(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 013 691 B9

(12) CORRECTED EUROPEAN PATENT SPECIFICATION
Note: Bibliography reflects the latest situation

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see page(s) 4, 5

(51) Int Cl.⁷: **C08G 63/85**, C08G 63/80, C08G 63/181

(48) Corrigendum issued on:
15.06.2005 Bulletin 2005/24

(45) Date of publication and mention of the grant of the patent:
26.01.2005 Bulletin 2005/04

(21) Application number: **99125390.7**

(22) Date of filing: **20.12.1999**

(54) **Process for the preparation of polyester resin**

Verfahren zur Herstellung von Polyesterharzen

Procédé pour la préparation d'une résine polyester

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

(30) Priority: **23.12.1998 IT MI982803**

(43) Date of publication of application:
28.06.2000 Bulletin 2000/26

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(56) References cited:
EP-A- 0 752 437
US-A- 4 590 259
US-A- 5 334 669

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to an improved process for the production of polyester resin having a high intrinsic viscosity.

[0002] The catalysts normally used in polycondensation of aromatic polyester resin in the molten state are in general compounds of antimony (principally as antimony oxide and antimony triacetate). Catalysts based on germanium oxide are also usable but only in certain cases given the high cost of the catalyst.

[0003] Titanium compounds (in particular titanium alkoxides) have also been proposed as catalysts. These catalysts have a high activity but lead to the formation of polymer with a yellowish colouration and further, have problems of instability due to hydrolysis during synthesis of PET from terephthalic acid. The kinetics of polycondensation of the resin to the solid state is moreover detrimentally affected by the presence of titanium compounds. Because of these disadvantages titanium catalysts have not in practice found application.

[0004] Currently the tendency of the market and the authorities competent for safeguarding the environment is to require ever more insistently a PET having a low content of residual metal catalysts. It is not however in practice possible to reduce the quantity of antimony catalysts because their activity is not very high.

[0005] The use of titanium catalysts is not satisfactory because of their low activity in the solid state polycondensation.

[0006] A necessity therefore exists to have available inexpensive catalysts other than those of antimony, which will not be a health hazard and which will provide good catalytic activity without presenting possible problems of colouration of the polymer.

[0007] Recently titanium dioxide and silica in the ratio Ti/Si of 9:1, and tetraisopropyl (dioctyl) titanate phosphite have been proposed as hydrolysis resistant catalysts having few problems of yellowing when compared to titanium alkoxides. The activity of these catalysts (expressed as ppm by weight of Ti/kg polymer) is very much higher than that obtainable with antimony oxide or triacetate.

[0008] These catalysts also have the serious disadvantage in that their use is, in practice, precluded due to the low kinetics when they are employed for the solid state polycondensation of the resin.

[0009] With respect to antimony catalysts, in the case of PET, the kinetics of solid state polycondensation are about 50% less (for the same conditions).

[0010] EP-A-0 752 437 discloses a solid state polycondensation process of polyester resin in the presence of pyromellitic dianhydride and Sb/Co catalysts.

[0011] US-A-5 334 669 discloses a solid state polycondensation process of polyester resin in the presence of pyromellitic dianhydride without detailing the catalysts used.

[0012] US-A-4 590 259 discloses a solid state polycondensation process of polyester resin with a Ti catalyst and in the absence of any dianhydride of a tetracarboxylic acid.

[0013] It has now been unexpectedly found that it is possible to utilise titanium catalysts in the polycondensation reaction of the polyester resin in the molten state and to obtain kinetics of the solid state polycondensation comparable and possibly better than those of polymers prepared utilising antimony catalysts if the solid state polycondensation is conducted in the presence of a dianhydride of a tetracarboxylic acid, preferably aromatic.

[0014] Pyromellitic dianhydride is preferred. The dianhydrides are added to the polyester resin in quantities of about 0.05 to 2% by weight.

[0015] The solid state polycondensation reaction is effected according to known methods by operating at a temperature between 160° and 230°C for times sufficient to obtain an increase of at least 0.1 dl/g of intrinsic viscosity for the starting resin. The viscosity of the starting resin is in general between 0.4 - 0.7 dl/g. It is, however, possible to start from resins with viscosity lower than 0.4 dl/g, for example, 0.2 - 0.3 dl/g.

[0016] The dianhydride is mixed with the resin in the molten state operating for example in extruders with relatively short residence times (several tens of seconds).

[0017] Polycondensation in the molten state of the polyester resin is achieved according to conventional methods using quantities of titanium catalysts equal to 20-60 ppm by weight of titanium with respect to the polymer.

