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**Specification for a Patent
Application—Translation
from Belgian Patent 654, 791**

By Ciba Societe Anonyme

Published December 1982

Prepared for the United States Department of Energy
Under Contract Number DE-AC04-76-DP00613.

**Kansas City
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SPECIFICATION FOR A PATENT
APPLICATION--TRANSLATION FROM
BELGIAN PATENT 654,791

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SPECIFICATION FOR A PATENT APPLICATION--TRANSLATION FROM BELGIAN
PATENT 654,791

BDX-613-2877, Published December 1982

Prepared by Ciba Société Anonyme

This entire article has been translated from the Flemish as it was submitted as a patent with the Minister of Economic Affairs and Energy, Kingdom of Belgium, regarding the process for the preparation of diallyl phthalate prepolymer solutions.

DDK:TR24/i

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A prime contractor with the United States
Department of Energy under Contract Number
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TRANSLATION:

Kingdom of Belgium

International Classification: --

Ministry of Economic Affairs
and Energy

Opened to the Public on April 23, 1965

BELGIAN PATENT NO. 654,791

The Minister of Economic Affairs and Energy

With reference to the law of May 24, 1854 concerning patents;

With reference to the Union Convention for the Protection of Industrial Property;

With reference to the procès-verbal of 23 October 1964 at 3:45 p.m. at the Industrial Property Department;

DECREES:

Article 1. *Granted to the company called: CIBA SOCIÉTÉ ANONYME, in Bale (Switzerland), represented by the Office of Parette (Fred. Maes) in Brussels, a patent for: PROCESS FOR THE PREPARATION OF DIALLYL PHTHALATE PREPOLYMER SOLUTIONS, which they declare to have been the subject of a patent application filed in Switzerland on 25 October 1963.*

Article 2. *This patent is issued without prior examination, at the applicant's own risk, without guarantee of the factualism, newness, or merit of the invention or the accuracy of the description and without prejudice to the rights of third parties.*

One of the copies of the specification of the invention (descriptive report and drawings, if any), signed by the party concerned and filed in support of his patent request, shall remain attached to the present decree.

Brussels, 23 April 1965
By special authority of the
Director General

/signature/

J. HAMELS

SPECIFICATION

Filed in support of an application for a

PATENT

Case 5378/E

BELGIUM

Submitted by the company called:

CIBA SOCIÉTÉ ANONYME

for:

Process for the preparation of diallyl phthalate prepolymer solutions

Which is the subject of a prior patent application filed in SWITZERLAND on 25

October 1963

A process is known for preparing prepolymers of a diallyl phthalate such as diallyl *o*-phthalate which are still soluble in organic solvents like lower ketones, esters, halogenated hydrocarbons, or aromatic hydrocarbons, by controlled polymerization of diallyl phthalate in substance [in bulk? -- *Tr. Ed.*] in the presence of catalysts forming free radicals, such as organic peroxides. The prepolymer formed is precipitated from its solution in the unreacted monomer by the addition of agents in which the monomer is soluble but in which the prepolymer, on the other hand, is insoluble. Such processes are described, for example, in U. S. Patent No. 3,030,341 filed 6 May 1959, and in Austrian Patent No. 225,424 filed 20 May 1960. In this way, only low diallyl phthalate conversions (25 to 30% by weight) to the prepolymer are obtained. For higher conversions, there is already yellowing and the polymer is insoluble in organic solvents.

To obtain higher conversions, German Patent No. 1,067,216 filed on 12 March 1958 proposed using substituted benzyl alcohols as chain length regulators.

The process described in Swiss Patent No. 363,807 filed on 2 April 1957 pursues the same goal, but hydrogen peroxide is used as the polymerization catalyst and serves at the same time to regulate chain growth. The higher conversions obtained in this case are a little over 50% by weight, while large quantities of catalyst and regulator are necessary -- for example, over 6% by weight of benzoyl peroxide and over 30% by weight of regulator, relative to the quantity of monomer.

The prepolymer prepared in accordance with this known process is used in most cases, for example, to prepare laminated products, and is advantageously in the form of solutions in organic solvents which also still contain fractions of the monomer. The preparation of such industrially ready-to-use solutions is expensive, however, because diallyl phthalate prepolymerization in an organic solvent has still not been successful in arriving directly at such solutions. It has always been necessary to go through the expensive route of first isolating the prepolymer from the reaction mixture -- by precipitation, for example -- and then dissolving this polymer in the organic solvent along with the desired amount of monomer.

Surprisingly, it has now been found that there is an inexpensive way to obtain industrially ready-to-use solutions of diallyl phthalate prepolymers if the polymerization is carried out in the presence of a liquid ketone such as acetone or methyl ethyl ketone as the solvent, and a free radical-forming catalyst like hydrogen peroxide, while small amounts of strong acids are added so that this polymerization solution always remains slightly acidic and so that its pH has a value of 2 to 5.

