

DESCRIPTION

PROCESS FOR PRODUCING AN ESTER

TECHNICAL FIELD

The present invention relates to a process for
5 producing an ester such as a plasticizer to be used for
vinyl chloride resins.

BACKGROUND ART

Heretofore, a process for producing an ester to be
used for e.g. a plasticizer, by an esterification
10 reaction of an acid and an alcohol, has been widely
industrially carried out. In such a process for
producing an ester, an acid catalyst such as sulfuric
acid or p-toluene sulfonic acid, or an organic metal
catalyst of e.g. Ti or Sn, has been commonly used as a
15 catalyst. And, in a case where an acid catalyst such as
p-toluene sulfonic acid is to be used, the reaction can
be effected at a relatively low temperature, but there is
a problem such that by-products are substantially formed.
When an organic metal catalyst is used, formation of by-
20 products is little, but there is a problem that it is
necessary to elevate the reaction temperature, whereby
the energy cost tends to be high.

This esterification reaction is a typical
equilibrium reaction, and in order to increase the field
25 of the desired ester, it is common to employ a method
wherein the starting material alcohol is used usually in
excess of the theoretical amount (stoichiometric amount),

and by-product water accompanying the esterification reaction is continuously withdrawn out of the system. As a method for removing water out of the system, a method is employed wherein the starting material alcohol and water are azeotropically distilled, and the distillate is cooled, whereupon only water is separated by phase separation, and the alcohol is refluxed to the reactor. The azeotropic point of the alcohol and the by-product water is not higher than the boiling point of the alcohol, and if the reaction is carried out under normal pressure or reduced pressure at the initial stage of the reaction, the boiling state will continue at a temperature lower than the desired reaction temperature, and the temperature of the reaction solution will not increase until the water is azeotropically removed and decreased, i.e. the reaction rate will not rise, thus leading to a problem that it takes long time for the reaction. Further, there is a problem that as the evaporation latent heat is deprived by azeotropy, the energy to raise the reaction temperature is required wastefully.

JP-A-55-38334 and JP-A-6-157405 disclose a method wherein a dehydration column to remove water from a refluxed alcohol is installed to increase the reaction rate at the terminal stage of the reaction. However, by this method, no improvement in the reaction rate at the initial stage of the reaction is observed, and there is a

problem that a special installation such as a dehydration column is required. Further, WO95/29888 discloses a method of shortening the reaction time by changing the charging ratio of an alcohol and an acid. Namely, a
5 method is disclosed in which the reaction rate is increased by increasing the boiling point of the reaction solution i.e. the reaction temperature by adding an alcohol in an amount smaller than the theoretical amount and then stepwisely adding it while monitoring the amount
10 of the alcohol. However, also by this method, there is a problem such that the reaction rate tends to be slow as compared with a case where an excessive alcohol is added.

DISCLOSURE OF THE INVENTION

The purpose of the present invention is to provide a
15 process for producing an ester from an organic carboxylic acid and/or an anhydride thereof and a C₄₋₁₈ alcohol, wherein the reaction time is shortened by elevating the reaction rate at the initial stage of the reaction, and the energy cost is reduced thereby bringing about an
20 economical advantage.

The present invention is characterized in that the reaction is effected under a pressure of from 0.02 to 5 kg/cm²G in a process for producing an ester from an organic carboxylic acid and/or an anhydride thereof and a
25 C₄₋₁₈ alcohol. Further, the present invention resides in a method for producing an ester, which is characterized in that in addition to effect the reaction under such a

pressure condition, the reaction is effected by supplying the starting material C₄₋₁₈ alcohol in a temperature range from the boiling point under the pressure in the reactor to a temperature lower by 20°C than that.

5 BEST MODE FOR CARRYING OUT THE INVENTION

Now, the present invention will be described in detail.

The organic carboxylic acid and/or an anhydride thereof to be used in the present invention may, for
10 example, be an aliphatic monocarboxylic acid such as acetic acid, propionic acid or butyric acid and/or an anhydride thereof, an aliphatic dicarboxylic acid such as adipic acid, sebacic acid, oleic acid or fumaric acid and/or an anhydride thereof, an aromatic dicarboxylic
15 acid such as phthalic acid, isophthalic acid or telephthalic acid and/or an anhydride thereof, or an aromatic polycarboxylic acid such as trimellitic acid, pyromellitic acid or biphenyltetracarboxylic acid and/or an anhydride thereof. Among them, phthalic acid,
20 isophthalic acid, terephthalic acid, trimellitic acid, biphenyltetracarboxylic acid and/or an anhydride thereof, is preferred, and phthalic acid and/or an anhydride thereof is most preferred. Namely, the present invention is particularly preferred as a process for obtaining a
25 diester of an aromatic dicarboxylic acid such as phthalic acid.

