

The invention is concerned with an improved process for the recovery of terephthalates of alkali metals or alkaline earth metals or of terephthalic acid and of-alkylene glycol by saponification of a polyalkylene terephthalate. The invention is concerned, more particularly, with the continuous production of terephthalates of alkali metals or alkaline earth metals from polyalkylene terephthalates.

The invention permits improved recycling of polyalkylene terephthalate waste originating, for example, from films, fibres or used bottles. The process of the invention furthermore permits the recovery of alkylene glycol with good purity for re-use.

Alkaline saponification of polyalkylene terephthalate in solution is described in the prior art (see, for example, patents US-A- 3.317.519 and US-A- 3.544.622); it is usually carried out in solution diluted in water or in glycol, usually under pressure.

In the patent application FR-A-2.672.049, the filers described a process for the manufacture of alkali metal or alkaline earth metal terephthalate by heating polyalkylene terephthalate with an alkali metal hydroxide or alkaline earth metal hydroxide in the absence or presence of water.

It has now been discovered that it is possible to carry out saponification, by means of an alkali metal hydroxide or an alkaline earth metal hydroxide, of polyalkylene terephthalate, with neither solvent nor diluent, in the molten state, whilst removing all the alkylene glycol formed, the alkali metal or alkaline earth metal terephthalate recovered being obtained in powder form.

Unexpectedly, it has been discovered that the saponification reaction between a polyalkylene terephthalate and an alkali metal or an alkaline earth metal hydroxide initiated by heating the mixture of reagents beforehand to a temperature of between 60 and 250°C happened by itself, without additional heating. The polyterephthalate continues to react until the end of the reaction, without even stirring, in order to form a product which is soluble in water, without any trace of the initial polymer.



The main advantage of the process of the invention is that it permits the continuous production of an alkali metal or alkaline earth metal terephthalate compound in powder form, and permits the removal of the stage for recovery of the alkylene glycol in purifying waters. The powdery solid obtained is easy to store, to transport and to re-dissolve subsequently in aqueous phase with a view to purifying it, and, if required, of converting it to terephthalic acid or ester.

The removal of alkylene glycol in gaseous form prior to dissolving the alkali metal terephthalate facilitates purification of this latter by dissolving, in particular, certain colorants and products which are soluble in alkylene glycol.

In the prior art, the glycols resulting from saponification were either extracted from the solution, with the aid of a solvent, following filtration of the terephthalic acid, or were salted out by saturating the solution by increasing the salinity of the medium, or were otherwise sent to the sewage treatment plant. These methods amounted to an additional operation which was costly in terms of reagents, equipment and time. The process according to the invention makes it possible to remove the glycol formed without supplying any additional reagent, either by entrainment using an inert gas, or by extraction at reduced pressure during the saponification reaction, thereby simplifying the desired outline of the production of alkali metal or alkaline earth metal terephthalate.

In the face of the prior art, the process according to the invention permits the treatment of polyester waste in small, non-localised, simple industrial units and subsequent collection of the saponification products, constituted mainly by mono- and di-alkali metal or alkaline earth metal terephthalates coming from different sources, in order to treat them in one and the same industrial installation, in order to purify them and to convert them into reusable terephthalic acid or ester by polycondensation. An operation of this kind is carried out in two separate stages and permits a reduction in investment and in collection and transportation costs for the plastics waste.

The process according to the invention enables alkali metal and alkaline earth metal terephthalates to be obtained industrially and more economically from which high purity

terephthalic acid or ester can be formed. The process proves itself to be particularly worthwhile for film, fibres or polyethylene terephthalate (PET) bottle recycling.

The process according to the present invention theoretically consists in carrying out saponification using an alkali metal or an alkaline earth metal hydroxide, without either solvent or diluent, in the molten state, the reaction being initiated by continuously passing a solid mixture of polyterephthalate and alkali metal or alkaline earth metal hydroxide into a heated kneader-extruder which is especially designed to remove vapours, and/or being carried out outside that first kneader-extruder, in a thermally controlled chamber, stirred and kept at a reduced pressure in order to remove the glycol formed, the glycol also being able to be entrained by a current of inert gas, but operating at a higher temperature.

