power consumption (current  $\times$  voltage) is very great. Hence, they are at a disadvantage commercially and their continuous operation actually is impossible.

As a result of research conducted for a method of preparing advantageously and effectively on a commercial scale, by eliminating the disadvantages of the conventional prior art methods, diesters from alkali solutions of alkali salts of an alkyl hydrogen dicarboxylate by means of electrolytic oxidation, it was noted that the foregoing electrolytic oxidation is an anodic reaction, and that in the conventional prior art methods, studies were made only with respect to the reaction mechanism and the operational conditions at the anode. However, the effects that the cathode had on the anodic reaction were overlooked by the prior-art workers in the field. As a result of much study regarding these effects, it was found that unless the reaction was carried out in a state in which the effects of the cathode are completely excluded, satisfactory results could not possibly be obtained, and that when carrying out the anodic reaction in this state, in which the effects of the cathode are excluded, it was necessary to effect the reaction while isolating the anodic compartment from the cathodic compartment. In addition, it was also found that a cation-exchange membrane should be used as such isolating means. Moreover, it was found that the objects of the present invention could not be obtained by other isolating means such as, for example, perforated membrane, unglazed pottery, sulphate paper, etc.

It was also found that if the reaction liquid was fed to the anodic compartment and alkali was added to the cathodic compartment so that the cathodic compartment liquid would become alkaline at the time of the start of the electrolysis, then it would be sufficient if water was fed thereto to maintain said alkalinity. Thus, the herein described troublesome side reactions in the vicinity of the cathode as well as the side reactions which brought about the other defects of the conventional methods could be essentially overcome.

It was also found that by means of the method of the present invention it was made possible for the first time to obtain the intended diesters in a regular manner and that a continuous operation could be carried out that would be satisfactory on a commercial scale. It was further

found that since the resistance of the liquid becomes exceedingly small as compared with the conventional methods, the reaction could be carried out at a low voltage which is advantageous commercially accordingly, the reaction could be carried out with marked advantage particularly in case of a continuous operation, and the power consumption could be reduced considerably.

It was also found that since there was no need for complicated and imperfect control means for controlling the alkali accumulation which formation was inevitable in the conventional methods the pH of the reaction liquid could be controlled easily and satisfactorily.

Moreover, a variation in the pH of the anodic liquid in the anodic compartment between the vicinity of the inlet and the vicinity of the outlet therefor could hardly be observed; instead, it was found that the pH would shift about 0.05 towards the acidic side which was favorable for the reaction and that the pH would shift about 0.2 towards the alkaline side which was unfavorable for the reaction when the membrane was not present. It was also found that since different solvents could be used in the cathodic compartment and the anodic compartment, the transmissibility of electricity could be enhanced, and also that it was possible to fix the substance that sets up impeding actions in the anodic compartment and in the cathodic compartment and thus prevent the occurrence of impeding actions.

Accordingly, it is an object of the present invention to provide a commercially advantageous and effective method of preparing in good yield and with regularity dialkyl dicarboxylates with low voltage and electric power while preventing the occurrence of undesirable side reactions.

Another object of the invention is to provide a method of preparing dialkyl dicarboxylates in which the defects of the conventional methods can be overcome and in which a continuous operation with regularity can be carried out satisfactorily over an extended period of time without the need for complicated operating means.

Other objects and advantages of this invention will be apparent from the description which follows.

According to the method of the present invention, cation-exchange membranes are used as partitions and at least one each of an anodic compartment and a cathodic compartment is constituted. To this anodic compartment a solution of an alkali salt of an alkyl hydrogen dicarboxylate whose pH has been adjusted to the vicinity of neutral or slightly acidic side is fed and while maintaining the cathodic compartment in an alkaline state electricity is passed. In the first place, when considered from the nature of this type of electrolytic oxidation reaction, while it is one of the requisites that the pH of the reaction liquid does not become alkaline as the reaction proceeds, according to the method of this invention, as shown in FIG. 1, concomitant with the electric discharge of  $R\cdot COO^-$  (wherein R is an alkyl group), the potassium ion  $K^+$ , for example, passes through the cation-exchange membrane 1 and moves to the cathode to form KOH. On the other hand, on the anode the carboxyl radical loses a molecule of  $CO_2$  to produce an alkyl radical as in the foregoing Equation 2 and forms diesters as in Equation 3.