The C₄₋₁₈ alcohol to be used in the present invention

may, for example, be an aliphatic primary alcohol such as butanol, hexanol, heptanol, n-octanol, 2-ethylhexanol, nonyl alcohol, decyl alcohol or lauryl alcohol, and a mixture thereof, an aromatic primary alcohol such as butyl benzyl alcohol or cresyl alcohol, a glycol such as ethylene glycol, propylene glycol or butane diol, a polyhydric alcohol such as pentaerythritol, and a mixture thereof. Among them, a C₇₋₁₃ aliphatic primary alcohol is preferred, and 2-ethylhexyl alcohol, nonyl alcohol or decyl alcohol is particularly preferred. The alcohol is used in an amount within a range of from the stoichiometrical amount to 2.0 times thereof relative to the organic carboxylic acid and/or an anhydride thereof, and industrially, it is more preferably 2.5 times of the stoichiometrical amount.

In the process of the present invention, it is necessary that the reaction is effected under a pressure of from 0.02 to 5 kg/cm²G. A preferred range of the pressure is from 0.03 to 2 kg/cm²G. If the pressure is less than 0.02 kg/cm²G, the mixture of the C₄₋₁₈ alcohol and by-product water tends to be azeotropic, and it tends to take a long time for the reaction. Further, in the present invention, the object can be achieved if the pressure at a predetermined reaction temperature is set to be at least the vapor pressure of the mixture of the C₄₋₁₈ alcohol and the by-product water. Accordingly, it is meaningless to increase the pressure beyond 5 kg/cm²G.

Further, in the present invention, it is preferred to supply the starting material alcohol as heated to the boiling point under the pressure in the reactor or to a temperature range lower by 20°C than that, in order to quickly raise the temperature in the reactor to the predetermined reaction temperature.

With respect to the manner of exerting the pressure, it is preferred to exert the pressure from the exterior by an inert gas such as nitrogen, from the initial stage of the reaction, from the viewpoint of the operation efficiency. The period for effecting the reaction under pressure is preferably a period from the initiation of the reaction till the conversion becomes 90%, preferably a period from the initiation of the reaction till the conversion becomes 80%. (Here, the conversion means the yield of the ester relative to the starting material organic carboxylic acid. For example, when the starting material organic carboxylic acid is an aromatic dicarboxylic acid such as phthalic acid, the reaction of the carboxylic acid to a monoester is carried out relatively quickly and almost completely in many cases, and here, it represents the reaction from the carboxylic acid to the diester.)

The esterification reaction is an equilibrium reaction, and accordingly, it is necessary to increase the yield of the ester by removing by-product water in the later half of the reaction. Accordingly, as

mentioned above, it is preferred that during a period until the conversion becomes 90%, preferably 80%, a pressure is exerted at the initial stage of the reaction and from a proper point of time, the pressure is
5 initiated to be reduced to gradually accelerate removal of water, so that the reaction pressure becomes within a range of from 0.02 to 5 kg/cm²G as prescribed by the present invention, and at the terminal stage of the reaction wherein the conversion exceeds 90%, the pressure
10 is made negative.

The process of the present invention can be carried out in the absence of a catalyst. However, an acid catalyst such as sulfuric acid, an aliphatic sulfonic acid or an aromatic sulfonic acid such as p-toluene
15 sulfonic acid or an organic metal catalyst of e.g. Ti or Sn, such as an alkyl titanate such as tetrabutyl titanate or tetraisopropyl titanate, tin tetramaleate, butyl tin maleate, may be used. Among them, an organic catalyst of e.g. Ti or Sn is preferred, and an alkyl titanate is most
20 preferred.

In the process of the present invention, the reaction temperature is set to be a temperature higher than the azeotropic point at normal pressures of the C₄₋₁₈ alcohol and the by-product water, accomplished by
25 pressurizing, particularly preferably within a range of from 120 to 250°C. If it is lower than 120°C, the reaction rate tends to be low, and if it exceeds 250°C,

the reaction solution tends to be colored, or a by-product is likely to be formed to hinder e.g. a plasticizer performance. In the process of the present invention, a preferred range of the reaction temperature is influenced by the catalyst. However, a preferred range of the reaction temperature in a case where an acid catalyst is employed, is from 120 to 160°C, and a preferred range in a case where no catalyst or an organic metal catalyst is employed, is from 160 to 250°C, more preferably from 180 to 230°C.