Generally speaking, the process of the invention can be defined by the fact that

- a) the initial composition comprising mainly polyalkylene terephthalate is mixed with an alkali metal or an alkaline earth metal hydroxide **which is in practice anhydrous** in the absence of solvent;
- b) the mixture obtained is heated, said mixture being at least in part in the molten state, in order to initiate saponification of the polyalkylene terephthalate;
- c) the alkylene glycol formed during the saponification reaction is removed; and
- d) the alkali metal or alkaline earth metal terephthalate is collected in the form of a powdery product.

The process of the invention will be described in greater detail hereinafter.

The polyalkylene terephthalate which may be in the form of film, fibre or bottle waste is previously ground or shredded and mixed thoroughly with an alkali metal or an alkaline earth metal hydroxide in powder, granule, chip or pellet form, these reagents being metered in such a way that the alkali metal or alkaline earth metal reagent is in stoichiometric proportion or slightly in excess of the carboxylic groups of polyalkylene terephthalate. The reagents are introduced, e.g. by force of gravity, into a **reactor which can be a kneader-extruder operating** continuously.

In the case of a continuous kneader-extruder, introducing reagents at the start of the kneading chamber permits advantage to be taken of the entire duration of the residence time in the kneader. Without departing from the scope of the invention, it is also possible to introduce all or some of the reagents later or at different places.

The introduction throughput is variable and is a function of the reaction conditions, the size and type of kneader-extruder and the residence time of the reagents necessary to initiate saponification. Usually, it is between 50 and 10,000 kg/h with a kneader-extruder of 5 inches x 36 inches taken by way of reference.

By employing the hysteresis effect an additional advantage is obtained with the process of the present invention in being able to achieve very high throughput in a kneader-extruder reactor of small volume by initiating saponification and by inducing continuation of the reaction through to completion, **this latter** being able to be carried out in simplified equipment by virtue of **exploiting** the exothermic nature of the reaction.

Mixing and homogenisation of the reagents which are necessary in order to initiate saponification is done at a temperature of between 60 and 250°C, and preferably of between 100° and 200°C, and more specifically of between 120° and 160°C, in order to avoid the formation of secondary degradation products.

More particularly, the reaction takes place at a satisfactory speed of about 150°C, and it is preferable to control the temperature by circulation of **liquid** coolant. The reactor is supplied with a mixture of polyalkylene terephthalate (in particular, P.E.T.) and hydroxide (in particular, sodium) using a metering device.

Mixing in the kneader-extruder reactor can be carried out using various arrangements of blades along two parallel shafts rotating in the same or different directions within a double-screw kneader-extruder. Usually, making a wise selection with respect to the arrangement of the blades involves, firstly, at the intake to the mixing chamber, self-cleaning endless screws to ensure the introduction of **reagents** which are supplied by force of gravity, and secondly

various types of mixing-, forward motion-, shearing- and delay blades to provide optimum mixing, homogenisation and kneading capability suited to the saponification process.

According to one preferred embodiment of the invention, saponification is initiated by associating heating and **the hysteresis effect on the mixture** of polymer **and of** alkali metal or alkaline earth metal hydroxide. Depending on the degree of hysteresis, the temperature of **the mixture** is increased by the mechanical working, thereby making it possible to **utilise the energy produced by working the material** and to reduce the residence time in the kneader-extruder reactor.

According to one variant of the process, the alkylene-glycol is removed continuously from the kneader-extruder reactor at reduced pressure and/or by entrainment by means of an inert gas, possibly nitrogen, then condensed by cooling.

According to another variant of the process, at the outlet from the kneader-extruder reactor, the reaction mixture is degassed, **the glycol being removed at reduced pressure and/or by entrainment by means of an inert gas current**; the vapours of the glycol formed are **then** condensed. This second stage of the process of the invention is preferably carried out by keeping the mixture issuing from the kneader-extruder reactor at a temperature of between 50° and 200°C for a period of time which is sufficient to produce saponification, e.g. from 5 to 30 minutes. That step can be carried out by passing the mixture into a single-screw reactor or onto a heated conveyor or otherwise into a chamber which enables the temperature to be maintained and the glycol formed to be collected.