The new process has the additional advantage of allowing diallyl phthalate polymerization up to high conversions which are clearly greater than in the case

of the known processes. It is extremely surprising that diallyl phthalate can even be polymerized with a good yield in a solvent. In fact, in U. S. Patent No. 3,030,341 filed on 6 May 1959, it was possible to obtain conversions of only 25 to 30% with hydrogen peroxide as the polymerization catalyst at a polymerization time of over ten hours, either in substance [bulk?] or in the presence of small quantities of lower aliphatic alcohols; for conversions of over 30 to 35%, there was already yellowing in accordance with this known method.

What is even more surprising is that in the method in accordance with the invention, in which the polymerization is carried out in a ketone as the solvent at temperatures which are, for example, only slightly above 60°C, conversions of over 60% can be obtained at approximately the same reaction time.

The diallyl phthalate prepolymers which are obtained in accordance with the new process are different from the prepolymers obtained in accordance with the known processes in that the average molecular weights are smaller (1,000). It is assumed that a certain small fraction of the ketone is incorporated into the prepolymers and that these latter are consequently so-called telomerization products with the formula:

in which Y and Z represent atoms and groups of atoms formed by splitting of the ketone as telogen (Z is generally a hydrogen atom and Y is the residue of the ketone molecule), and in which n is a small whole number, generally from 2 to 50. The prepolymerization products and telomerization products obtained in accordance with the process of the invention can be used for the same practical applications as the known diallyl phthalate prepolymerization products. The solutions of the prepolymers in a liquid ketone -- acetone, for example -- which are obtained after the polymerization is stopped, also have the important advantage of being very slightly viscous and stable, and of being directly usable for shaping into pressed products and laminated products without the necessity (as in the processes known up until now) of carrying out preliminary isolation of the prepolymer.

The subject of the present invention is therefore a process for preparing solutions containing the prepolymerization products of a diallyl phthalate with the following formula, in the dissolved state in a liquid ketone at room temperature:

or containing the products of the copolymerization of such diallyl phthalates with other copolymerizable monomers, in addition to the monomers which may not have been reacted.

The process in conformance with the invention is characterized by the fact that the solution of a diallyl phthalate alone or a diallyl phthalate and another copolymerizable monomer in a liquid ketone at ambient temperature -- preferably in a lower aliphatic ketone -- is reacted with heating in the presence of a free radical-forming catalyst -- preferably hydrogen peroxide -- as well as in the presence of a small amount of a strong acid until at least 60% and advantageously at least 90% of the monomer initially present in the reaction solution has been converted to the prepolymer.

Diallyl isophthalate, diallyl terephthalate, and particularly diallyl *o*-phthalate can be used as the diallyl phthalates.

The liquid ketone at room temperature serves at the same time as regulator and solvent for the reaction.

Aromatic ketones like acetophenone, cycloaliphatic ketones like cyclopentanone, cyclohexanone, and methylcyclohexanones, and especially lower aliphatic ketones like acetone, methyl ethyl ketone, methyl isopropyl ketone, diisopropyl ketone, methyl isobutyl ketone, and diisobutyl ketone can be used. If necessary, some of the ketone can be replaced by an inert organic solvent.

The usual free radical-forming catalysts are used as the polymerization catalysts. We can mention hydrazine derivatives such as hydrazine hydrochloride, aliphatic azo compounds like α, α' -azoisobutyronitrile, and organic peroxides or persalts such as peracetic acid, acetyl peroxide, chloroacetyl peroxide, trichloroacetyl peroxide, benzoyl peroxide, chlorobenzoyl peroxide, benzoylacetyl peroxide, propionyl peroxide, fluorochloropropionyl peroxide, lauryl peroxide, cumene hydroperoxide, *tert*-butyl hydroperoxide, di-*tert*-butyl peroxide, di-*tert*-amyl peroxide, and *para*-menthane hydroperoxide; it is preferable to use hydrogen peroxide.

It is advantageous to use on the order of 0.05 to 10% by weight of the catalyst relative to the overall weight of the monomer(s). The catalyst can be added all at once at the beginning, or by portions as the prepolymerization progresses.

The reaction should be carried out in an acid medium, advantageously in the pH range of 2 to 4. For this purpose, a small amount -- preferably from 0.05 to 5% by weight relative to the total weight of the monomer(s) -- of a strong acid such as hydrochloric acid, perchloric acid, benzenesulfonic acid, or especially *p*-toluenesulfonic acid, is added.

The reaction is carried out at high temperature, preferably in the temperature range of 50 to 150°C. It is carried out under such pressures that the reaction partners remain in the liquid phase. The process can be carried out continuously or discontinuously.