Further, after completion of the esterification reaction of the present invention, purification is carried out by a known method such as distillation of an excessive alcohol, removal of the catalyst, neutralization, washing with water, treatment with activated carbon or activated clay, or filtration, to obtain an ester as the product.

EXAMPLES

Now, the present invention will be described in further detail with reference to Examples and Comparative Examples. However, the present invention is not limited to the following Examples unless it exceeds its gist.

The following Examples show cases wherein phthalic acid which is an aromatic dicarboxylic acid, is used as the organic carboxylic acid. In the case of this phthalic acid, the reaction to a phthalic acid monoester is carried out extremely quickly and completely. In the

following Examples, the conversion represents a conversion to a phthalic acid diester. Namely,

Conversion (%) = $[1 - (\text{mols of a phthalic acid monoester calculated from an acid value}) / (\text{mols of the starting material phthalic anhydride})] \times 100$

EXAMPLE 1

A 20 four necked flask equipped with a stirrer, a distillation column, a condenser, an oil-water separator and an alcohol-reflux line, was preliminarily heated by an oil bath and pressurized with nitrogen gas to 1000 mmHg (0.316 kg/cm²G). 459g (3.1 mol) of phthalic anhydride heated and melted at a temperature of at least 140°C, was charged over a period of 35 minutes by means of a pump. Simultaneously, 1009 g (7.75 mol) of 2-ethyl hexanol of 170°C was fed, so that the initial 807 g was charged over a period of 40 minutes, and the remaining 202 g was charged over a period of 40 minutes. Further, 0.63 mg (0.05 wt% relative to phthalic acid dioctylester as the product) of tetraisopropyl titanate was added as a catalyst after completion of the charging of phthalic anhydride.

Refluxing of 2-ethyl hexanol was continued, while maintaining the pressure at 1000 mmHg from the time (this is taken as the starting point of the reaction) at which charging of phthalic anhydride and 2-ethyl hexanol was initiated (by-product water and 2-ethyl hexanol were separated by an oil-water separator, and the water was

removed out of the system, and 2-ethyl hexanol was returned to the flask via the reflux line). Upon expiration of 40 minutes from the initiation of the reaction, the pressure was gradually reduced, and the pressure upon expiration of about 60 minutes from the initiation of the reaction (about 20 minutes after initiation of the reduced pressure) was about 900 mmHg (about 0.184 kg/cm²G). At that time, the acid value was 37.5 mgKOH/g. Further, upon expiration of 85 minutes from the initiation of the reaction, the pressure in the reactor became negative, and the conversion exceeded 92%. And, the reaction was terminated at the time when the acid value of the reaction solution became 0.1 mgKOH/g (conversion of 99.92%). The pressure at that time was 550 mmHg (-0.276 kg/cm²G), and the time required finally for this reaction was 150 minutes.

EXAMPLE 2

Using the same apparatus as in Example 1, 459 g of phthalic anhydride, 1009 g of 2-ethyl hexanol and 0.63 ml of tetraisopropyl titanate were charged in a similar manner. In the same manner as in Example 1, while maintaining the pressure at 1000 mmHg (0.316 kg/cm²G) from the initiation of the reaction, the temperature of the reaction solution was raised from 170°C to 220°C over a period of 35 minutes. Then, while maintaining the temperature of the reaction solution at 220°C, vacuuming was initiated by means of a vacuum pump. From 75 minutes

after initiation of the reaction (40 minutes after initiation of vacuuming), the temperature was lowered to 185°C over a period of 80 minutes while continuing vacuuming, and this temperature was maintained until completion of the reaction (the time when the acid value of the reaction solution became 0.1 mgKOH/g = a conversion of 99.92%). The pressure upon expiration of 60 minutes from the initiation of the reaction was 800 mmHg (0.053 kg/cm²G), the acid value was 40.1 mgKOH/g, the pressure at the time of the completion of the reaction was 200 mmHg (-0.737 kg/cm²G), and the time required finally for this reaction was 180 minutes.

