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(21) International Application Number: PCT/IN20 12/000760
(22) International Filing Date: 21 November 2012 (21.11.2012)
(25) Filing Language: English
(26) Publication Language: English
(51) International Patent Classification: C08G 63/85 (2006.01)
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Declarations under Rule 4.17:
— as to the identity of the inventor (Rule 4.17(7))
— as to inventorship (Rule 4.17(iv))

Published:
— without international search report and to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: PROCESS FOR PREPARATION OF POLY-ESTERS AND CO-POLY-ESTERS
(57) Abstract: The present invention provides a process for the preparation of a dispersion containing finely dispersed hydrated TiO2. Further, there are also provided improved processes for solvolysis and polymer synthesis that employ the finely dispersed hydrated TiO2.
FIELD OF DISCLOSURE:
The present disclosure relates to the process of manufacturing of polyester/co-polyester using nano-structured hydrated TiO₂ as a poly-condensation catalyst.

BACKGROUND:
Method to manufacture poly-esters/co-polyester through poly-condensation reaction is well known in the art. The poly-condensation reaction to manufacture poly-esters/co-polyester can be carried out in solid and liquid phase. Poly-condensation reaction of polycarboxylic acids and polyols carried in any phase leads to formation of poly-ester group, the entire process being termed as poly-esterification. The poly-esterification reaction is catalyzed by strong acids.

The catalyst mostly used for liquid phase poly-esterification reaction of polycarboxylic acids and polyols to produce respective poly-esters/co-polyesters are strong mineral acids such as hydrochloric acid, sulfuric acid or aryl sulfonic acids as well as metal salts of strong mineral acids which hydrolyze readily in the presence of water, such as zinc and tin chlorides. Also, antimony based compounds like antimony trioxide, antimonic acid, antimony glycoloxide, antimony triacetate or antimony tri chloride and other commonly used Lewis acids, besides silver, include titanium tetrachloride (TiCl₄); zinc dichloride (ZnCl₂); boron tri fluoride (BF₃); aluminum and alkyl aluminum halides (AlX₃ and RₙAlX₃₋₃), where X= -F,-Cl,-Br or -I; phosphorus and antimony penta fluorides (PF₅ and SbF₅); and tin di and tetrachlorides (SnCl₂ and SnCl₄) are used as poly-condensation catalysts. However, use of strong mineral acids as well as other acids has certain drawbacks associated with them. One of the major drawbacks associated with their use is substantial dehydration of the polyols used in the poly-condensation reactions resulting in lower
yield of poly-ester/co-poly esters. To overcome this problem, higher proportions of poly-
ols are used and this results in higher cost of production.

Another drawback is that the poly-ester and/or co-polyester obtained by making use of
these catalysts are strongly acidic because of the entrapped acid catalyst in the final poly-
esters/co-polyesters. Furthermore, due to the inherent corrosive nature of these materials,
the cost of protecting processing machinery used in the poly-ester/co-polyesters manufact-
uring results in increased cost of production. Still furthermore, on account of excessive
exposure to strong acids, these processes are not very safe for the personnel handling the
manufacturing process.

To overcome the disadvantages associated with the use of these catalysts for the poly-
condensation reactions involving poly-carboxylic acids and polyols, use of titanium com-
ounds have been proposed in the art. The class of titanium compounds used in the art
includes hydrated TiO₂ and titanium salts of hydro halide acids such as TiCl₄ or TiBr₄.
The methods to produce hydrated TiO₂ are well known in the art.

US 3056817A, discloses the use of hydrated TiO₂ as such without dehydro-drying as
poly-condensation catalyst for the poly-esterification reactions. The drawback associated
with this application is that the hydrated TiO₂ produced employing the method described
in the application has an active metal (Ti) content starting from 100 ppm and above based
on the esterifiable acid and the reaction is carried out at elevated temperatures.