For the other monomers which may be prepolymerized conjointly with the diallyl phthalate, it is appropriate to use those containing a carbon-carbon double bond, and in particular a $H_2C=C-$ group. We can mention: polymerizable olefins such as butene, isobutylene, amylene, hexylene, and butadiene; halogenated olefins like vinyl fluoride, fluoroprene, vinylidene fluoride, difluoroethylene, trifluoroethylene, tetrafluoroethylene, difluoromonochloroethylene, dichloromono-fluoroethylene, trifluorochloroethylene, difluorodichloroethylene, perfluoropropene, perfluorobutene, vinyl chloride, vinylidene chloride, trichloroethylene, chloroprene, tetrachloroethylene, and perchloropropene; vinyl ethers such as vinyl methyl ether, vinyl ethyl ether, and vinyl phenyl ether; vinyl aryl compounds like styrene, α -methylstyrene, and other substituted styrenes; compounds of the acrylic acid series such as the esters obtained from acrylic acid or methacrylic acid and alcohols or phenols, for example, methyl acrylate, ethyl acrylate,

butyl acrylate, dodecyl acrylate, methyl methacrylate, acrylonitrile, methacrylonitrile, acrylic acid amides and methacrylic acid; analogous derivatives of α -fluoroacrylic, α -chloroacrylic, crotonic, maleic, or fumaric acid; and allyl compounds other than diallyl phthalates, such as diallyl succinate, triallyl cyanurate, and chloroallyl acetate.

It is, of course, also possible to prepare ternary, quaternary, etc. copolymers by prepolymerizing diallyl phthalates with two or more other different monomers. In addition, coprepolymers can also be prepared by prepolymerization of different diallyl phthalates.

The prepolymer solutions which are obtained in accordance with the invention can be used as is for very diverse purposes.

They are most particularly suitable for the preparation of press-molded pieces and laminated products, for which purpose peroxide-based hardeners, fillers, reinforcing agents, unmolding agents, pigments, coloring agents, stabilizers, and, if necessary, other monomers and/or other prepolymers are added.

The invention is described in more detail in the nonlimiting examples which follow. In these examples, the percentages are expressed by weight and the temperatures are indicated in degrees centigrade. The viscosities were measured at 20°C.

Example 1

A mixture consisting of 1.127 g of diallyl *o*-phthalate, 984.5 g of methyl ethyl ketone, 3.7 g of *p*-toluenesulfonic acid, and 16.6 g of hydrogen peroxide (at 65%) is boiled while stirring for nine hours under reflux at an internal temperature of 81°. At the end of two, four, six, and eight hours, another 2 g each time of hydrogen peroxide (at 65%) are added. The reaction mixture is

then cooled. 2.143 g of a yellow-colored solution are obtained. In this solution, no [sic] precipitate can be observed after the addition of 0.9 cc of methanol to 3 g of the reaction mixture. The viscosity of the solution is 90 cP. A sample of this solution is evaporated under vacuum. A solid substance remains which is flexible and a little sticky. The solution obtained contains only a little unpolymerized diallyl phthalate and can be used as is for the preparation of laminated products or powders for press-molding. If desired, the acetone solution obtained can be neutralized before use by shaking it with precipitated CaCO_3 and then filtering.

Example 2

A mixture of 980 g of diallyl *o*-phthalate, 856 g of acetone, 3.2 g of *p*-toluenesulfonic acid, and 9.6 g of hydrogen peroxide (at 65%) is boiled while stirring for 13 hours under reflux at an internal temperature of 68°. At the end of two, four, six, and ten hours, another 8 g of hydrogen peroxide (at 65%) are added each time. The reaction mixture is then cooled. 1.764 g of a yellow-colored solution are obtained. In this solution, a precipitate is observed after the addition of 0.9 cc of methanol to 3 g of the reaction mixture. The viscosity of the solution obtained is 34 cP. After evaporating a sample under vacuum, a sticky elastic solid substance is obtained. The solution can be used as is for the preparation of laminated products or powders for press-molding.

Example 3

A mixture of 220.5 g of diallyl *o*-phthalate, 24.5 g of methyl methacrylate (stabilized with hydroquinone, 214 g of acetone, 0.8 g of *p*-toluenesulfonic acid, and 2.4 g of hydrogen peroxide (at 65%) is boiled while stirring for 12

hours under reflux at an internal temperature of 67°. At the end of two, four, six, eight, and ten hours, another gram of hydrogen peroxide (at 65%) is added each time. After the reaction is interrupted by cooling, 398 g of a yellow-colored solution are obtained; the viscosity is 45 cP. In this solution, a precipitate is observed after the addition of 1.2 cc of methanol to 3 g of the reaction mixture. This solution can be used as is for the preparation of laminated products and powders for press-molding.