By way of illustration, the output of the kneader-extruder reactor communicates with a **sealed heating chamber equipped with a double-screw**, by the intermediary of a sealed distributor. The mixture continues to react; the glycol is extracted at reduced pressure **and/or by entrainment**. The residence time in that screw can be between 10 minutes and 2 hours. Output of the finished product can be done by a sealed extractor. The terephthalate obtained can then be stored, or, in the case of an alkali metal terephthalate, placed in aqueous solution for subsequent purification. According to one particular embodiment of the process of the invention, the initiation or start of the saponification reaction is carried out in a kneader-

extruder with two co-rotating screws, and the reaction takes place in a powder kneader, which can be equipped with a screw or with "Z-shaped" arms, in a current of inert gas in order to entrain the glycol formed which is condensed outside the reactor.

The continuous removal, preferably at reduced pressure, of the glycol formed during saponification constitutes another improvement according to the invention; it allows more complete saponification to be obtained in comparison with prior art methods of operation, and it allows the reaction speed to be increased. In this way, 95% or more, by weight, of the polyterephthalate is converted into terephthalic acid salt.

Unlike prior art processes which produce **diluted solutions of alkali metal or alkaline earth metal terephthalates**, the process according to the invention makes it possible to obtain terephthalates in concentrated state, in the form of a powdery solid which is easier to store and transport.

Another major advantage of the process according to the invention is its reduced sensitivity to any other polymers which may be present, such as polyolefins or polyvinylchloride, mixed with the polyterephthalate. Therefore, the process of the invention is particularly suitable for recycling PET waste from ground or shredded used bottles or flasks.

During the saponification of the polyterephthalate waste coming from packaging, films, fibres or bottles, various other impurities can be present, such as fillers, additives, colorants, wrappings, labels, etc. The process of the invention makes it possible to separate all these impurities by dissolving the saponification product in water and by filtering the aqueous solution, possibly with one or more adsorbents, before acidifying the aqueous solution in order to precipitate the terephthalic acid.

The following examples are given by way of illustration and in no way limit the present invention.

EXAMPLE 1

56 kg/h of PET chips of shredded film (average particle size approximately 4 x 1.5 cm; apparent density approximately 0.10) and 28 kg/h technical quality caustic soda pellets, these flow rates enabling the PET/Na OH weight ratio to be kept constant to about 2, is added continuously, by means of two volumetric metering devices, into a 5" x 36" (15kw) kneader-extruder manufactured by AOUSTIN under licence from READCO, and comprising two endless screws which rotate in the same direction and a temperature controlled oil circulation heating system for the body of the kneader. The temperature of the oil circulating in the two-layer casing of the kneader is between 150 and 160°C at the beginning and is reduced to 120-130°C as soon as the state of equilibrium is reached. The revolutionary speed of the double screw is 70 revs/min. Under these conditions, the average residence time of the material within the mixer is estimated at 6 minutes. A sample of the material taken from the product issuing from the kneader-extruder indicates a saponification rate of more than 60%.

This product is then degassed at reduced pressure (10mmHg) in order to remove the ethylene glycol formed, and it is kept at a temperature of between 80 and 130°C for 30 minutes by passing it over a conveyor in a heating tunnel.

In this way, a powdery solid is obtained which is mainly constituted by mono- and di-sodium terephthalate. The final saponification rate is greater than 97 per cent, whilst all the PET used is converted.

EXAMPLE 2

In the same apparatus as that of Example 1, and adopting a similar procedure, 235 kg/h of chipped PET waste in the form of fine grains (a few mm) of apparent density 0.6 and 110 kg/h of pelleted caustic soda is treated. Under these conditions, all things being equal in other respects to Example 1, the residence time of the material within the mixer is less than 2 minutes, the saponification rate obtained under these conditions being approximately 40 per cent.

The product coming from the kneader-extruder with double co-rotating screws is then introduced into a 4.5 m continuous single screw kneader which is kept at a temperature of approximately 150°C and which is swept with a current of nitrogen in order to entrain the vapours of the ethylene glycol formed which are also condensed and recovered.

The powdery solid produced is poured into an excess of water in order to obtain an aqueous solution diluted (e.g. 140 g/l) with sodium terephthalates. This solution is passed into a column containing active carbon; it is then acidified in sulphuric acid in order to obtain a pH value of approximately 2.5 to 3. The terephthalic acid which precipitates is filtered and washed in water, then dried.