Moreover, since the  $OH^-$  of the cathodic compartment cannot enter the anodic compartment because the partition is a cation-exchange membrane, it can restrain the formation of oxy acids, the by-products resulting from the reaction of Equation 7.

With respect to the alkali salt of an alkyl hydrogen dicarboxylate that is used in this invention, compounds in which the monoester is composed of a dicarboxylic acid of 3-13 carbon atoms and a lower aliphatic alcohol of 1-3 carbon atoms and said alkali salt is an alkali metal salt, particularly a Na salt or a K salt, are satisfactorily used. Included as such dicarboxylic acids are, for example, the malonic, succinic, 2-methyl succinic,

glutaric, adipic, pimelic, suberic, azelaic, sebacic and brassylic acids. Also the lower aliphatic alcohols for the esters thereof include methyl alcohol, ethyl alcohol and propyl alcohol (normal and iso).

Accordingly, the alkali salts of alkyl hydrogen dicarboxylates as used in the present invention include the Na and K salts of the alkyl hydrogen dicarboxylate such as, for example, methyl hydrogen malonate, ethyl hydrogen malonate, methyl hydrogen adipate, ethyl hydrogen adipate, propyl (n-, iso-) hydrogen adipate, methyl hydrogen azelate, ethyl hydrogen azelate, propyl (n-, iso-) hydrogen azelate, methyl hydrogen sebacate, ethyl hydrogen sebacate, propyl (n-, iso-) hydrogen sebacate, methyl hydrogen pimelate, ethyl hydrogen pimelate, propyl hydrogen pimelate, methyl hydrogen suberate, ethyl hydrogen suberate, propyl hydrogen suberate, methyl hydrogen brassylate, ethyl hydrogen brassylate, methyl hydrogen-2-methyl succinate, ethyl hydrogen 2-methyl succinate, etc. These compounds may either be used singly or two different compounds may be combined and used. If different monoesters of alcohols are used, a diester will of course be obtained whose ester portions at the two ends will be different as in Equation 3, for example, methyl propyl sebacate.

Thus, according to the method of this invention, the diesters which can be prepared with advantage include, for example, dimethyl succinate, diethyl succinate, methylenedibutyl succinate, propyl (n-, iso-) hydrogen sebacate, dipropyl (n-, iso-) sebacate, methyl propyl (n-, iso-) sebacate, dimethyl brassylate, diethyl brassylate, dimethyl n-tridecane-1:13-dicarboxylate, diethyl n-tridecane-1:13-dicarboxylate, dimethyl thapsiate, diethyl thapsiate, methyl ethyl thapsiate, dimethyl n-hexadecane-1:16-dicarboxylate, diethyl n-hexadecane-1:16-dicarboxylate, dimethyl 3-methyl-n-tridecane dicarboxylate, diethyl 3-methyl-n-tridecane dicarboxylate, etc.

In accordance with the method of the present invention when preparing a neutral or slightly acidic solution of the alkali salts of an alkyl hydrogen dicarboxylate such as described hereinbefore, the salts may be dissolved in an aqueous solution or a water-water soluble lower aliphatic alcohol mixture and the pH adjusted with an alkyl hydrogen dicarboxylate, an alkali, and water or a water-water-soluble lower aliphatic alcohol mixture may be mixed so as to obtain the desired concentration and pH. The alkali used in this instance include those which can form a sodium or a potassium salt such as, for example, caustic soda, caustic potassium, sodium carbonate, sodium bicarbonate, potassium carbonate, potassium bicarbonate, etc. And as the water-soluble lower aliphatic alcohols, included are, for example, methyl alcohol, ethyl alcohol, propyl alcohol (n-, iso-), butyl alcohol (n-, iso-, tert-), etc. In case a water-water-soluble lower aliphatic alcohol mixture is used, if the concentration of the alcohol is high, a minute amount of the alcohol passes through the partitioning membrane and moves into the cathodic cell where it disperses. To compensate for this portion the anodic liquid is suitably replenished with a minute amount of alcohol.

For effecting the isolation of the anodic compartment from the cathodic compartment, which is an important feature of the present invention, a cation-exchange membrane is used.