US 6451959, discloses the use of hydrated TiO₂, comprising a solid Ti compound, which
is dehydro-dried by heating (either in air or vacuum) as well as dehydrated with the help
of higher boiling solvent than water. For the hydrated TiO₂ to be effective in improving
the properties of the final poly-ester like substantially less colour and improved synthesis
time it is used along with a co-catalyst. The preferable concentration of the Ti atom is be-
tween 1 to 50 ppm based on the weight of the poly-ester and the preferable concentration
of the metal atom present in the co-catalyst is in the range of 1 to 250 ppm based on the
weight of the poly-ester. However, the drawback associated is that, the final poly-ester to exhibit excellent product qualities like substantially less colour in the final poly-ester and reduced synthesis time the use of co-catalyst becomes imperative.

US 3463742, discloses the use of hydrated TiO$_2$, dehydro-dried by washing with a solvent that can take away water (e.g. methanol) as well as dehydro-dried by azeotropic removal of water using azeotropic solvent that has lower boiling point. Further, a colloidal dispersion of the hydrated TiO$_2$ in an appropriate alcohol (e.g. butanol) or an appropriate glycol (e.g. mono ethylene glycol) is disclosed. However, for the invention to provide improved properties to the final poly-ester, like substantially improved colour and reduced synthesis time the concentration of the active Ti atom should be 20000 ppm and above which is a drawback associated with the invention.

OBJECTS:

Some of the objects of the invention are as follows:

To provide a process for the manufacture of poly-esters/eo-polyesters that employs a nano-structured hydrated TiO$_2$ based poly-condensation catalyst.

To provide a process to produce substantially colourless poly-esters/co-poly esters.

SUMMARY:

These and other objects of the invention are to a great extent dealt with the invention herein after disclosed.

In accordance with one of the aspect of the present invention, there is provided a process for synthesis of poly-esters/co-polyesters, comprising charging a reactor with at least one pair of poly-ester/co-polyester forming materials selected from the group of pairs consisting of a 'polyol-dicarboxylic acid' pair, a 'polyol-dicarboxylic ester' pair; subjecting the pair to a method step selected from the group consisting of esterification and ester-interchange reaction in the presence of a catalyst system comprising a combination of a
finely dispersed hydrated TiO$_2$ catalyst, and an antimony based catalyst; wherein the amount of the antimony based catalyst is at least 45% lesser than the amount of antimony based catalyst that is required for carrying out said esterification and ester-interchange reactions, if they were to be carried out using the antimony based catalyst alone, to obtain a poly-ester/co-poly ester.

Typically, the poly-esters/co-poly esters produced by the process of the present invention has L* value greater by at least 3 units than the poly-ester/co-poly ester prepared by using antimony based catalyst alone.

Typically, the poly-esters/co-polyesters produced by the process of the present invention, the antimony based catalyst is antimony trioxide.

According to another aspect of the present invention there is provided a process for solvolysis of poly-esters/co-polyesters, carried out in the presence of finely dispersed hydrated TiO$_2$ and essentially in the absence of zinc based catalysts, to obtain low molecular weight solvolysate and further re-polymerizing the low molecular weight solvolysate wherein, said polyesters/co-polyesters are selected from the group consisting of virgin polyesters and recyclable waste polyesters.

Typically, for the solvolysis of poly-esters/co-polyesters according to the process of the present invention, the zinc based catalyst is zinc acetate.

Typically, the solvent is selected from the group consisting of water, monohydric alcohol and polyol.

Typically, the monohydric alcohol is further selected from the group consisting of methanol, ethanol, propanol and butanol.

Typically, the polyol is further selected from the group consisting of 1,2 ethane diol, 1,3 propane diol, and 1,4 butanediol.
Typically, the amount of finely dispersed hydrated TiO$_2$ as elemental Ti ranges between 6 to 10 ppm; preferably 8 ppm based on weight of polyesters/co-poly esters.

Typically, the dicarboxylic acid is selected from the group consisting of ethanedioic acid, propanedioic acid, butanedioic acid, pentanedioic acid, hexanedioic acid, heptanedioic acid, octanedioic acid, nonanedioic acid, decanedioic acid, undecanedioic acid, dodecanedioic acid, (Ortho-) Phthalic acid, Isophthalic acid, Terephthalic acid, naphthalene 1,6 di carboxylic acid, 4, 4’ bis (diphenyl dicarboxylic acid ) Muconic acid, Traumatic acid, Glutaconic acid, Fumaric acid and Maleic acid.

