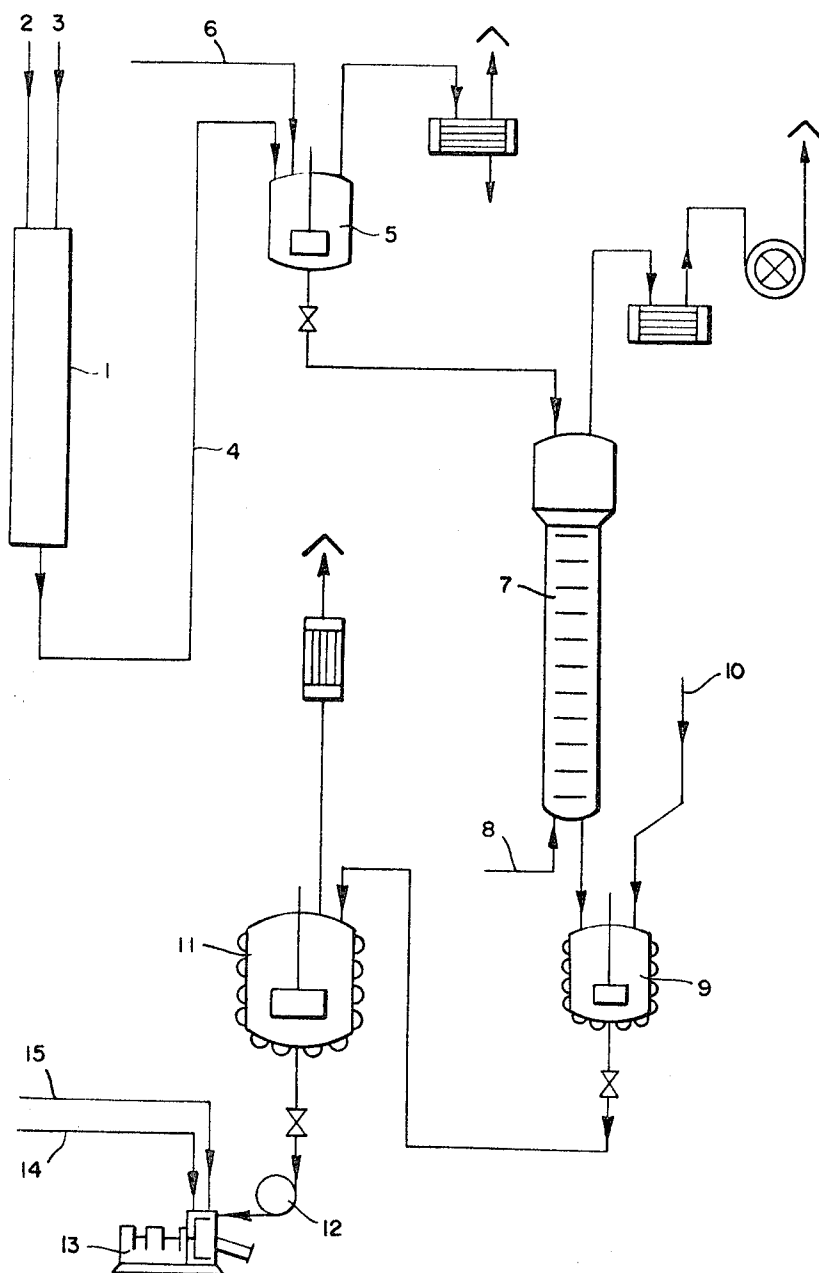


June 10, 1969

H. GOELZ ET AL
CONTINUOUS PRODUCTION OF 1,4,5,6,7,7-HEXACHLOROBICYCLO-
[2,2,1]-5-HEPTENE-2,3-DICARBOXYLIC ACID
Filed May 11, 1966

3,449,412



INVENTORS:

HORST GOELZ
HUBERT SUTER
FRIEDRICH BRUNNMUELLER
ALBERT PALM
BY

Marzall, Johnston, Cook & Root
ATT'YS

1

3,449,412

CONTINUOUS PRODUCTION OF 1,4,5,6,7,7-HEXACHLOROBICYCLO-[2,2,1]-5-HEPTENE-2,3-DICARBOXYLIC ACID

Horst Goelz, Schwetzingen, and Hubert Suter, Friedrich Brunnmueller, and Albert Palm, Ludwigshafen (Rhine), Germany, assignors to Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany
Filed May 11, 1966, Ser. No. 549,352

Claims priority, application Germany, May 14, 1965, B 81,929

Int. Cl. C07c 61/26

U.S. Cl. 260—514

9 Claims

This invention relates to the continuous production of 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid and to the continuous processing of the reaction mixture.