In this connection a cation-exchange membrane which is either a homogeneous membrane, a heterogeneous membrane, or a united membrane may be used; for example, strongly acid cation-exchange resin membranes such as the polystyrene sulfonic acid resin membrane, the styrene sulfonic acid-butadiene type resin membrane, the polyethylene-styrene sulfonic acid type resin membrane, the interpolymers resin membrane, etc. The weakly acid cation-exchange resin membranes such as the divinyl benzene acrylate, the divinyl benzene methacrylate and the divinyl benzene maleic anhydride types may also be used. According to this invention, while at least

one each of an anodic and cathodic compartment comprising at least one cation-exchange membrane, in commercial practice it is advantageous to adopt a multicellular arrangement, as shown in FIG. 2, by using at least two or more cation-exchange membranes 1, 1', 1'' . . . to form at least three or more compartments wherein the two end compartments are made cathodic and, the compartments adjoining thereto anodic and thereby forming in alternation cathodic and anodic compartments. It is of course possible to make the compartments at their ends anodic, but since it is advantageous to use platinum as the anodes, and since only one surface of an expensive plate would be utilized, the compartments at the two ends should be made cathodic.

To the thus constituted anodic cells is fed a neutral or slightly acidic solution containing an alkali salt of an alkyl hydrogen dicarboxylate, is fed to the anodic compartment and the solution used as a concentration of 20-40% by weight, preferably 25-35% by weight, and a pH of preferably 6-7. On the other hand, the cathodic compartments are maintained in an alkaline state. Since alkalis are formed in the cathodic compartments by the alkali metal ions which have moved over from the anodic compartment by passing through the cation-exchange membranes, the alkalinity of the former may be maintained merely by adding water during the continuance of the reaction to adjust the alkaline concentration preferably to 0.5-3% by weight. Such an alkali may be, for example, caustic soda, potassium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate and potassium bicarbonate. The alkali metal of the alkaline substance that is added to the cathodic compartment at the start may be the same or different from the alkali metal that is derived from the alkali salt of an alkyl hydrogen dicarboxylate of the anodic cells.

The object of the present invention are satisfactorily attained by passing an electric current described above and carrying out the electrolytic oxidation. While the electric current used will be varied depending on the scale of the electrolytic compartments, the reaction temperature of the electrolytic oxidation of the anodic compartment, the concentration of the anodic liquid, the kind and dimensions of the partitioning membrane, etc., the method of this invention can be carried out continually over an extended period of time regularly at a low voltage and low power requirements which are of great advantage over the conventional methods. For example, in a 160-hour operation for obtaining dimethyl thapsiate from an aqueous solution of a potassium salt of methyl hydrogen azelate, the voltage and power required by the conventional methods were on the order of 12.3 volts and 12.4-37.7 kwh. (increasingly become greater as the reaction proceeded) per kg. of dimethyl thapsiate, and furthermore, as already mentioned hereinbefore, numerous technical difficulties were encountered. In contrast, the method of the present invention can be carried out satisfactorily by the use of a voltage of 9 volts and a consumption of power on the order of 4.62 kwh. (practically constant with the passage of time) per kg. of dimethyl thapsiate produced when operating for the same number of hours under identical conditions, the technical difficulties of the conventional methods being moreover surmounted.

Either a batch or a continuous process may be applied to the practice of the method of this invention. In the conventional methods the continuous operation over an extended period on a regular basis was substantially impossible, but in accordance with the present invention it is possible to operate continuously over an extended period very advantageously and effectively, and especially when the continuous operation is carried out using the aforesaid multicellular system. Such a continuous method may be carried out by feeding continuously, while passing an electric current, a neutral or slightly acidic

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solution containing an alkali salt of an alkyl hydrogen dicarboxylate to the anodic compartment and water to the alkaline solution in the cathodic compartment, taking out on the other hand the liquid containing the formed diesters from which the said-dieters are separated, then after depleting the residual liquid with the materials consumed and adjusting the pH in concomitance therewith, recycling said liquid again to the anodic compartment, while discharging continuously the cathodic compartment liquid.

In order to take out continuously the oil produced comprising mainly diesters which floats normally at the top of the anodic compartment, any means by which the floating oil can be continuously taken out as quickly as possible can be utilized. However, from the operational standpoint the removal by means of, for example, the overflow method is convenient. On the other hand, when the liquid phase containing the diesters collects at the bottom (on account of its pH or specific gravity) of the oil formed, it can be taken out by providing a suitable outlet at the bottom. When using a water and water-soluble lower aliphatic alcohol mixture, if the concentration of the alcohol is relatively high, the resulting oil containing the diesters formed dissolves in the liquid and becomes in its entirety a liquid phase containing the diesters formed. In this case, the extraction and separation may be performed by using a methanol-insoluble lower aliphatic hydrocarbons, for example, hexane. When the concentration of the alcohol is relatively low, for example, about 10% by weight, such a necessity does not arise. The adjustment of the concentration and pH of the residual liquid may be carried out by adding an alkyl hydrogen dicarboxylate and an alkaline substance, or it can also be accomplished by the addition of an alkali salt of an alkyl hydrogen dicarboxylate and a small amount of an alkyl hydrogen dicarboxylate.