Typically, the polyol is selected from the group consisting of 1,2 ethane diol, or 1,3 propane diol, or 1,4 butane diol or with cyclo hexane dimethanol, 2 methyl 1,3 propane diol, glycerine, polyethylene glycol, polypropylene glycol, poly (tetramethylene ether) glycol, pentaerythritol, trimethylolethane, trimethylolpropane (tris (1:1:1 tri hydroxy methyl ) propane) , 1,2,6-hexanetriol, sorbitol and inositol.

In accordance with another aspect of the present invention, there is provided a process for preparation of a dispersion containing hydrated TiO$_2$, said process comprising:

« hydrolyzing inorganic titanium compound of formula:

\[
\text{Ti}(X)_{1-4};
\]

wherein X is independently Fluorine or Chlorine or Bromine or Iodine or Astatine, in the presence of an alkali/alkaline earth metal hydroxide solution, to obtain a mixture containing a TiO$_2$ catalyst; and

- obtaining the TiO$_2$ catalyst in different forms, from the mixture by removing respective salts of neutralization.

Typically, the inorganic titanium compound is titanium tetrachloride.

Typically, the TiO$_2$ catalyst obtained is in the form of dispersion.
Typically, the method step further comprises of filtering off the dispersion to obtain a wet cake which is further dispersed in a carrier medium.

Typically, the carrier medium is selected from a group consisting of butanol, ethanol, acetone and mono ethylene glycol.

Typically, the alkali or alkaline earth metalis selected from the group consisting of Lithium, Sodium, Potassium, Rubidium, Caesium, Francium, Beryllium, Magnesium, Calcium, Strontium, Barium, and Radium.

Typically, the poly-ester Poly-ethylene terephthalate (PET) or its copolymer obtained by the process of the present invention is substantially colourless.

DETAIL DESCRIPTION OF THE DISCLOSURE:

A Catalyst is an inherent ingredient which is used in poly-condensation reaction to improve the process parameters or the product properties. Conventional catalysts used in poly-condensation reaction have drawbacks associated with their use namely substantial dehydration of the polyols resulting in lower yield of poly-ester/co-poly esters. Furthermore, some of these catalysts are corrosive in nature, this leads to adverse chemical reaction on the manufacturing vessels. This necessitates replacement of costly manufacturing equipment thereby increasing the maintenance and operation cost. Also, there is a potential danger to the health of the personnel handling these corrosive catalysts.

Thus there is a need to develop catalysts which have improved catalytic efficiency to improve the process efficiency or the final product properties and which are potentially less harmful to the health of the personnel using these catalysts.

The present disclosure envisages the use of nano-structured hydrated TiO₂ based poly-condensation catalyst in combination with antimony based to overcome the drawbacks associated with the use of the conventional catalysts used for the synthesis of poly-esters/co-polyesters. Also, disclosed is a process that employs the said catalyst system to
obtain poly-esters/co-polyesters having improved properties particularly, substantial decrease in the b* value. Besides, the disclosure further discloses the use of nano-structured hydrated TiO₂ for solvolysis of poly-esters/co-polyesters as a standalone catalyst thereby completely obviating the use of zinc based catalysts.

The processes of the present disclosure are disclosed herein below:

A process to synthesize poly-ester/co-polyester in accordance with the present invention comprises charging a reactor with at least one pair of poly-ester/co-polyester forming materials selected from the group of pairs consisting of a 'polyol-dicarboxylic acid' pair, a 'polyol-dicarboxylic ester' pair; subjecting the pair to a method step selected from the group consisting of esterification and ester-interchange reaction in the presence of a catalyst system comprising a combination of a finely dispersed hydrated TiO₂ catalyst, and an antimony based catalyst; wherein the amount of the antimony based catalyst is at least 45% lesser than the amount of antimony based catalyst that is required for carrying out said esterification and ester-interchange reactions, if they were to be carried out using the antimony based catalyst alone, to obtain a poly-ester/co-polyester. The dicarboxylic acid used in the preparation of poly-esters/co-polyesters employing the said catalyst system comprises aliphatic/aromatic saturated, unsaturated and branched chain dicarboxylic acids like ethanedioic acid, propanedioic acid, butanedioic acid, pentanedioic acid, hexanedioic acid, heptanedioic acid, octanedioic acid, nonanedioic acid, decanedioic acid, undecanedioic acid, dodecanedioic acid, (Ortho-)Phthalic acid, Isophthalic acid, Terephthalic acid, naphthalene 1,6 di-carboxylic acid, 4, 4’ bis (diphenyl dicarboxylic acid), Muconic acid, Traumatic acid, Glutaconic acid, Fumaric acid, Maleic acid and the like and the polyols comprises 1,2 ethane diol, or 1,3 propane diol, or 1,4 butane diol or with cyclo hexane dimethanol, 2 methyl 1,3 propane diol, glycerine, polyethylene glycol, polypropylene glycol, poly(tetramethylene ether) glycol, pentaerythritol, trimethylolpropane (tris (1:1:1 tri hydroxy methyl) propane), 1,2,6-hexanetriol, sorbitol, inositol, and the like. The antimony based catalyst used in the pro-
cess of the present invention is antimony trioxide. By using a combination of the catalyst system as disclosed in the present invention, poly-ester/co-poly ester with L* value greater by at least 3 units are synthesized. Further, these poly-esters/co-polyesters have better optical properties.

Another process disclosed is a process for solvolysis of poly-esters/co-poly esters. The solvolysis of poly-esters/co-polyesters is carried out in the presence of finely dispersed hydrated TiO$_2$ and essentially in the absence of zinc based catalysts, to obtain low molecular weight solvolysate. The low molecular weight solvolysate is further re-polymerized. The polyesters/co-polyesters are selected from the group consisting of virgin polyesters and recyclable waste polyesters. As described, the process is carried out in the absence of zinc based catalyst, typically zinc acetate. The solvent used for the process of solvolysis is selected from the group consisting of water, monohydriz alcohol and polyol. Typically, the monohydrizic alcohol is selected from the group consisting of methanol, ethanol, propanol and butanol and the polyol is selected from the group consisting of 1, 2 ethane diol, 1, 3 propane diol, and 1, 4 butanediol. The amount of finely dispersed hydrated TiO$_2$ as elemental Ti ranges between 6 to 10 ppm; preferably 8 ppm based on weight of polyesters/co-poly esters.

The finely dispersed hydrated TiO$_2$ is prepared by a process by hydrolyzing inorganic titanium compound of formula:

$$\text{Ti (X)}_{1.4}^+$$

wherein X is independently Fluorine or Chlorine or Bromine or Iodine or Astatine, in the presence of an alkali/alkaline earth metal hydroxide solution, to obtain a mixture containing a TiO$_2$ catalyst which, can be obtained in different forms, from the mixture by removing respective salts of neutralization. The inorganic titanium compound used for the present invention is titanium tetrachloride. Preferably, the TiO$_2$ catalyst obtained is in the form of dispersion which is filtered off to obtain a wet cake which is further dispersed in
a carrier medium selected from a group consisting of butanol, ethanol, acetone and monoethylene glycol. The alkali or alkaline earth metal which is used in the form of hydroxide solution is selected from the group consisting of Lithium, Sodium, Potassium, Rubidium, Caesium, Francium, Beryllium, Magnesium, Calcium, Strontium, Barium, and Radium.

The poly-ester/co-polyester formed in accordance with the process of the present invention is substantially colourless.

TECHNICAL ADVANCEMENT:
- Produce substantially colourless poly-esters, especially Poly-ethylene terephthalate (PET).
- Partial or full replacement of antimony based catalyst which is environmentally hazardous with a more benign Ti based catalyst.
- Desired product properties is possible at very low concentration (1 to 8 ppm) of the active metal (Ti) atom content in the Ti based catalyst, making the production process economical and environment friendly.

The details of the invention will further be explained by the way of examples which do not limit the scope of the invention. The individual components in the formulations as given in the examples are maintained in ppm and percentage by weight unless otherwise specified.

Example-1: Preparation of cataSyst-1.

The reaction of TiCl₄ and calcium hydroxide was carried out in water. Calcium hydroxide (28 gm) was dissolved in 500 ml water and to it was added 20 ml TiCl₄ over a period of 30 minutes. The reaction mixture was then allowed to settle for approximately 60 minutes. The settled solid was then filtered, washed several times with water at room temperature till the chloride content was found to be nil. The wet slurry was then dispersed in mono ethylene glycol (MEG).
The weight % of Ti was analyzed by spectrophotometric method and calcium content by AAS method. The product solution was referred to as catalyst-1. The results are tabulated in Table-1.