[0018] Since the catalytic activity of titanium is much higher that that obtainable with antimony catalysts (less ppm of metal per kg of polymer) it is possible to reduce the polycondensation times in the melt for the same ppm of metal used, thus increasing the productivity of the installation.

[0019] Titanium compounds usable as catalysts generally comprise titanium alkoxides, in particular, titanium tetraethoxy, tetrapropoxy and tetrabutoxy, and tetraisopropyl (dioctyl) titanate phosphite and the acetyl acetonates of titanium, such as titanium acetylacetoyl and titanium diacetyl acetoxide and titanium dioxide-silica mixture.

[0020] The polyester resins in the synthesis of which the titanium catalysts are usable are obtained by polycondensation according to known methods from a diol with 2-12 carbon atoms and aromatic dicarboxylic acids preferably terephthalic acid or by transesterification of their lower aliphatic diesters for example dimethyl terephthalate and subsequent polycondensation. Diols usable are for example ethylene glycol, propylene glycol, butylene glycol and 1,4 - cyclohexanedimethylol.

[0021] Preferred resins are polyethylene terephthate and ethylene terephthalic copolymers in which up to 20% by weight of units deriving from terephthalic acid are substituted by units of isophthalic and/or napthalene dicarboxylic acid.
[0022] Polyester resins obtainable with the process of the invention find application in all fields in which polyester resins are normally used. In particular they are used for the preparation of containers by injection blow moulding or extrusion blow moulding and in the preparation of expanded materials.
[0023] In table 1 there are recorded the polycondensation conditions of bis-hydroxyethyl terephthalate (BHET) and the results obtained by using a titanium catalyst (mixture of titanium dioxide and silica; Ti/Si ratio 9:1; C-94 from Akzo Nobel) and an antimony catalyst (antimony triacetate S21 from Atochem).

Table 1

		Test With Antimony	Test With Titanium
Polycondensation Temperature (°C) (Starting value)		267	267
Vacuum (mbar)		1-5	1.0
Polycondensation Time		4h 30'	4h 30'
Final Polycondensation Temperature (°C)		269	270
Quantity of Catalyst (ppm metal)		240	60
Intrinsic Viscosity (dl/g)		0,653	0,673
Activity (IV_f/hrs*ppm Me)		0,000602	0,002481
Activity Ti/Activity Sb		4,123077	-
Terminal Acid Groups Eq/T		13	13.8
Colour	L*	71	76
	a*	-2.86	-2.48
	b*	-1.27	4.73

[0024] From the data of the table it is apparent that the titanium catalyst is four times more active than the antimony catalyst (activity expressed as increment of intrinsic viscosity per ppm of metal per hour of reaction).
[0025] The colour index b* of the polymer obtained with the titanium catalyst is significantly higher than in the polymer containing the antimony catalyst (the disadvantage can however be easily eliminated by adding to the catalyst small percentages of a cobalt compound or other organic colorants).
[0026] In table 2 are recorded the LV. data relating to the solid state polycondensation (195° C in a nitrogen current) of the polymer obtained with the antimony catalyst and that with the titanium catalyst.

Table 2

Time (Hours)	Test With Antimony		Test With Titanium	
	without PMDA	with 0.4%w PMDA	without PMDA	with 0.4%w PMDA
0	0.653	0.653	0.673	0.673
2	0.717	0.804	0.695	0.845
4	0.754	1.020	0.732	0.982
6	0.813	1.328	0.755	1.350

Table 3

	Test With Antimony	Test With Titanium
Polycondensation Temp (°C)	267	267
Vacuum (mbar)	1-2	1-2
Polycondensation Time	4h 15'	5h

Table 3 (continued)

		Test With Antimony	Test With Titanium
Final Polycondensation Temp (°C)		270	270
Quantity of Catalyst (ppm Me)		219	28
Intrinsic Viscosity (dl/g)		0.670	0.655
Activity (IV_f/hrs* ppm Me)		0.000737	0.0046429
Activity Ti/Activity Sb		6.2980011	-
Terminal Acid Groups (Eq/T)		27.20	21.23
Colour	L*	67.74	70.14
	a*	-3.03	-2.92
	b*	-1.52	5.24

Analytical Measurements

[0027] The intrinsic viscosity of the polyester resin was measured in solution of 0.5g of resin in 100ml of 60/40 mixture by weight of phenol and tetrachloroethane at 25°C according to ASTM D4603-86.