In order to illustrate the invention further, the following examples are given, it being understood that these are intended to be merely illustrative of the invention and not in limitation thereof.

#### A. The construction of the electrolyzer

Two sheets of cation-exchange membranes were used as partitions by which the electrolyzer was divided into 3 isolated compartments, of which the compartments at the two ends were made the cathodic compartments and the middle was made the anodic compartment.

##### Cathodic compartment:

Length—20 cm.

Height—29 cm.

Width—5.2 cm.

Inside capacity—3 liters

Fitted at the bottom with an inlet for water and at the top with an overflow outlet.

##### Anodic compartment:

Length—20 cm.

Height—29 cm.

Width—2.6 cm.

Inside capacity—1.5 liters

Fitted with a glass tube, a cooler, an inlet for the anodic liquid at the bottom and an overflow outlet at the top.

##### Cation-exchange membrane:

Effective area—20 cm.×20 cm., 400 cm.<sup>2</sup>

Selemon CMG-10 styrene sulfonic acid-butadiene type (produced by Asahi Glass Kabushiki Kaisha, Japan).

Thickness—0.21–0.25 mm.

Specific resistance 300Ω·cm.

Transference number TNa<sup>+</sup> 0.91

Anode: Platinum wire 0.5 mm. diameter, 159 cm. long, surface area 25 cm.<sup>2</sup>.

Cathode: Thin plate of nickel, stainless steel or iron 19 cm.×20 cm., 380 cm.<sup>2</sup>.

#### B. Operation

As shown in the flow sheet of FIG. 3, one example comprises preparing by means of the material tank 1 and the adjusting tank 2 a neutral or slightly acidic solution containing in a suitable concentration an alkali salt of alkyl hydrogen dicarboxylate, which is used as the anodic compartments liquid of the electrolytic reaction vessel 3, and on the other hand, filling the cathodic compartments of the electrolytic reaction 3 at first with a dilute aqueous alkaline solution containing a small amount of an alkali, and then passing an electric current. An anodic liquid is introduced into the anodic compartment from the bottom thereof at the rate of 3–5 l./hr. from the material tank 1. The oil produced containing the intended diesters which rises to the surface of the anodic compartment liquid along with the evolution of carbon dioxide that attends the progress of the reaction is caused to flow out from the overflow outlet at the top and is conducted to an oil and water separation tank 4. The diesters which have been separated here are conveyed to a receiving tank 5, whereas the residual liquid after having its concentration and pH adjusted is recycled to the electrolytic reaction vessel 3 via the material tank 1. Since the anodic and cathodic compartments are separated by means of an ion-exchange membrane, when left as it is without any countermeasures being taken the concentration of alkali of the cathodic solution becomes higher as the reaction proceeds resulting in a decrease in the selective permeability of the membrane so that the adjustment of the pH becomes difficult of accomplishment. To prevent this, water is fed to the cathodic compartment to dilute the cathodic compartment liquid and thus maintain the concentration of alkali at 0.5–3%. In this case, the alkaline water which flow out from the cathodic compartment is recovered at the outside of the vessel.

The oil of the receiving tank 5 is adjusted to pH 9 by means of a caustic alkali solution, extracted with a solvents using aliphatic and aromatic hydrocarbons, preferably such as benzene, toluene, hexane, etc., after which the monoesters mixed in said oil is separated as an aqueous solution of alkali salt, the extract washed with water, and after recovering the solvent followed by dehydration, rectification is effected to obtain the intended purified diesters.

*Example 1.*—Using 3,200 g. of methyl hydrogen azelate and 1,230 g. of potassium carbonate an aqueous solution having a concentration of 30% and a pH of 7 was prepared, and by operating as described in section B, above, with the electrolyzer described in A, above, employing a direct current of 9 volts and 20 amperes dimethyl thapsiate was obtained.