Example 4

A mixture of 245 g of diallyl phthalate, 214 g of acetone, 0.7 g of perchloric acid (at 70%), and 4.8 g of hydrogen peroxide (at 65%) is boiled while stirring for 15 hours under reflux at an internal temperature of about 65°. At the end of two, four, six, eight, and ten hours, another gram of hydrogen peroxide (at 65%) is added each time. The reaction mixture is then cooled. 480 g of a yellow-colored solution are obtained. In this solution, a precipitate can be observed after the addition of 0.9 cc of methanol to 3 g of the reaction mixture. The viscosity of the solution is 20 cP. After the solution is evaporated under vacuum at 70°, a practically solid, sticky resin is obtained. The solution can be used as is for the preparation of laminated products. If necessary, it can be neutralized with sodium carbonate before use.

Example 5

A mixture of 1.078 g of diallyl isophthalate, 942 g of acetone, 3.59 g of *p*-toluenesulfonic acid, and 21 g of hydrogen peroxide (at 65%) is boiled while stirring for five hours under reflux at an internal temperature of 65°. At the end of four hours, another 4 g of hydrogen peroxide (at 65%) are added. After

cooling, 2.010 g of a slightly viscous clear yellow solution are obtained. In this solution, a precipitate is observed when 1.0 cc of methanol is added to 3 g of the reaction mixture. The viscosity is 15 cP. This solution is not indefinitely stable. At the end of the week the viscosity has risen to 27 cP. The solution can be used as is for the preparation of laminated products.

Example 6

A mixture of 245 g of diallyl phthalate, 214 g of diisobutyl ketone, 0.8 g of *p*-toluenesulfonic acid, and 3.6 g of hydrogen peroxide (at 65%) is heated for two hours at 100° while stirring. At the end of an hour another gram of hydrogen peroxide (at 65%) is added. After cooling, a clear, viscous, slightly yellowish solution is obtained. With this solution, a precipitate is observed when 0.8 cc of methanol is added to 3 g of the reaction mixture. The prepolymer can be precipitated from this solution with methanol. This solution can also be used as is for the preparation of laminated products.

Example 7

A mixture of 245 g of diallyl phthalate, 214 g of cyclohexanone, 0.8 g of *p*-toluenesulfonic acid, and 4.8 g of hydrogen peroxide (at 65%) is heated for 15 hours at 65° while stirring. At the end of two, four, six, eight, ten, and twelve hours, one gram of hydrogen peroxide (at 65%) is added each time. After cooling, a viscous yellow liquid is obtained which contains a little water. After evaporating the solution, a solid resin is obtained with a 120% yield (relative to diallyl phthalate used), which allows us to deduce that a certain quantity of cyclohexanone was incorporated during the polymerization. This product can also be used for the preparation of laminated products.

CLAIMS

I. Process for the preparation of solutions which contain, in the dissolved state in a liquid ketone at room temperature, the prepolymerization products of a diallyl phthalate with the formula:

or the coprepolymerization products of such diallyl phthalates with other copolymerizable monomers, in addition to possibly unreacted monomer, and which can be used directly or after preliminary isolation of the prepolymer in the preparation of press-molded shapes and laminated products, said process being remarkable notably by virtue of the following characteristics, considered separately or in combination.

(1) In the presence of a free radical-forming catalyst as well as in the presence of a small quantity of a strong acid as reaction accelerator, a solution of a diallyl phthalate alone or of a diallyl phthalate and another copolymerizable monomer in a liquid ketone at room temperature is reacted with heating.

(2) A lower aliphatic ketone is used as the solvent.

(3) Acetone or methyl ethyl ketone is used as the solvent.

(4) Diallyl *ortho*-phthalate is used as the diallyl phthalate.

(5) Hydrogen peroxide is used as the catalyst.

(6) *p*-Toluenesulfonic acid is used as the reaction accelerator.

(7) The strong acid used as the reaction accelerator is used in the amount of 0.05 to 5% by weight relative to the total weight of the monomer or monomers.

(8) The prepolymerization is carried out in a temperature range of 50°C to 150°C.

(9) The reaction is continued until at least 60% by weight of the monomer initially present in the reaction solution has been converted to the prepolymer.

(10) The reaction is continued until at least 90% of the monomer initially present in the reaction solution has been converted to the prepolymer.

II. New industrial products in the form of solutions of the prepolymerization products of a diallyl phthalate in a liquid ketone at room temperature which are obtained by implementing the process defined above.

Brussels, 23 October 1964

For: CIBA SOCIÉTÉ ANONYME

For: Office PARETTE (Fred. Maes)

SPECIFICATION

Sixteen pages

Additions:

Deletions: