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(54) Process of centrifugally removing inorganic compounds from polyester glycol recovery bottoms

Verfahren zur Zentrifugalentfernun von anorganischen Verbindungen aus Rückständen der Glykolrückgewinnung aus Polyestern

Procédé pour la séparation par centrifuge de composés minéraux de résidus de la récupération de glycols à partir de polyesters

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(56) References cited:
US-A-4 013 519
US-A-4 046 688

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Description

The present invention relates to a process for removing inorganic compounds from polyester glycol recovery bottoms formed as a by-product in the manufacture of poly(ethylene terephthalate) using a centrifuge to separate the inorganic compounds from the bottoms. This process improves not only the removal of inorganic compounds, but also provides for insolubilizing inorganics, such as antimony, and then centrifugally removing the resulting antimony precipitate. In particular, the process includes forming the glycol recovery bottoms by distilling spent glycol produced as a by-product of polyester to have a solids concentration of from 15% to 45% by weight, and centrifuging the glycol recovery bottoms to remove the inorganic compounds. In addition to the centrifugal removal of inorganic compounds, the addition of a precipitating reagent to the glycol recovery bottoms before the centrifuging of the glycol recovery bottoms insolubilizes other inorganic compounds which can also be centrifugally removed. In particular, it has been found that adding a mole ratio of about 2 P/Sb as phosphoric acid before centrifuging permits the removal of antimony and increases the amount of removal of TiO₂.

Prior Art

Poly(ethylene terephthalate) (PET) is a commercial film and fiber forming polyester which is generally manufactured by reacting a lower dialky ester of a dicarboxylic acid such as dimethyl terephthalate (DMT) with a molar excess of ethylene glycol (EG) in the presence of a catalyst (such as compounds of manganese, zinc, calcium, magnesium, for example). A dehydrating agent such as TiO₂ is also added. These components undergo ester interchange to yield bis(hydroxyethyl)terephthalate (BHET) and methanol. Phosphorus is preferably added to sequester the ester interchange catalyst. Alternatively, BHET may be produced by the direct esterification of terephthalic acid (TA) also with an excess of ethylene glycol (EG). The BHET is then polymerized by a polycondensation reaction in the presence of a suitable polymerization catalyst (such as an antimony compound). From this reaction PET and spent ethylene glycol are formed. Because the polycondensation reaction is reversible, the excess spent glycol is removed as it is evolved, thus forcing the reaction toward the formation of the polyester. Large quantities of spent ethylene glycol distillate, hereinafter "spent glycol", are produced during the polymerization reaction.

Unfortunately, the spent glycol contains impurities which make it unsuitable, as is, for the manufacture of PET or for other uses such as the production of polyols, polyurethane foams, and unsaturated polyester resins, etc. For instance, a typical spent glycol contains mostly ethylene glycol, along with various quantities of diethylene glycol, water, polyester oligomers, and inorganic compounds. Contained in the inorganic organic compounds are titanium dioxide, phosphorus, and about 10 to 500 ppm of antimony. Accordingly, it is standard practice in the industry to purify the spent glycol, recovering distilled glycol and reusing the recovered glycol in the manufacture of PET. A by-product of this purification is a mass known in the industry as polyester glycol recovery bottoms, in which is contained inorganic compounds. The inorganics are concentrated 30 to 50 times in the bottoms by the ethylene glycol recovery process. The presence of some inorganic compounds such as antimony compounds or titanium dioxide makes the by-product unusable. Removal of these inorganic compounds has proved troublesome to date.

In prior art processes, the spent glycol is passed through a light-ends removal column (water stripper column) under reduced pressure and at a column top temperature of about 75°C. The glycol is then fractionally distilled in one or more columns or in flash or thin-film evaporators under vacuum conditions, ranging from about 20 to 200 mm mercury absolute pressure and at a temperature of from about 130-160°C. The glycols including ethylene and diethylene glycol are recovered from the spent glycol as a overhead steam. The glycols are further distilled to separate the ethylene glycol from the diethylene glycol. In a typical distillation 90 to 95% by weight of the ethylene glycol present in the spent glycol is recovered in the overhead stream, the balance remaining in the bottoms and dehydrated to diethylene glycol.