1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid has hitherto been the most valuable acid component for the production of self-extinguishing polyester resins. In order to obtain water-clear polyester resins, very high purity requirements are placed on the 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid.

1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic anhydride and 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid itself which have been prepared by prior art methods are always contaminated by compounds containing chlorine. These partly originate from the impurities in the starting materials. Thus for example commercial grade hexachlorocyclopentadiene contains about 3% of byproducts, such as hexachlorobutadiene and octachlorocyclopentene. On the other hand, they may be attributed to the fact that the reaction is incomplete. According to U.S. patent specification No. 3,214,444 it is extremely difficult, if not impossible, to carry the reaction of the chlorohydrocarbons to completion, even when pure hexachlorocyclopentadiene is used as the starting material. The reaction of equimolar amounts of hexachlorocyclopentadiene with maleic anhydride is incomplete even after a reaction period of seven to eight hours at a temperature of 150° C. According to U.S. patent specification No. 2,903,463, at a temperature above 170° C., a reversed Diels-Alder reaction takes place which is attended by discoloration of the product. It is known that the reaction of hexachlorocyclopentadiene with maleic anhydride may be carried out in the presence of a solvent. According to various literature references, the solvents may be hydrocarbons, for xylene, toluene or hexane, or chlorinated hydrocarbons, for example mouene or hexane, or chlorinated hydrocarbons, for example monochlorobenzene, o-dichlorobenzene, m-dichlorobenzene and carbon tetrachloride. Since the diene synthesis proceeds exothermally, the process is often carried out with vapor cooling. Using solvents necessitates recycling the assistant in the industrial form of the process. This assistant then in turn has to be separately purified.

Quite apart from the circulation of the solvent, all other chlorohydrocarbons have to be removed from the product, both unreacted hexachlorocyclopentadiene and the byproducts, for example hexachlorocyclopentene. These chlorohydrocarbons not only cause detrimental discoloration or further decomposition products, but they are also skin irritants and produce a type of dermatitis.

The prior art methods have made it clear how difficult it is to separate the product of the process from the reaction mixture in a satisfactory yield so that it is free from injurious impurities. For example a method has been described in which hexachlorocyclopentadiene is removed together with the solvent toluene by steam distillation. Repeated recrystallization of the 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic anhydride or

2

acid prepared therefrom, in some cases using other assistants, for example ethylene chloride (German patent specification No. 1,154,097) or aliphatic acids (British patent specification No. 878,003) have also been described. In these methods numerous washings and filtrations are naturally necessary and these require a great deal of time and labor. It is also known that purification may be carried out by azeotropic distillation. Substances, for example glycols or maleic anhydride, which form an azeotrope with the impurities containing chlorine, are added. Apart from the additional expense of using a distillation step in the process, the method is limited by the requirement that the constant boiling point of the azeotrope be kept so low that other undesirable byproducts are not formed. Moreover when glycols are used the adduct is converted into a partial ester. This disadvantage of the method can only be tolerated if immediate processing into polyester is carried out.

The object of the present invention is a process for the continuous production of pure 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid from hexachlorocyclopentadiene and maleic anhydride in which the reaction and the purification of the product of the process can be carried out far more simply than in the prior art methods, which may be carried out on a large scale in a simple way and which requires only small expenditure on protective measures against the physiological effects of the chlorohydrocarbons.

We have found that colorless and very pure 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid is obtained from hexachlorocyclopentadiene and maleic anhydride by heating at atmospheric, subatmospheric or superatmospheric pressure followed by hydrolysis, by supplying the reactants together and continuously to a reactor kept at a temperature of 120° to 200° C., preferably 135° to 180° C., passing it therethrough at a mean residence time of two to seven hours, particularly three to five hours, with or without simultaneous stirring, any free space above the reaction mixture in the reactor being advantageously filled with an inert gas, allowing the effluent reaction product to flow into water at a temperature of at least 70° C., treating the solution thus obtained by blowing in superheated steam until it is freed from chlorohydrocarbons, adding to the solution a low saturated fatty acid, which may be chlorinated, cooling the solution and separating the crystalline 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid.