<table>
<thead>
<tr>
<th>No</th>
<th>Calcium content</th>
<th>Titanium content</th>
<th>Water content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst-1</td>
<td>750 ppm</td>
<td>20,000 ppm</td>
<td>26</td>
</tr>
</tbody>
</table>

Table-1: Analysis of catalyst-1.


Monoethylene glycol (MEG) (22.2kg) and purified terephthalic acid (PTA) (51.6 kg) (1:1.15 molar ratios) were esterified under nitrogen pressure of 1.7 kg/cm² and at a temperature of 260°C. At the end of poly-esterification process, 610 ml of 20% TiO₂ slurry was added. Further, 18 gm of catalyst slurry from Example-1 was then added at the end of poly-esterification process and the reaction mixture was transferred to a poly-condensation reactor where vacuum was applied gradually till the final vacuum of around 1mm Hg was obtained in 45 min. The temperature was gradually increased to around 285°C. As the reaction progressed, increase in the torque (up to 0.5Nm) was observed due to viscosity build-up, and the power of the agitator was increased accordingly. The vacuum supply to the reactor was stopped after a reaction time of 95 min was reached as indicated by corresponding rise in the torque. The reactor was further pressurized with nitrogen and polymer was drained as strands and quenched in water bath. The strands were then cut into chips in a pelletizer, which were further dried to remove moisture. The obtained chips were then analyzed for molecular weight distribution, intrinsic viscosity, end group analysis and DSC. The polymer thus obtained was used as a control.

Example-3: Polyester manufactured using Sb₂O₃ as a catalyst (290 ppm) and used as a control.

Monoethylene glycol (MEG) (22.2kg) and purified terephthalic acid (PTA) (51.6 kg) (1:1.15 molar ratios) were added to the poly-condensation reactor. The Catalyst slurry of
antimony trioxide in mono ethylene glycol (MEG) was (total antimony concentration 290 ppm as Sb) added to the slurry and the poly-esterification reaction was carried out under nitrogen pressure of 1.7 kg/cm² and at temperature of 260°C. At the end of poly-esterification process, 610 ml of 20% TiO₂ slurry was added. The oligomer thus obtained was then transferred to the poly-condensation reactor. Vacuum was applied slowly to the poly-condensation reactor till the final vacuum of around 1mm Hg was obtained in 45 min. The temperature was gradually increased to around 285°C. As the reaction progressed, the viscosity increased due to polymerization, hence correspondingly the torque (about 0.5Nm) and power of the agitator was increased. After a certain reaction time (as given in table-2) there was a rise in torque. The vacuum was then removed at a specific torque value and the reactor was further pressurized with nitrogen. Polymer thus obtained was drained as strands and quenched in water bath. The strands were then cut into chips in a pelletizer, which were further dried to remove moisture. The chips were measured for their intrinsic viscosity, (L, a, b) values and molecular weight distribution and labeled as control polyester. The strands were further cut and the results are tabulated in Table-2.

Example 4: Polyester manufactured in the presence of both cataSyst-1 with half the amount of antimony trioxide (2 ppm Ti and 150 ppm antimony)

Monoethylene glycol (MEG) (22.2kg) and purified terephthalic acid (PTA) (51.6 kg) (1:1.15 molar ratios) were added to the poly-condensation reactor. The Catalyst slurry of antimony trioxide in MEG (total antimony concentration 150 ppm as Sb) was added to the slurry and the poly-esterification reaction was carried out under nitrogen pressure of 1.7 kg/cm² and at a temperature of 260°C. At the end of poly-esterification reaction the catalyst as obtained in Example-1, (6 gms) in 610ml of 20% TiO₂ slurry was added. The reaction mixture obtained was then transferred to the poly-condensation reactor maintained under vacuum till the final vacuum of around 1mm Hg was obtained in 45 min. The temperature was gradually increased to around 285°C. As the reaction progressed, the viscosity increased due to polymerization; hence torque (about 0.5Nm) and power of the agitator were correspondingly increased. After a certain reaction time (as given in ta-
ble-2) there was a rise in the torque. Vacuum supply to the poly-condensation reactor was then removed after a specific torque value was obtained and the reactor was further pressurized with nitrogen. The polymer obtained was drained as strands and quenched in water bath. The strands were then cut into chips in a pelletizer, which were further dried to remove moisture. The dried chips were then measured for their intrinsic viscosity, (L, a, b) values and molecular weight distribution and used as a control polyester. The strands were later cut and the results tabulated in Table-2.