As the glycols are fractionally distilled, most of the residual impurities remain in the bottom of the column or the evaporator taking the form of a waxy granulated mass and will be referenced to as "glycol recovery bottoms or bottoms". A typical bottom includes about 98% terephthalate esters and glycols (ethylene and diethylene) and about 2% of inorganic compounds of Sb and P including TiO₂.

The terephthalate ether and diethylene glycol of the polyester bottoms are known to have commercial applications in markets including polyol/polyurethane and unsaturated polyester resins which use crude terephthalate streams as raw materials. However, specifically the inorganic compounds of Sb and TiO₂, have been found intolerable in such applications. No known problem has ever been associated to date with phosphorus in downstream end uses. Without such commercial applications, polyester glycol recovery bottoms containing these inorganic compounds require disposal by burying or incinerating. However, antimony is known to be highly toxic. The Environmental Protection Agency (EPA) has taken the position that the presence of antimony constitutes an environmental and subsequent health hazard. A maximum acceptable limit of 5 PPM of antimony has been established by the EPA for effluent discharged into a waterway. A problem with incinerating polyester bottoms is the high volatility of antimony oxides. Pretreating for burying or incinerating to mitigate antimony-related problems becomes enormously expensive.
The following references are directed to various methods for purifying spent glycol and methods of separating the inorganic impurities from the glycol recovery bottoms.

U. S. Patent 2,788,373 to Mills, Jr. et al discloses a process for recovering ethylene glycol from spent glycol using an acid to precipitate out soluble solid matter. In particular, the spent glycol is first diluted with water and a mineral acid such as phosphoric acid is added to precipitate out soluble solid matter usually terephthalate salts. The precipitated solid matter is removed by decantation or filtration.

U. S. Patent 4,013,519 to Happer et al discloses recovering antimony from the polyester bottoms by alkaline hydrolysis, acidification and filtration to remove antimony sulfide precipitate from spent glycol. Such a process is disclosed to remove terephthalic acid from the polyester bottoms without contamination by the antimony. The uncontaminated terephthalic acid can be recycled for polyester manufacture or other use.

U. S. Patent 4,046,688 to Cunningham et al discloses a process to recover dissolved antimony using a strong acid and/or a strong base in an ion exchange resin to absorb the antimony. This process is done after the spent glycol has been filtered to remove suspended solids.

U. S. Patent 4,100,253 to Dougherty et al discloses a process to recover antimony from spent glycol by incineration.

In particular, the polyester bottoms are incinerated to produce an ash and then the ash is contacted with water to form an ash-water from which the antimony compounds can be recovered.

U. S. Patent 4,118,582 to Walker discloses a process to recover antimony from spent glycol by precipitating the antimony with an alkali metal borohydride. The process can be enhanced by adding a strong inorganic base.

Improvements which remove just antimony but not titanium dioxide, for example, partially solves the foregoing problem. However, one goal of the present invention is to remove both the antimony and titanium dioxide.

There remains a need to develop a process for the purification of polyester glycol recovery bottoms which minimizes the problems of disposal of the polyester bottoms so the polyester bottoms can be recycled for other uses. Especially desired is an improved process wherein contaminates present in glycol recovery bottoms, such as antimony and titanium dioxide can be economically removed.

Summary of the Invention

The present invention provides a process which is effective and economical in purifying polyester glycol recovery bottoms by separating out solid inorganic precipitates from the bottoms using a centrifuge. Furthermore, the present invention uses phosphoric acid as the precipitating agent in the glycol recovery bottoms and uses the precipitating agent in specific amounts and in a unique manner so as to insolubilize inorganics including antimony for precipitation as well as improve the removal of other inorganic compounds. In particular, the present invention comprises distilling the spent glycol to form polyester glycol recovery bottoms having a specific solids concentration, then centrifuging the glycol recovery bottoms to remove the inorganic compounds. A precipitating agent i.e. phosphoric acid, is added to the glycol recovery bottoms before centrifuging to form an inorganic precipitate that can be removed by centrifuging.