It is a special advantage of the process that the use of a solvent may be dispensed with. It is therefore possible to carry out the reaction at a relatively high temperature and at the same time to shorten the reaction time without discoloration of the reaction product. Carrying out the reaction in the absence of solvents makes the industrial embodiment more elastic because in the even of disturbance the reaction time and the reaction temperature may be rapidly correlated to one another. Another advantage of the new process is that after the diene synthesis it is possible to carry out the chemical reaction of hydrolysis of the anhydride and the physical purification by steam distillation in a common operation. The physiologically injurious chlorohydrocarbons are collected in the steam distillate and can be removed without danger. It is also an advantage that recrystallization of the precipitate may be dispensed with.

Hexachlorocyclopentadiene and maleic anhydride are usually supplied to the reactor in a molar ratio of from 0.8:1.3 to 1.3:0.8, preferably in a molar ratio of from 0.9:1.1 to 1.1:0.9.

The reaction temperature and the residence time are interdependent. At temperatures only slightly above 120° C., residence times of up to seven hours are required, whereas at reaction temperatures of 200° C., a residence

time of two hours is sufficient. It is preferred to use reaction temperatures of 135° to 180° C. and residence times of three to five hours. The reactor may be one or more stirred vessels, for example in cascade arrangement. The process may however be carried out in reaction tubes. In this case the preferred tubes are those whose diameter/length ratio is from 1:30 to 1:100, particularly from 1:50 to 1:60. A stirrer, preferably rotating at slow speed, may also be used in the reaction tube to mix the reaction materials. The process is usually carried out at atmospheric pressure; it may however also be carried out at subatmospheric pressure, for example down to 20 mm. Hg, or superatmospheric pressure, for example up to 5 atmospheres gauge.

Nitrogen, carbon dioxide, rare gases or methane are suitable for example as the inert gas atmosphere in the reactor.

After the reaction mixture has left the reactor it is passed at atmospheric or slightly subatmospheric pressure, for example at 300 mm. Hg, or at superatmospheric pressure, for example at 2 atmospheres gauge, into water at a temperature of more than 70° C., advantageously at 80° to 100° C., preferably a ratio of 1:1 to 2:1 being maintained. When superatmosphere pressure is used, water having a temperature of more than 100° C. may also be used, e.g. 130° C.

Steam which has been superheated, for example up to 200° C., is passed through the solution obtained by hydrolysis until the chlorohydrocarbons present have been expelled. This is generally achieved (when the chlorohydrocarbons are present in the usual amounts) at a weight ratio of aqueous dicarboxylic acid solution to steam of 1:4 to 1:8.

The treatment with superheated steam is preferably carried out in columns, for example in sieve plate columns or baffle plate columns, to which the solution to be treated is supplied at the top and into which the superheated steam is injected at the bottom. Generally ten theoretical trays are adequate and often less than ten theoretical trays are sufficient.

The solution of 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid which has been steamed in this way then has added to it at the temperature reached in the steaming (but at least more than 70° C.) and at atmospheric pressure a saturated lower fatty acid which may be chlorinated. Examples of suitable fatty acids are formic acid, acetic acid and propionic acid, the homologues which follow these being less recommendable on account of their odor. Chloroacetic acid or chloropropionic acid may also be used. These acids are usually added in 0.05 to 1, particularly 0.05 to 0.2, times the weight of the 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid. Monocarboxylic acids are as a rule added as aqueous solutions whose concentration is measured so that the ratio of 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid to solvent is in the weight range from 0.8:1 to 1:0.8, preferably 1:1, and the concentration of the monocarboxylic acid in the aqueous phase is mainly 5 to 20% by weight.

Separation of the 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid after the solution has been cooled preferably to 10° to 60° C. may be carried out by methods conventionally used for separating crystals from mother liquor, for example by means of centrifuges or filters.

An embodiment of the process will now be described in greater detail by way of example with reference to the accompanying drawing in which a suitable plant is shown diagrammatically. The diene synthesis takes place in a reaction tube 1 to which maleic anhydride and hexachlorocyclopentadiene are supplied in liquid form through lines 2 and 3. A cascade of stirred vessels may be used instead of the reaction tube 1. The reaction product is passed through line 4 to a stirred vessel 5 into which hot water is passed at the same time through line 6. The

solution obtained by hydrolysis in the stirred vessel 5 is supplied to the steaming column 7, while at the same time superheated steam is injected through line 8. The 1,4,5,6,7,7 - hexachlorobicyclo - [2,2,1] - 5 - heptene-2,3-dicarboxylic acid solution which has been treated with steam is supplied to a container 9 and mixed therein with an aqueous solution of a low fatty acid supplied through line 10. The resultant solution is cooled. This is advantageously carried out in a stirred vessel 11 from which the crystal slurry is supplied by means of a pump 12 to a centrifuge 13. Water or a dilute solution of the low fatty acid (used for washing) is supplied through lines 14 and 15.