<table>
<thead>
<tr>
<th>Example No.</th>
<th>Catalyst</th>
<th>Composition</th>
<th>Time for Melt poly-condensation (Minutes)</th>
<th>$\eta_r$ [dl/g]</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Catalyst-1</td>
<td>6ppm</td>
<td>107</td>
<td>0.629</td>
<td>80.3</td>
<td>-0.4</td>
<td>6.6</td>
</tr>
<tr>
<td>3</td>
<td>Control: antimony</td>
<td>290ppm</td>
<td>101</td>
<td>0.610</td>
<td>76.7</td>
<td>-0.8</td>
<td>5.2</td>
</tr>
<tr>
<td>4</td>
<td>Catalyst-1 + antimony</td>
<td>2ppm + 150ppm</td>
<td>104</td>
<td>0.635</td>
<td>79.8</td>
<td>-0.8</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Table-2: Properties of the polymer chips.

MELT SPINNING OF THE CHIPS

Exaimple-5&6:

Polyethylene terephthalate chips (PET chips) prepared in examples-3 and 4 were melt extruded at a temperature of 283 to 290° C to obtain filaments or fibers (130/36 POY). The processing parameters applied for the melt spinning were as follows:

- quench air temperature of 19°C,
- quench air velocity of 0.42 m/s,
The mechanical properties of the filaments prepared were studied in terms of their tenacity and elongation. The results of these studies are tabulated in Table-3 below.

<table>
<thead>
<tr>
<th>Spinning parameters</th>
<th>Example-5: Spinning of polymer chips manufactured in Example-3, using antimony catalyst (290 ppm)</th>
<th>Example-6: Spinning of polymer chips manufactured in Example-4, using catalyst-1 (2 ppm and antimony (Sb)-150ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winding Speed (mpm)</td>
<td>2900</td>
<td>2900</td>
</tr>
<tr>
<td>Draw Tension</td>
<td>28.8</td>
<td>29.7</td>
</tr>
<tr>
<td>Tenacity (gpd)</td>
<td>2.56</td>
<td>2.55</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>151.3</td>
<td>147</td>
</tr>
</tbody>
</table>

Table-3: Properties of partially oriented yarn (POY) spun from the polymer chips.

It is evident from Table-3 that the mechanical properties of filament yarn prepared in example-5 and 6 are comparable.

Example-7: Depolymerization or Glycolization

The initiation of the process is with a heel of virgin PTA and MEG under normal polyesterification conditions. Popcorn waste and lump waste of polyesters/co-polyesters were added (about 5.64 kg (94% popcorn + 6% lump waste) out of the batch size of 55kg) to-
wards the end of poly-esterification reaction to initiate their de-polymerisation along with zinc-acetate as a catalyst. An additional 30 min hold time was provided before transferring the oligomers formed to the poly-condensation reactor. Also, in the poly-condensation step, apart from Sb catalyst and 0.30% TiO$_2$, blue toner KP-32 was added.

Example-8: Depolymerization or Glycoliziation

The initiation of the process is with a heel of virgin PTA and MEG under normal poly-esterification conditions. Popcorn waste and lump waste of polyesters/co-poly esters were added (about 5.64 kg (94% popcorn+ 6% lump waste) out of the batch size of 55kg) towards the end of poly-esterification to initiate their de-polymerization along with Ti catalyst. An additional 30 min hold time was provided before transferring the oligomers formed to the poly-condensation reactor. Further, in the poly-condensation step 0.30% TiO$_2$, and blue toner KP-32 was added.