Furthermore, according to the present invention inorganic compounds are removed from polyester glycol recovery bottoms which include, in addition to the inorganic compounds, polyester materials, terephthalate esters and glycols. The polyester glycol bottoms are formed in the recovery of spent glycol produced as a by-product in the manufacture of polyester to which inorganic compounds are added, wherein the spent glycol contains glycol, terephthalate esters and the inorganic compounds, and the spent glycol has a solids concentration of less than 5% by weight. The improvement of the present invention comprises the steps of: distilling the spent glycol to form the glycol recovery bottoms such that the glycol recovery bottoms having a solids concentration of from 15 to 45% by weight, preferably 20 to 35% by weight; and centrifuging the glycol recovery bottoms to remove the inorganic compounds. The flow rate of the glycol recovery bottoms into the centrifuge is preferably from 1 gal/min to 20 gal/min (3.8 l/min to 76 l/min).

In the foregoing process, phosphoric acid is added as the precipitating reagent to the glycol recovery bottoms before centrifuging to precipitate the inorganics (which include antimony and titanium dioxide) which is then removed by centrifuging. It is preferred that the mole ratio of the phosphorus of the phosphoric acid to antimony is from about 1.0 to about 3.0.

Brief Description of the Drawing

Figure 1 depicts a flow sheet of a specific embodiment of the process of this invention.
Figure 2 shows various graphs illustrating the relationship of TiO₂ removal and feed rate.
Figure 3 shows a graph illustrating the relationship of antimony removal and the mole ratio of phosphorus to antimony.

Figure 4 shows a graph illustrating the relationship of TiO₂ removal and the mole ratio of phosphorus to antimony.
Description of the Preferred Embodiments

A typical spent glycol formed as a by-product in a commercial poly(ethylene terephthalate) manufacturing plant contains about 70 to 97% by weight ethylene glycol, 0.5 to 1% by weight diethylene glycol, up to 3% by weight terephthalate oligomers, up to 25% by weight water, and inorganic compounds including about 50-500 ppm antimony, in the form of dissolved organic antimony compounds, up to 200 ppm titanium in the form of titanium dioxide (TiO2), and up to about 200 ppm phosphorus in the form of phosphorous or phosphoric acid or their organic esters, and trace quantities of other contaminants. Distillation procedures, such as fractional and flash distillation, are conventionally used to remove water and other low-boiling materials from the spent glycol and recover most of the ethylene glycol present in the spent glycol.

In accordance with the present invention, inorganic compounds present in the glycol are rendered insoluble, if required, and then centrifugally removed after the spent glycol has been distilled to from glycol recovery bottoms having a solids concentration of from 15% to 45% by weight to allow for the efficiency of centrifuging during the removal of the inorganic compounds.

The spent glycol is first passed through a light-end distillation column where all low-boiling components are removed, including water which may be present in amounts up to 25% by weight. This column generally operates under a vacuum of about 250 mm mercury absolute pressure (33 kPa) with column top temperature of about 75°C.

After the water and other low-boiling materials have been removed from the spent glycol, the spent glycol is transferred to a second distillation column or an evaporator wherein the spent glycol is distilled at a vacuum of about 175 mm mercury absolute pressure (23 kPa) and a temperature from 130°C to 150°C to remove a certain portion of ethylene glycol such that the residual product referenced herein as glycol recovery bottoms has a solids concentration from 15% to 45% by weight. Within the specified solids concentration range, the resulting glycol recovery bottoms contains ethylene glycol, diethylene glycol, and solids including the terephthalate oligomers and the inorganic compounds.

The glycol recovery bottoms are then transferred to a storage tank and phosphoric acid as the precipitating reagent is added under controlled conditions. The precipitating agent is generally added to the hot glycol recovery bottoms in the storage tank.

Intimate mixing of the glycol recovery bottoms and precipitating reagent is important, both as they are brought together and during the course of the reaction. Reaction efficiency suffers unless there is intimate mixing of the components. For that reason, the spent glycol is continuously agitated during the course of mixing the precipitating agent with the spent glycol.