1,4,5,6,7,7 - hexachlorobicyclo - [2,2,1] - 5 - heptene-2,3-dicarboxylic acid obtained by the process contains 1 mole of water of crystallization in addition to any adherent water. This product may be used direct for the production of high grade colorless self-extinguishing polyesters.

The following examples will further illustrate this invention. The parts specified (unless otherwise stated) are by weight. Parts by weight bear the same relation to parts by volume as the gram to the liter.

EXAMPLE 1

Referring to the drawing, 379 parts per hour of liquid maleic anhydride at 70° C. is passed through line 2 and 955 parts per hour of 97.5% hexachlorocyclopentadiene which has been heated to 155° C. is passed through line 3 into a reaction tube 1 having a capacity of 3.4 parts by volume, whose diameter/height ratio is 1:58, which is arranged vertically and which has a jacket for cooling liquid to carry away heat. The molar ratio of maleic anhydride to hexachlorocyclopentadiene is 1.1:1. A temperature of about 140° C. is set up in the mixture. The temperature rises to about 175° C. by the exothermic reaction. It is kept at about 160° C. by cooling. After a reaction time of four hours, the melt thus obtained flows in an amount of 1334 parts per hour from the lower end of the reaction tube 1 through line 4 into a receiver 5 fitted with a stirrer and condenser. 570 parts of hot water at a temperature of 80° to 90° C. is supplied per hour to the receiver 5 through line 6. The aqueous solution of 1,4,5,6,7,7 - hexachlorobicyclo - [2,2,1] - 5 - heptene - 2, 3-dicarboxylic acid formed is supplied to the top of a sieve tray column 7 having ten sieve trays. 8000 parts per hour of steam, supplied through line 8 at a temperature of 150° C., flows countercurrent to the supply of 1904 parts per hour of the aqueous 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3 - dicarboxylic acid solution. 2040 parts per hour of steamed 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid solution is withdrawn from the bottom of the column 7 and passed into a stirred vessel 9 into which at the same time a 50% aqueous solution of acetic acid is introduced through line 10 in an amount of 400 parts per hour. The solution is passed into one of two crystallizing vessels 11 (used alternately) in which it is cooled to 15° C. with a residence time of about five hours. Within twelve hours, 14,640 parts of crystal slurry is sucked off by a pump 12 and supplied to a centrifuge 13. The crystal slurry is washed in the centrifuge with 2700 parts of 15% acetic acid solution supplied through line 14 and 12,600 parts of water supplied through line 15. About 1300 parts of 1,4,5,6,7,7 - hexachlorobicyclo - [2,2,1] - 5 - heptene - 2, 3-dicarboxylic acid per hour is obtained which contains 4.3% of water of crystallization and to which about 3.7% of water adheres.

Anhydrous 1,4,5,6,7,7-hexachlorobicyclo - [2,2,1] - 5-heptene-2,3-dicarboxylic acid is obtained by drying the 1,4,5,6,7,7 - hexachlorobicyclo - [2,2,1] - 5 - heptene - 2, 3-dicarboxylic acid containing water of crystallization for two hours at 100° to 110° C. The yield is about 91% on the hexachlorocyclopentadiene supplied, the conversion being 94%. The space-time yield is 8.56 kg. per liter of reaction space per day.

EXAMPLE 2

An apparatus is used which is similar to that in Example 1 but a cascade of three vessels each provided with a stirrer and a jacket for cooling or heating fluid and whose capacity is from 0.9 to 1.2 parts by volume is provided instead of the reaction tube 1. 406 parts per hour of liquid maleic acid is supplied through line 2 at 70° C. and 982 parts per hour of 97.5% hexachlorocyclopentadiene at room temperature is supplied through line 3 to the series of vessels.

The molar ratio of maleic anhydride to hexachlorocyclopentadiene is 1.15:1. The volume of the vessels and their cooling and heating means are so dimensioned that the reaction mixture has a mean residence time of sixty-five minutes at 165° C. in the first vessel, fifty-eight minutes at 165° C. in the second vessel and seventy-seven minutes at 170° C. in the third vessel of the series.