<table>
<thead>
<tr>
<th>Process recipe &amp; conditions</th>
<th>Example-7</th>
<th>Example-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst, ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>De-polymerization catalyst= zinc acetate-105ppm, Polymerization catalyst = Sb$_2$O$_3$-250 ppm</td>
<td>De-polymerization catalyst= Ti-8ppm, Polymerization catalyst= nil</td>
</tr>
<tr>
<td>BlueToner (KP-32), ppm</td>
<td>15</td>
<td>7</td>
</tr>
<tr>
<td>Optical Brightner,(OB)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TiO$_2$, (%)</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Estimated Temp, °C</td>
<td>260</td>
<td>260</td>
</tr>
<tr>
<td>Estimate Time, (min)</td>
<td>333</td>
<td>321</td>
</tr>
<tr>
<td>Polymerization Time, (min)</td>
<td>132</td>
<td>137</td>
</tr>
<tr>
<td>Polymerization Temperature, °C</td>
<td>290</td>
<td>290</td>
</tr>
</tbody>
</table>
Final vacuum, mm Hg | 0.07 | 0.07
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer chip properties:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intrinsic viscosity (I.V.), dl/g</td>
<td>0.625</td>
<td>0.633</td>
</tr>
<tr>
<td>L*</td>
<td>64.0</td>
<td>68.7</td>
</tr>
<tr>
<td>a*</td>
<td>-1.7</td>
<td>-2.6</td>
</tr>
<tr>
<td>b*</td>
<td>-4.3</td>
<td>3.6</td>
</tr>
<tr>
<td>-COOH, meq/kg</td>
<td>21</td>
<td>18</td>
</tr>
<tr>
<td>Number of polymer chips per gram of sample</td>
<td>76</td>
<td>79</td>
</tr>
</tbody>
</table>

Table-4: De-polymerization or Glycolization with different catalysts.

From the table it is evident that 8 ppm of Ti catalyst has replaced both 105 ppm of depolymerization catalyst, zinc acetate and 250 ppm of Sb₂O₃ at comparable reactivity. Also, an improvement in L* colour value of 4.7 units is obtained but with some compromise on b* color value, which is taken care of by addition of optical brightener during the spinning process.

CHARACTERIZATION OF POLYMER CHIPS:

1. Intrinsic viscosity: The intrinsic viscosity of the polymer samples was determined in 1,1,2,2-tetrachloroethane/phenol 40/60 wt% mixed solution at 25±1 0.1 °C using a Ubbelohde viscometer. About 0.125 g of chips was dissolved in 25 ml of solvent mixture. (The concentration was -0.5 % by weight) The I.V. was obtained from the measurement of relative viscosity η_r for a single polymer concentration (0.5%) by using the Billmeyer equation (see F.W. Billmeyer, J. of Polymer Sci. IV, 83 (1949) shown below. I.V.= [η] = 0.25 (η_r - 1 + 3 ln η_r)/c (valid for the range c = 0.5 - 0.65 g/dl)
2. End-group analysis: Samples of the polymer or fiber (-0.5 g) were dissolved in
25 ml of o-cresol at 100-110°C and the solution was further diluted with chloro-
form. The carboxyl terminal groups were determined by titration at room tempera-
ture using methanolic KOH (0.02 N) and bromo phenol blue as indicator. The val-
ues were expressed as mg of KOH per gram of sample.

3. Colour: Hunter Lab Color Flex (Model No 45/0, serial No. CX 0969) was used
for colour measurements. The colour of the transparent amorphous chips were
categorized using the CIE tri-stimulus L*, a* and b* values. L* indicates the
brightness of the samples, with a high value signifying high brightness, L* = 100
stands for perfectly white; L* = 0 is perfectly black. The, a* value indicates the
greenness or redness of the sample (- value indicates greenness; + value indicates
redness). The b* value indicates blueness or yellowness (- value indicates blue; +
indicates yellow).
Claims:

1. A process for synthesis of poly-esters/co-polyesters, comprising charging a reactor with at least one pair of poly-ester/co-poly ester forming materials selected from the group of pairs consisting of a 'polyol-dicarboxylic acid' pair, a 'polyol-dicarboxylic ester' pair; subjecting the pair to a method step selected from the group consisting of esterification and ester-interchange reaction in the presence of a catalyst system comprising a combination of a finely dispersed hydrated TiO₂ catalyst, and an antimony based catalyst; wherein the amount of the antimony based catalyst is at least 45% lesser than the amount of antimony based catalyst that is required for carrying out said esterification and ester-interchange reactions, if they were to be carried out using the antimony based catalyst alone, to obtain a poly-ester/co-poly ester.