The chemical equation for the reaction of trivalent antimony with phosphoric acid is

\[ \text{Sb}_2\text{O}_3 + 2\text{H}_3\text{PO}_4 \rightarrow 2\text{SbPO}_4 + 3\text{H}_2\text{O} \]

By stoichiometric principles, one mole of phosphorus will react with one mole of antimony. Under the prescribed ratio of 1:1 of P to Sb, about 50% of the dissolved antimony compound can be precipitated as antimony phosphate. When the mole ratio of P to Sb was increased to about 2:1, up to 90% or more of the dissolved antimony compounds can be precipitated. Figure 3 illustrates the relationship of the percent antimony removal to the mol ratio of P/Sb. As shown by the graphs, the antimony removal percentage levels off dramatically when the mole ratio exceeds 2:1. The data basis for the graph is contained in the subsequent Example 3.

The glycol recovery bottoms containing the precipitated antimony in addition to the other inorganic compounds is then fed into a centrifuge for the removal of the inorganic precipitates. The present invention is directed to the removal of titanium dioxide and the antimony precipitate. Each of these inorganic contaminates can be removed individually or in combination. By processing through the centrifuge, the inorganic contaminates are concentrated in an "underflow" which is then collected.

Centrifuges suitable for use in the present invention generally have feed rates dependent on the centrifuge capacity, are rotatable at rpm from 3000 to 6600 rpm and have a variable overflow/underflow ratio, generally from about 80/20 to about 95/5 being preferred. All centrifuge processes result in an "underflow" or a "cake" or a cut of material which is being centrifuged out as unwanted material. The size or fraction of the underflow is controllable, but is found to be dependent of the centrifuging efficiency of the overflow or the mainstream.

Reduction of underflow to as low as possible is desirable. Some centrifuges are designed to recirculate the underflow to further remove the insolubles. Increase in the overflow/underflow ratio directly affects the amount of contaminant removed. For example, in the case of removing only precipitates such as TiO2 from the spent glycol, it was found that for an overflow/underflow ratio of 33/67, 98% removal of the TiO2 could be attained at a feed rate of 1.5 gal/min (5.7 l/min). For an overflow/underflow ratio of 50/50, 89% removal rate would occur at 2 gal/min (7.6 l/min). For an overflow/underflow ratio of 80/20, a 53% removal could be attained at a feed rate of 5 gal/min (18.9 l/min), a 31% removal at a feed rate of 7.5 gal/min (28.4 l/min) and only a 15% removal at a feed rate of 10 gal/min (37.9 l/min). For an overflow/underflow ratio of 90/10, only 14% removal rate could be attained at a feed rate of 5 gal/min (18.9 l/min). In view of
the dependency of the removal rate and flow rate, the ratio of overflow/underflow is dependent on the processing rate and the economics of removing the inorganic compounds versus disposal of the underflow.

When phosphoric acid is added to precipitate the antimony, it was surprisingly found the percentage of TiO₂ removal increased. In particular, it was found that in excess of 99% TiO₂ removal was achieved when a molar ratio of P/Sb was about 2:1 and the centrifuge was operated at about 2.45 gal/min (9.3 l/min), and an overflow/underflow of about 80/20. Without the phosphoric acid, only about 75% by weight of the TiO₂ was removed as shown in Figure 2.

The centrifuged precipitate can be further processed to recover usable materials. For example, the recovered antimony can be oxidized, in a furnace, for instance, to convert it to antimony oxide. The claimed antimony oxide may be recycled for reuse. Incineration also allows for the recovery of the TiO₂ which remains in the ash product.

After centrifuge treatment of the glycol recovery bottoms to remove the inorganic contaminants, the overflow is further distilled to recover as much ethylene glycol as is possible for the manufacture of PET. The deposit of still bottoms contains the remaining impurities including terephthalate esters and glycols. The still bottoms absent the inorganic contaminant are of commercial value and can be sold to the polyol/polyurethane industry and the unsaturated polyester resin industry.

Experimental Procedure

A specific embodiment of the process of the present invention is depicted by 10 in Figure 1 and may be generally performed as follows:

- Spent glycol taken from the manufacture of poly(ethylene terephthalate) containing by weight about 76% ethylene glycol, 0.7% diethylene glycol, 2.0% oligomers, 20.3% water and 1% inorganic compounds including antimony, titanium and phosphorus compounds was fed into a distillation column 12 wherein the water and other low-boiling impurities are removed from the spent glycol. Feed rate into the column was about 25 gal/min (95 l/min). Removal occurred at a head temperature of about 75°C and under a vacuum at about 250 mm mercury absolute pressure (33 kPa).

- The spent glycol was then fed into a flash evaporator 14 wherein glycol is removed at a head temperature of about 140°C and under a vacuum of about 175 mm mercury absolute pressure (23 kPa) such that the remaining glycol recovery bottoms reaches a solids concentration between about 15 and 45% by weight. The glycol recovery bottoms are then transferred to an atmospheric storage tank 16 wherein phosphoric acid is added to the glycol recovery bottoms. The tank 16 is heated to about 140°C and continuously agitated.

- From the storage tank, the glycol recovery bottoms are fed into a Dorr-Oliver Model PC-9 centrifuge 18 wherein the insoluble inorganic compounds are separated from the glycol recovery bottoms. Testing of the glycol bottoms for remaining inorganic compounds can be performed at this point. Subsequent to the centrifuging, the centrifuge overflow is fed into a thin-film evaporator 20 wherein additional glycols are separated from the bottoms. The glycol streams from both evaporators are sent to a fractionating column 22 operated under reduced pressure where the purified ethylene glycol is taken off as overhead stream and diethylene glycol is taken off as a side stream.

Example 1 (comparative)

Various centrifuge parameters were employed to demonstrate the present invention for removal of the inorganic contaminant titanium dioxide. Throughout the 9 experiments, the glycol recovery bottoms fed from the storage tank to the centrifuge contained from 64% to 72% by weight ethylene glycol, 5% diethylene glycol, solids as designated which include the inorganic contaminants.

Experiment 1 employs an overflow/underflow ratio of 90/10, a flow rate of 5 gal/min (18.9 l/min) and a solids concentration of the spent glycol of about 22%.

Experiments 2 and 3 were similar to Experiment 1 except the overflow/underflow ratio was held at 85/15 and the solids concentration was 27% and the flow rate was varied.

In Experiments 4-6, the solids concentration was 23% by weight and the overflow/underflow ratio was 80/20 while the flow rates varied from 10 to 5 gal/min (37.9 to 18.9 l/min).

Experiments 7 was similar to Experiment 1 except the overflow/underflow ratio was 75/25, flow rate was 3.6 gal/min (13.6 l/min).
Similarly, Experiments 8 and 9 varied all three parameters.

<table>
<thead>
<tr>
<th>Table I</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>% Solids Concentration</td>
</tr>
<tr>
<td>Overflow/underflow ratio</td>
</tr>
<tr>
<td>Flow Rate (gal/min)</td>
</tr>
<tr>
<td>TiO₂ In Feed (ppm)</td>
</tr>
<tr>
<td>Overflow (ppm)</td>
</tr>
<tr>
<td>% Removal</td>
</tr>
</tbody>
</table>

The % TiO₂ removal using the centrifuge is shown in Figure 2. Clearly shown are the highest rates of removal of TiO₂ are attained at low overflow/underflow ratios, low flow rates and solids concentration of about 30%.

Example 2

Various precipitating reagents were employed to demonstrate those suitable for precipitating out antimony from a glycol slurry. To a solution of glycol-solubilized antimony containing about 200 ppm Sb, is added at 90°C an excess of each reagent listed in Table II.

<table>
<thead>
<tr>
<th>Table II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitating Reagent</td>
</tr>
<tr>
<td>Trimethyl Phosphate</td>
</tr>
<tr>
<td>Tridecyl Phosphate</td>
</tr>
<tr>
<td>Sodium Bisulfite</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
</tr>
<tr>
<td>Phosphoric Acid</td>
</tr>
</tbody>
</table>

From these results, it is clear that phosphoric acid outperformed the other precipitating reagents.
Example 3

Various mole ratios of phosphorus to antimony were employed to demonstrate the preferred ratio. In Experiments 1 and 5 (controls), no phosphoric acid was added to a antimony-containing glycol slurry. Experiments 2 and 6 used a mole ratio of about 0.8, Experiments 3 and 7 about 1.6, Experiments 4 and 8, 2.35 and 2.6 respectively and Experiment 9 a mole ratio of 3.85.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/Sb mole ratio</td>
<td>0</td>
<td>0.77</td>
<td>1.56</td>
<td>2.35</td>
<td>0</td>
<td>0.76</td>
<td>1.60</td>
<td>2.60</td>
<td>3.85</td>
</tr>
<tr>
<td>% Sb Removal</td>
<td>0</td>
<td>43</td>
<td>82</td>
<td>87</td>
<td>0</td>
<td>35</td>
<td>68</td>
<td>79</td>
<td>81</td>
</tr>
</tbody>
</table>

The results of Example 3 are shown in Figure 3. The graphs clearly show that antimony removal continues to increase beyond the stoichiometric ratio of 1:1 up to about 2:1 where the removal rate dramatically levels off.

Example 4

Various levels of phosphoric acid were employed to demonstrate the unexpected synergism created by adding the phosphoric acid to remove both the titanium and antimony. In these experiments, phosphoric acid was added to the spent glycol prior to the centrifuge. The glycol was fed at 2.45 gal/min (9.3 l/min) into a centrifuge having an overflow/underflow ratio of 80/20 and operating at 4800 rpm.

Experiments 1, 2 and 3 contained only trace amounts of phosphoric acid while experiments 4 and 5 contained more than 2 mole ratio of P/Sb.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>P/Sb Ratio</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
<td>&gt;2.0</td>
<td>&gt;2.0</td>
</tr>
<tr>
<td>%TiO2 Removal</td>
<td>97.5</td>
<td>94</td>
<td>99.7</td>
<td>100</td>
<td>99.2</td>
</tr>
<tr>
<td>%Sb Removal</td>
<td>6</td>
<td>11</td>
<td>18</td>
<td>85</td>
<td>98.4</td>
</tr>
</tbody>
</table>

Surprisingly, in experiments 4 and 5 the removal rates of the TiO2 increased to nearly 100% while the %Sb removal remained good. These results were illustrated in Figure 4.

Thus, it is apparent that there has been provided in accordance with the invention, a method of removing inorganic contaminants from recovery polyester bottoms using a centrifuge that fully satisfies the objects, aims and advantages as set forth above.

Claims

1. A process for producing recyclable polyester glycol recovery bottoms by removing inorganic compounds from polyester glycol recovery bottoms, said inorganic compounds including antimony and titanium dioxide and said recovery bottoms including, in addition to the inorganic compounds, polyester materials, terephthalate esters and glycols, said polyester glycol recovery bottoms formed in the recovery of spent glycol produced in the manufacture of polyester to which inorganic compounds are added, wherein the spent glycol contains glycol, terephthalate esters and inorganic compounds, said spent glycol having a solids concentration of less than 5% by weight, which process comprises essentially of the steps of:

a) distilling the spent glycol to obtain, as a bottoms product, the polyester glycol recovery bottoms such that the glycol recovery bottoms have a solids concentration of from 15% to 45% by weight;
b) adding phosphoric acid to the glycol recovery bottoms in sufficient quantity to precipitate out any solubilized inorganic compounds; and
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c) centrifuging said glycol recovery bottoms with a centrifuge to remove the inorganic compounds leaving recyclable polyester glycol recyclable bottoms.

2. The process of claim 1 wherein the glycol recovery bottoms is distilled to have a solids concentration of from 20 to 35% by weight.

3. The process of either of claims 1 and 2 wherein the flow rate of the glycol recovery bottoms into the centrifuge is from 1 gal/min to 20 gal/min (3.8 l/min to 76 l/min).