During the operation the electrical resistance was substantially constant throughout the reaction which was carried out in a regular manner. After operating for 160 hours, the consumption of monoesters was 13,600 g. and the dimethyl thapsiate obtained was 6,222 g.

When the results of the foregoing electrolytic oxidation, according to the method of the present invention, extending over 160 hours from the start of the reaction was divided into five sections comprising section I (20 hours), section II (35 hours), section III (35 hours), section IV (35 hours) and section V (35 hours), and the reaction conditions, composition of the oil formed, and the changes in amount of oil formed per unit electric current by sections were investigated, they were as shown in Table I, below. The oil formed, as shown in the table, however, has been shown in this instance by the oil distilled off during rectification.

TABLE I

	Section I	Section II	Section III	Section IV	Section V	Total
Material:						
Material monoester (g.)	3,200					
Material monoester replenished (g.)	1,820					
Reaction Conditions:		3,100	2,720	3,100	3,300	17,240
Reaction time (hr.)	20	35	35	35	35	160
Amount of electric current (ah.)	400	700	700	700	700	3,200
Current density (a./dm. <sup>2</sup> )	80	80	80	80	80	
Oil Formed:						
Rate of formation (g./ah.)	2.90	3.00	2.99	2.99	2.97	
Oil formed (g.)	1,180	2,100	2,090	2,094	2,080	9,524
Methyl-7-octenoate (g.) 50-70° C./5 mm. Hg.*	186 (16.0%)	357 (17.0%)	341 (16.3%)	355 (16.0%)	349 (16.8%)	1,568
Methyl-8-oxyoctanoate (g.) 120-130° C./5 mm. Hg.*	222 (19.0%)	420 (20.0%)	370 (17.7%)	387 (18.5%)	337 (16.2%)	1,734
Dimethyl thapsiate (g.) 180-185° C./3 mm. Hg.*	755 (65.0%)	1,320 (63.0%)	1,379 (66.0%)	1,372 (65.5%)	1,394 (67.0%)	6,222
High boiling fractions						
Yield:						
Monoester consumed (g.)						
Oil formed/Monoesters consumed (percent)						13,600
Dimethyl thapsiate/monoester consumed (percent)						70.0
Yield (percent of theory)						45.8
						58.8

\*Indicates the principal distillation range of each of the fractions.

On the other hand, when, for purpose of comparison, the same experiment was repeated with the operation being continued for 160 hours without using the partitioning membranes, the results obtained, when likewise divided into five sections, were as shown in Table II, below.

Again, when a comparison is made of the yields (the number of grams of oil formed in one hour per ampere), it can be seen that according to the method of the present invention a practically constant yield of about 3.0 g./ah. was regularly obtained, whereas in the control a yield of less than one half of this value could only be obtained,

TABLE II.—CONTROL

	Section I	Section II	Section III	Section IV	Section V	Total
Material:						
Material monoester (g.)	1,900					
Material monoester replenished (g.)	1,006					
Reaction Conditions:		2,046	1,821	1,385	2,023	10,181
Reaction time (hr.)	20	35	35	35	35	160
Amount of electric current (ah.)	400	700	700	700	700	3,200
Current density (a./dm. <sup>2</sup> )	80	80	80	80	80	80
Oil Formed:						
Rate of formation (g./ah.)	1.59	1.50	1.24	0.93	0.95	
Oil formed (g.)	636	1,050	865	650	664	3,865
Methyl-7-octenoate (g.)	150 (23.6%)	215 (20.5%)	180 (20.8%)	155 (23.8%)	159 (23.9%)	859
Methyl-8-oxyoctanoate (g.)	163 (25.7%)	240 (22.9%)	192 (22.2%)	184 (28.3%)	194 (29.2%)	973
Dimethyl thapsiate (g.)	323 (50.7%)	495 (47.1%)	355 (44.5%)	228 (35.2%)	225 (34.0%)	1,656
High boiling fractions (g.)		100 (9.5%)	108 (12.5%)	82 (12.7%)	86 (12.9%)	
Yield:						
Monoester consumed (g.)						
Oil formed/monoester consumed (percent)						5,700
Dimethyl thapsiate/monoester consumed (percent)						67.8
Yield (percent of theory)						29.0
						37.2