Claims

1. A process for the preparation of polyester resins having an intrinsic viscosity greater than 0.7 dl/g starting from resins with an intrinsic viscosity of 0.2-0.7 dl/g obtained by polycondensation of diols with 2-12 carbon atoms and aromatic dicarboxylic acids or by transesterification of the lower alkyl esters of the dicarboxylic acids and subsequent polycondensation, using in the polycondensation phase a catalyst comprising a titanium compound, **characterised in that** the polyester resin obtained from the polycondensation is added with a dianhydride of a tetracarboxylic acid and subsequently subjected to solid state polycondensation to obtain an intrinsic viscosity increase of at least 0.1 dl/g and **in that** the quantity of titanium catalyst is equal to 20-60 ppm by weight of titanium with respect to the polymer.

2. A process according to claim 1, in which the titanium compound is chosen from the group comprising alkoxides of titanium, acetyl acetonates of titanium, dioxides of titanium and titanate phosphites.

3. A process according to claims 1 or 2, in which the dianhydride is the pyromellitic dianhydride.

4. A process according to any of claims 1-3, in which the polyester resin is polyethylene terephthalate and co-polyethylene terephthalate in which up to 20% by weight of units deriving from terephthalic acid are substituted by units deriving from isophthalic and/or naphthalene dicarboxylic acid.

Patentansprüche

1. Verfahren zur Herstellung von Polyesterharzen mit einer inneren Viskosität über 0,7 dl/g, wobei von Harzen mit einer inneren Viskosität von 0,2-0,7 dl/g ausgegangen wird, welche durch Polykondensation von Diolen mit 2-12 Kohlenstoffatomen und aromatischen Dicarbonsäuren oder durch Umesterung der niedrigeren Alkylester der Dicarbonsäuren und anschließende Polykondensation erhalten werden, wobei in der Polykondensationsphase ein eine Titanverbindung umfassender Katalysator verwendet wird, **dadurch gekennzeichnet, dass** zu dem durch Polykondensation erhaltenen Polyesterharz ein Dianhydrid einer Tetracarbonsäure hinzugefügt wird und das Polyesterharz anschließend einer Festphasenpolykondensation unterzogen wird, um einen Anstieg der inneren Viskosität von mindestens 0,1 dl/g zu erhalten, und dass die Menge an Titankatalysator 20-60 Gewichts-ppm Titan, bezogen auf das Polymer, entspricht.

2. Verfahren gemäß Anspruch 1, wobei die Titanverbindung ausgewählt ist aus der Gruppe, umfassend Titanalkoxide, Titanacetylacetonate, Titandioxide und Titanatphosphite.

3. Verfahren gemäß Anspruch 1 oder 2, wobei das Dianhydrid das Pyromellithsäuredianhydrid ist.

4. Verfahren gemäß einem der Ansprüche 1-3, wobei das Polyesterharz Polyethylenterephthalat und Copolyethylenterephthalat ist, bei welchem bis zu 20 Gew.% der von Terephthalsäure abgeleiteten Einheiten durch Einheiten ersetzt sind, die von Isophthal- und/oder Naphthalindicarbonsäure abgeleitet sind.

Revendications

1. Procédé de préparation de résines polyesters ayant une viscosité intrinsèque supérieure à 0,7 dl/g à partir de résines ayant une viscosité intrinsèque de 0,2 - 0,7 dl/g obtenues par polycondensation de diols de 2-12 atomes de carbone et d'acides dicarboxyliques aromatiques ou par transestérification d'esters d'alkyle inférieur d'acides dicarboxyliques, suivie d'une polycondensation, utilisant dans la phase de polycondensation un catalyseur comprenant un composé de titane, **caractérisé en ce que** l'on ajoute à la résine polyester obtenue par la polycondensation un dianhydride d'un acide tétracarboxylique, puis on la soumet à une polycondensation à l'état solide pour obtenir une augmentation de la viscosité intrinsèque d'au moins 0,1 dl/g, et **en ce que** la quantité de catalyseur à base de titane est égale à 20-60 ppm en masse de titane par rapport au polymère.

2. Procédé selon la revendication 1, dans lequel le composé de titane est choisi dans le groupe comprenant des alkylates de titane, des acétylacétonates de titane, des dioxydes de titane et des phosphites de titanates.

3. Procédé selon les revendications 1 ou 2, dans lequel le dianhydride est le dianhydride pyromellitique.

4. Procédé selon l'une quelconque des revendications 1-3, dans lequel la résine polyester est un poly(téréphtalate d'éthylène) et un co-poly(téréphtalate d'éthylène) dans lequel jusqu'à 20 % en masse d'unités dérivées de l'acide téréphtalique sont remplacées par des unités dérivées de l'acide isophtalique et/ou d'acide naphtalènedicarboxylique.