4. The process of claim 3 wherein the centrifuge has an overflow/underflow ratio from 33/67 to 95/5.

5. The process of claim 4 wherein the centrifuge has an overflow/underflow ratio from 80/20 to 95/5.

Patentansprüche

1. Verfahren zur Herstellung recyclingfähiger Polyester-Glycolrückgewinnungssäfte durch Entfernen anorganischer Verbindungen aus Polyester-Glycolrückgewinnungssäften, wobei zu den anorganischen Verbindungen Antimon und Titandioxid gehören und die Rückgewinnungssäfte neben den anorganischen Verbindungen Polystematerialien, Terephthalatester und Glycole umfassen, wobei die Polyester-Glycolrückgewinnungssäfte bei der Rückgewinnung verbrauchten Glycols gebildet werden, das bei Herstellung von Polyester entsteht, zu dem anorganischen Verbindungen hinzugefügt werden, wobei das verbrauchte Glycol eine Feststoffkonzentration von weniger als 5 Gew.-% hat, wobei das Verfahren im wesentlichen die Schritte umfaßt:

a) Destillieren des verbrauchten Glycols, wobei man als Sumpfprodukt die Polyester-Glycolrückgewinnungssäfte erhält, so daß die Glycolrückgewinnungssäfte eine Feststoffkonzentration von 15 bis 45 Gew.-% haben;

b) Hinzufügen von Phosphorsäure zu den Glycolrückgewinnungssäften in einer ausreichenden Menge, um alle gelösten anorganischen Verbindungen auszufallen; und

c) Zentrifugieren der Glycolrückgewinnungssäfte mit einer Zentrifuge, um die anorganischen Verbindungen zu entfernen, wobei recyclingfähige Polyester-Glycolrückgewinnungssäfte zurückbleiben.

2. Verfahren gemäß Anspruch 1, wobei die Glycolrückgewinnungssäfte so destilliert werden, daß sie eine Feststoffkonzentration von 20 bis 35 Gew.-% haben.

3. Verfahren gemäß einem der Ansprüche 1 und 2, wobei die Fließgeschwindigkeit der Glycolrückgewinnungssäfte in die Zentrifuge 1 gal/min bis 20 gal/min (3,8 l/min bis 76 l/min) beträgt.


5. Verfahren gemäß Anspruch 4, wobei die Zentrifuge ein Überlauf/Unterlauf-Verhältnis von 80/20 bis 95/5 hat.

Revendications

1. Procédé de production d'un résidu de polyesterglycol de récupération recyclable par élimination de composés inorganiques d'un résidu de polyesterglycol de récupération, lesdits composés inorganiques comprenant de l'antimoine et du dioxyde de titane et ledit résidu de récupération comprenant, en plus des composés inorganiques, des polyesters, des esters téraphtaliques et des glycols, ledit résidu de polyesterglycol de récupération étant formé lors de la récupération du glycol épaisé engendré dans la production d'un polyester auquel des composés inorganiques sont ajoutés, dans lequel le glycol épaisé contient du glycol, des esters téraphtaliques et des composés inorganiques, ledit glycol épaisé ayant une concentration en matières solides inférieure à 5 % en poids, Procédé qui comprend essentiellement les étapes consistant :

a) à distiller le glycol épaisé pour obtenir, comme produit résiduaire, le résidu de polyesterglycol de récupération de telle sorte que le résidu de glycol de récupération ait une concentration en matières solides de 15 % à 45 % en poids ;

b) à ajouter de l'acide phosphorique au résidu de glycol de récupération en une quantité suffisante pour séparer par précipitation tous les composés inorganiques solubilisés ; et
c) à centrifuger le résidu de glycol de récupération au moyen d’une centrifugeuse pour éliminer les composés inorganiques en laissant le résidu de polyster glycol recyclable.

2. Procédé suivant la revendication 1, dans lequel le résidu de glycol de récupération est distillé pour parvenir à une concentration en matières solides de 20 à 35 % en poids.

3. Procédé suivant chacune des revendications 1 et 2, dans lequel la vitesse d’écoulement du résidu de glycol de récupération dans la centrifugeuse est comprise dans l’intervalle de 1 gallon/min à 20 gallons/min (3,8 l/min à 76 l/min).

4. Procédé suivant la revendication 3, dans lequel la centrifugeuse a un rapport courant de débordement/courant de soutirage de 33/67 à 95/5.

5. Procédé suivant la revendication 4, dans lequel la centrifugeuse a un rapport courant de débordement/courant de soutirage de 80/20 à 95/5.
FIG. 1

FIG. 2

% TiO₂ REMOVAL

OVERFLOW/UNDERFLOW RATIO

FEED RATE (GAL/MIN)

85/15 90/10 80/20 50/50 33/67