As is apparent from a comparison of the foregoing Tables I and II, it can be seen that when the operation was continuously carried out for the same number of hours under identical conditions, in case of the control (Table II) (the method without the partitioning membranes) a production of only 3,965 grams of oil was obtained, whereas according to the method of the present invention (Table I) a production of 9,524 grams of oil was obtained and moreover with a reaction efficiency that is markedly superior. In addition, the amount occupied by dimethyl thapsiate, the intended diester, in the oil formed was about 65% by weight according to the method of the present invention in contrast with about 50.7% by weight in Section I according to the control experiments illustrated in Table II. Further, as is apparent from a comparison of Sections II-V of two methods, according to the method of this invention (Table I) the amount formed in each section is practically constant, showing that the reaction proceeds regularly, whereas in Table II (control) the amount forced decreases with the passage of time, showing that the reaction does not proceed regularly. It can also be seen that while it is exceedingly disadvantageous to carry out the operation continuously for more than about 60 hours according to Table II (control), according to the method of this invention (Table I) even after operating for 160 hours, it still is possible to obtain the product regularly in good yield.

this yield moreover being not only nonuniform but also manifesting a marked decrease with the passage of time.

It is also apparent that the formation of the undesirable high boiling fractions is of such a very minute amount according to the method of the present invention that it can be substantially ignored, whereas in Table II (control) the formation of the high boiling fractions is a considerable amount making it not ignorable, the proportion (shown together in the table as a percentage) occupied in the oil formed increasing with the passage of time. When a comparison is made in particular as regards the formation of impurity in the form of the oxy acid, according to the method of this invention it was about 20% at most, being usually about 17%, whereas in Table II (control) it reached about 29%, showing moreover a tendency to increase with the passage of time.

As is apparent from the foregoing results, it can be seen that since according to the method of the present invention the reaction is carried out regularly in good yield, the method is operable under constant electric power conditions. On the other hand, in the method illustrated in Table II (control), in order to obtain the production of oil in commercially profitable amounts, operation under constant power conditions is impossible, it being necessary that the voltage and electric power be increased with the passage of time. Especially, when the operation is carried out by the method without the partitioning membranes and moreover by the batch proc-

ess as has actually been attempted heretofore, with the requirement for a still greater voltage and electric power progressively with the passage of time, commercially satisfactory results can hardly be obtained.

In addition, as regards the oil formed in the anodic liquid inclusive of the diesters that are solubilized and accumulated therein, when the amount accumulated are shown by sections as in the foregoing Tables I and II, they are as in the following Tables I' and II', respectively.

TABLE I'

	Section I	Section II	Section III	Section IV	Section V
Quantity of reaction liquid (g.)-----	8.780	10.000	10.890	10.050	9.800
Quantity of oil formed (g.)-----	280.5	351.2	309.9	328.3	324.5
Concentration in liquid (percent)-----	3.19	3.51	2.64	3.28	3.31

TABLE II'.—CONTROL

	Section I	Section II	Section III	Section IV	Section V
Quantity of reaction liquid (g.)-----	7.450	8.900	10.930	11.070	10.100
Quantity of oil formed (g.)-----	149	355.8	467.1	669.0	815.7
Concentration in liquid (percent)-----	2.00	4.00	4.27	6.04	8.06

As indicated by the corresponding Sections II-V of the foregoing two tables, i.e., Tables I' and II', the proportion occupied in the anodic liquid of the oil that accumulates therein is low and practically constant in each of the sections as compared with the case of the control which shows a marked progressive increase with the passage of time. This brings about an increase in the resistance of the liquid and becomes one of the causes for the requirement for high voltage and high electric power. Again, the phenomena in the control of an increase in the high boiling fractions (see Table II) and an increase in the oil accumulated (see Table II') results from the formation of alkali in the vicinity of the cathode, as already mentioned hereinbefore.

*Example 2.*—A water-methanol solution (concentration of methanol 10% by weight) of the same composition, same concentration and same pH was used instead of the aqueous solution of Example 1. Except that a direct current of 10-11 volts was used while replenishing the anodic compartment with methanol to compensate for the minute quantity of the methanol which moves to the cathodic compartment, otherwise the same techniques were followed as in Example 1. After a reaction time of 150 hours, dimethyl thapsiate was likewise obtained satisfactorily. The yield was 59% of theory.

*Example 3.*—Except that a water-methanol solution whose concentration of methanol was 50% was used and a direct current of 13-15 volts was used, otherwise the same procedures were followed as in Example 2, whereby was satisfactorily obtained likewise after a reaction time of 50 hours dimethyl thapsiate, the yield of which was 62% of theoretical yield. In a case such as this where the concentration of methanol is high, the oil formed containing the diesters does not rise to the top but forms a homogeneous layer. Consequently, instead of the oil and water separating tank 4 a continuous extractor using hexane as the extracting agent is employed, and the oil formed is transferred to the hexane. The extracting agent may be any lower chain hydrocarbon that is substantially insoluble in methanol, the preferred being hexane. This operation is unnecessary when the concentration of methanol is so low that the oil operation performed is immiscible when the concentration of methanol is so low that the oil portion formed is immiscible, such operation is unnecessary.

*Example 4.*—When the same techniques as in Example 1 were followed, except that an aqueous solution of the

potassium salt of methyl hydrogen sebacate the concentration of which was 30% by weight and with its pH adjusted to 7 was used and the reaction was carried out for 50 hours under the conditions that the electric current passed was at 9-11 volts and 20 amperes, dimethyl n-hexadecane-1:16-dicarboxylate was likewise satisfactorily obtained with the yield being 58% of theory.

*Example 5.*—The same techniques as in Example 1 were followed, except that an aqueous solution whose con-

centration was 30% and having a pH of 7 was prepared using the potassium salt of methyl hydrogen brassylate and the potassium salt of methyl hydrogen 2-methyl succinate in a proportion of 1 mol of the former to 1 mol of the latter, and then the reaction was carried out for 30 hours at 9-11 volts and 20 amperes, whereby was obtained likewise satisfactorily dimethyl 3-methyl-n-tridecane dicarboxylate.

Having thus described the invention, what we claim is:

1. A method of preparing a dialkyl dicarboxylate which comprises converting an alkali salt of said dicarboxylate into a diester by means of electrolytic oxidation, in a cell consisting of at least one anodic compartment and one cathodic compartment and a cationic exchange membrane, feeding a solution of said alkali salt of an alkyl hydrogen carboxylate having a pH of 6 to 7 and a concentration of 20 to 40% by weight to said anodic compartment, maintaining said cathodic compartment in an alkaline state and having an alkaline concentration of 0.5 to 3% by weight and passing an electric current through the system to effect electrolytic oxidation.

2. A method of preparing a dialkyl carboxylate which comprises converting an alkali salt of said dicarboxylate into a diester by means of electrolytic oxidation, in a cell consisting of at least three compartments using at least two cation exchange membranes, making the compartments on the two ends cathodic and the compartment adjacent thereto anodic, thus having cathodic and anodic compartments in alternation, feeding to said anodic compartment a solution of said alkali salt of an alkali hydrogen dicarboxylate having a pH of 6 to 7 and a concentration of 20 to 40% by weight, maintaining said cathodic compartments in an alkaline state and having an alkali concentration of 0.5 to 3% by weight and passing an electric current through the system to effect electrolytic oxidation.

3. A method of preparing a dialkyl dicarboxylate, which comprises converting an alkali salt of said dicarboxylate into a diester by means of electrolytic oxidation, in a cell consisting of one anodic compartment and a cathodic compartment and an anionic exchange membrane, passing an electric current through the system, continuously feeding a solution of said alkali salt of an alkyl hydrogen dicarboxylate having a pH of 6 to 7 and a concentration of 20 to 40% by weight to said anodic compartment and water to said cathodic compartment containing an alkaline solution having an alkali concentration of 0.5 to

13

3% by weight and concurrently continuously taking a liquid phase containing the formed diester from the anolyte separating the diester, continuously recycling the residual liquid to the anodic compartment after adjusting the concentration and pH thereof, and continuously discharging the cathodic compartment liquid. 5

4. The method of claim 1, wherein said electrolytic oxidation is carried out by using a solution of an alkali salt of an alkyl hydrogen dicarboxylate having a pH of from 6-7, a concentration of 20-40% by weight, and employing platinum as the anode. 10

5. The method of claim 1 in which said solution of an alkali salt is a solution selected from the group consisting of water and water-soluble lower aliphatic alcohols.

6. The method of claim 1, wherein the alkalinity of said cathodic compartment at the start of the electrolysis is maintained by means of a 0.5-3% by weight dilute aqueous solution of a substance selected from the group consisting of caustic soda, caustic potassium hydroxide, 15

14

sodium carbonate, sodium bicarbonate, potassium carbonate and potassium bicarbonate.

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