2. A process as claimed in claim 1, wherein the L* value of the poly-ester/co-polyester is greater by at least 3 units than the poly-ester/co-polyester prepared by using antimony based catalyst alone.

3. A process as claimed in claim 1, wherein the antimony based catalyst is antimony trioxide.

4. A process for solvolysis of poly-esters/co-polyesters, carried out in the presence of finely dispersed hydrated TiO₂ and essentially in the absence of zinc based catalysts, to obtain low molecular weight solvolysate and further re-polymerizing the low molecular weight solvolysate wherein, said polyesters/co-polyesters are selected from the group consisting of virgin polyesters and recyclable waste polyesters.

5. A process as claimed in claim 4, wherein the zinc based catalyst is zinc acetate.
6. A process as claimed in claim 4, wherein the solvent is selected from the group consisting of water, monohydric alcohol and polyol.

7. A process as claimed in claim 6, wherein the monohydric alcohol is further selected from the group consisting of methanol, ethanol, propanol and butanol.

8. A process as claimed in claim 6, wherein the polyol is further selected from the group consisting of 1, 2 ethane diol, 1, 3 propane diol, and 1, 4 butanediol.

9. A process as claimed in claims 1 and 4, wherein the amount of finely dispersed hydrated TiO$_2$ as elemental Ti ranges between 6 to 10 ppm; preferably 8 ppm based on weight of polyesters/co-poly esters.

10. A process as claimed in all of the preceding claims, wherein the dicarboxylic acid is selected from the group consisting of ethanedioic acid, propanedioic acid, butanedioic acid, pentanedioic acid, hexanedioic acid, heptanedioic acid, octanedioic acid, nonanedioic acid, decanedioic acid, undecanedioic acid, dodecanedioic acid, (Ortho-Phthalic acid, Isophthalic acid, Terephthalic acid, naphthalene 1 6 di carboxylic acid, 4, 4' bis (diphenyl dicarboxylic acid ) Muconic acid, Traumatic acid, Glutaconic acid, Fumaric acid and Maleic acid.

11. A process as claimed in all of the preceding claims, wherein the polyol is selected from the group consisting of 1,2 ethane diol, 1,3 propane diol, 1,4 butane diol, cyclo hexane dimethanol, 2 methyl 1,3 propane diol, glycerine, polyethylene glycol, polypropylene glycol, poly (tetramethylene ether) glycol, pentaerythritol, trimethylethelane, trimethylolpropane (tris (1:1:1 tri hydroxy methyl ) propane), 1,2,6-hexanetriol, sorbitol and inositol.

12. A process as claimed in all of the preceding claims, wherein the finely dispersed hydrated TiO$_2$ is prepared by a process comprising:

a) hydrolyzing inorganic titanium compound of formula:
Ti (X)_{1-4};

wherein X is independently Fluorine or Chlorine or Bromine or Iodine or Asta-tine, in the presence of an alkali/alkaline earth metal hydroxide solution, to obtain a mixture containing a TiO₂ catalyst; and

b) obtaining the TiO₂ catalyst in different forms, from the mixture by removing respective salts of neutralization.

13. A process as claimed in claim 12, wherein the inorganic titanium compound is titanium tetrachloride.

14. A process as claimed in claim 12, wherein the TiO₂ catalyst obtained is in the form of a dispersion.

15. A process as claimed in claim 14, further comprising the method step of filtering off the dispersion to obtain a wet cake which is further dispersed in a carrier medium.

16. A process as claimed in claim 15, wherein the carrier medium is selected from a group consisting of butanol, ethanol, acetone and mono ethylene glycol.

17. A process as claimed in claim 12, wherein the alkali or alkaline earth metal is selected from the group consisting of Lithium, Sodium, Potassium, Rubidium, Caesium, Francium, Beryllium, Magnesium, Calcium, Strontium, Barium, and Radium.