COMPARATIVE EXAMPLE 1

Charging was carried out in the same manner as in Example 1 except that the pressure was maintained at 700 mmHg (-0.079 kg/cm²G), and while the temperature raising rate of the oil bath was the same as in Example 1, the reaction solution was heated from 170°C. From 70 minutes after initiation of the reaction, the pressure was further reduced from 700 mmHg, and the temperature raising of the reaction solution was continued, so that upon expiration of 120 minutes from initiation of the reaction, the temperature of the reaction solution reached 210°C. Thereafter, the reaction was continued while maintaining the temperature of the reaction solution at 210°C, and the reaction was terminated when the acid value of the reaction solution became 0.1

mgKOH/g (= a conversion of 99.92%). The pressure at that time was 380 mmHg ($-0.500 \text{ kg/cm}^2\text{G}$), and the time required finally for this reaction was 210 minutes.

COMPARATIVE EXAMPLE 2

5 Charging was carried out in the same manner as in Example 1 except that the pressure was maintained at 700 mmHg ($-0.079 \text{ kg/cm}^2\text{G}$), and while the temperature raising rate of the oil bath was the same as in Example 1, the reaction solution was heated from 120°C . After 88
10 minutes from initiation of the reaction, the pressure was further reduced from 700 mmHg, and the temperature raising of the reaction solution was continued, and upon expiration of 140 minutes after initiation of the reaction, the temperature of the reaction solution
15 reached 210°C . Thereafter, the reaction was continued while maintaining the temperature of the reaction solution at 210°C , and the reaction was terminated when the acid value of the reaction solution became 0.1
20 mgKOH/g (= a conversion of 99.92%). The pressure at that time was 380 mmHg ($-0.500 \text{ kg/cm}^2\text{G}$), and the time required finally for this reaction was 228 minutes.

EVALUATION OF THE RESULTS

Calculation of the energy required for heating was carried out by means of a computer simulation from the
25 temperatures and the pressure conditions in Examples 1 and 2 and Comparative Examples 1 and 2. The software employed was "gPROMS" (Barton and Pantelides, 1994 Im-

perial Collage of Sience, Technology and Medicine). The time required for completion of the reaction is 65% in Example 1 and 79% in Example 2, when it is 100% in Comparative Example 2.

5 From this result, it is evident that with the conventional process (Comparative Example 2), it takes a long time for the reaction, and the energy required for heating is required to be substantial. Further, Example 2 is a case where optimization was carried out to save
10 the required energy. Also in this case, the reaction time was 85% of Comparative Example 1, and the necessary energy was about 70%. Further, it was 79% of Comparative Example 2, and the necessary energy was about 60%.

INDUSTRIAL APPLICABILITY

15 According to the process for producing an ester of the present invention, the reaction time can be shortened, and the energy can be reduced, as compared with a conventional process.

CLAIMS

1. A process for producing an ester from an organic carboxylic acid and/or an anhydride thereof and a C₄₋₁₈ alcohol, which is characterized in that the reaction is
5 effected under a pressure of from 0.02 to 5 kg/cm²G.
2. The process for producing ^{an} ester according to Claim 1, wherein the reaction is carried out at a temperature higher than the azeotropic point which a mixture of the C₄₋₁₈ alcohol and by-product water exhibits under normal
10 pressures.
3. The process for producing an ester according to Claim 1 or 2, wherein the reaction is effected under a pressure of from 0.02 to 5 kg/cm²G during a period from the initiation of the reaction till the yield of the ester
15 become 90%.
4. The process for producing an ester according to any one of Claims 1 to 3, wherein the organic carboxylic acid and an anhydride thereof are supplied in a molten or powder state, and the alcohol is supplied in a
20 temperature range from the boiling point under the pressure in the reactor to a temperature lower by 20°C than that.
5. The process for producing an ester according to any one of Claims 1 to 4, wherein the reaction temperature is
25 from 120 to 250°C.
6. The process for producing an ester according to any one of Claims 1 to 5, wherein a catalyst is an organic



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metal catalyst.

7. The process for producing an ester according to any
one of Claims 1 to 6, wherein the organic carboxylic acid
and/or an anhydride thereof is an aromatic dicarboxylic
5 acid and/or an anhydride thereof.

8. The process for producing an ester according to any
one of Claims 1 to 7, wherein the C₄₋₁₈ alcohol is an
aliphatic primary alcohol.

9. The process for producing an ester according to any
10 one of Claims 1 to 8, wherein the pressure is made
negative at the terminal stage of the reaction.

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