The melt flows from this third vessel in an amount of 1388 parts per hour through line 4 into the receiver 5 provided with stirrer and condenser. 600 parts per hour of water at 80° to 90° C. is supplied through line 6 to the receiver 5. The aqueous solution thus formed is supplied to the top of a baffle plate column 7 having ten trays. The hourly supply of 1988 parts of the said solution meets a counter-current stream of 9940 parts per hour of steam which is supplied through line 8 at a temperature of 140° C. About 2040 parts per hour of steamed 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid solution is withdrawn at the bottom of the column and supplied to a stirred vessel 9 at the same time as 380 parts per hour of a 50% aqueous solution of acetic acid. The resultant solution is cooled to 15° C. in a continuous crystallizer. 2420 parts per hour of crystal slurry is sucked off by the pump 12 and supplied to the centrifuge 13, in which the amount of crystals remaining is washed with 500 parts of 15% acetic acid solution supplied through line 14 and with 2000 parts of water supplied through line 15.

1360 parts per hour of water-moist 1,4,5,6,7,7-hexachlorobicyclo - [2,2,1]-5-heptene-2,3-dicarboxylic acid is obtained which after having been dried yields about 1250 parts of anhydrous 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid. The yield is accordingly 91.5% on the hexachlorocyclopentadiene used.

The space-time yield is 9.68 kg. per liter of reaction volume per day.

We claim:

1. A process for the production of pure 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid from hexachlorocyclopentadiene and maleic anhydride by heating, wherein the reactants are supplied together and continuously to a reactor kept at a temperature of 120° to 200° C., are passed through the same with a mean residence time of two to seven hours, the effluent reaction product is allowed to flow into water at a tempera-

ture of at least 70° C., the solution thus obtained is treated by injection of superheated steam to remove chlorohydrocarbons, a lower saturated fatty acid or a lower saturated chlorinated fatty acid, is added to the solution which is then cooled and the crystalline 1,4,5,6,7,7 - hexachlorobicyclo - [2,2,1] - 5 - heptene - 2,3 - dicarboxylic acid is separated.

2. A process as claimed in claim 1 wherein the reaction of hexachlorocyclopentadiene and maleic anhydride is carried out in the absence of a solvent.

3. A process as claimed in claim 1 wherein any free space above the reaction mixture in the reactor is filled with an inert gas.

4. A process for the production of 1,4,5,6,7,7-hexachlorobicyclo - [2,2,1] - 5 - heptene-2,3-dicarboxylic acid from hexachlorocyclopentadiene and maleic anhydride, wherein hexachlorocyclopentadiene and maleic anhydride are supplied together and continuously in a molar ratio of 0.8:1.3 to 1.3:0.8 to a reactor kept at a temperature of from 120° to 200° C., are passed through the same with a mean residence time of two to seven hours, the effluent reaction product is allowed to flow into water having a temperature of from 70° to 130° C., the solution thus obtained is treated by steam superheated up to 200° C. to remove chlorohydrocarbons, a lower saturated fatty acid or a lower saturated chlorinated fatty acid is added to the solution in an amount of 0.05 to 1 times the weight of the 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid, which solution is then cooled and the 1,4,5,6,7,7-hexachlorobicyclo-[2,2,1]-5-heptene-2,3-dicarboxylic acid is separated.

5. A process as claimed in claim 4 wherein the molar ratio of hexachlorocyclopentadiene to maleic anhydride is between 0.9:1.1 and 1.1:0.9.

6. A process as claimed in claim 4 wherein the resistance period is 3 to 5 hours.

7. A process as claimed in claim 4 wherein the reactor is kept at 135° to 180° C.

8. A process as claimed in claim 4 wherein the effluent reaction product is allowed to flow at atmospheric pressure into water at from 80° to 100° C.

9. A process as claimed in claim 4 wherein the fatty acid or chlorinated fatty acid is added in such an amount that in the resulting aqueous phase the concentration of the fatty acid or the chlorinated fatty acid is 5 to 20% by weight.

References Cited

UNITED STATES PATENTS

2,779,769 1/1957 Robitschek ----- 260—346.6

FOREIGN PATENTS

634,620 1/1962 Canada.

LORRAINE A. WEINBERGER, *Primary Examiner.*

P. J. KILLOS, *Assistant Examiner.*