The conversion of PET into terephthalic acid is greater than 97 per cent, and the purity of the acid obtained is greater than 99.5 per cent, **that acid being, for all intents and purposes, able to be used as an acid of polymeric quality.**

EXAMPLE 3

As in Examples 1 and 2, 38.6 kg/h caustic potash and 54 kg/h PET pellets coming from shredded used bottles and containing approximately 10 per cent, by weight, polyethylene and polyvinylchloride is treated. The rotational speed of the screws is 200 revs/min.

The saponification rate obtained under these conditions, all things being equal in other respects, and calculated with respect to the weight of PET used, is above 50 per cent at the outlet from the double-screw kneader-extruder, and above 95% after a treatment according to the same operating mode as in Example 2.

EXAMPLE 4

2000 kg ground PET polyester from films are cold mixed in a band mixer with 926 kg sodium at a minimum of 98%, that is to say approximately 10% above the stoichiometric quantity.

The mixture of reagents is fed by means of a metering device into a double-screw kneader-extruder which has been preheated to 150°C, the outlet is connected by a rotary obturator to a double Archimedes screw in a closed, thermally controlled chamber, in which the product stays for 1/2 hour - the whole being placed under vacuum - the outlet of the chamber passes via a sealed obturator in order to maintain the vacuum inside the chamber.

The device for metering the initial mixture is started; as soon as the kneader-extruder has reached a temperature of 150°C, the reaction takes place and the circulation of oil is regulated in such a way that the temperature does not exceed 150°. As soon as the endless screw is fed, a vacuum in the order of 20 mm of Hg is applied. The glycol distils and the sodium terephthalate is converted into a very fluid, non-sticky powder which is free of glycol. This glycol is recovered by condensation, and is of sufficient purity for use in liquid coolants.

The yields observed in relation to the PET contained in the initial product are as follows:

Extract of sodium terephthalate	2150 kg	(yield: 98 per cent)
Ethylene glycol	601 kg	(yield: 93%).

CLAIMS

1. A process for the recovery of an alkali metal or alkaline earth metal terephthalate from a composition mainly comprising a polyalkylene terephthalate, characterised in that
 - a) the initial composition is mixed with an alkali metal or alkaline earth metal hydroxide, which is in practice anhydrous, in the absence of solvent;
 - b) the mixture obtained is heated, said mixture being at least in part in the molten state, in order to initiate saponification of the polyalkylene terephthalate;
 - c) the alkylene glycol formed during the saponification reaction is removed; and
 - d) the alkali metal or alkaline earth metal terephthalate is collected in the form of a powdery product.
2. A process according to Claim 1, characterised in that all the operations are carried out discontinuously or continuously.
3. A process according to Claim 1 or Claim 2, characterised in that the saponification reaction is initiated in a reactor which employs the hysteresis effect and the subsequent temperature increase of the mixture.
4. A process according to one of Claims 1 to 3, characterised in that the initial mixture is passed into a kneader-extruder reactor where it undergoes a transfer of thermal energy by the effect of hysteresis, the saponification reaction thus initiated being carried out with or without heating inside or outside said kneader-extruder reactor.
5. A process according to one of Claims 1 to 4, characterised in that the saponification reaction is initiated by introducing a solid mixture of polyalkylene terephthalate and of alkali metal or alkaline earth metal hydroxide into a kneader-extruder reactor with or without double co-rotating screws.



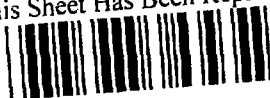
6. A process according to one of Claims 1 to 5, characterised in that the initial mixture continuously supplies a kneader-extruder reactor with double co-rotating screws with an arrangement of entry-, mixing-, forward motion-, shearing- and delay blades which permit homogenisation and heating of the reaction mixture sufficient to initiate the saponification process.
7. A process according to one of Claims 1 to 6, characterised in that the temperature for initiating the saponification reaction is between 60 and 250°C.
8. A process according to one of Claims 1 to 7, characterised in that the alkylene glycol formed during the saponification reaction is continuously removed.
9. A process according to one of Claims 1 to 8, characterised in that the alkylene glycol formed is removed by entrainment means by means of an inert gas and/or by extraction at reduced pressure.
10. A process according to one of Claims 1 to 9, characterised in that the alkylene glycol formed is removed at least in part from the kneader-extruder reactor.
11. A process according to one of Claims 1 to 10, characterised in that the polyalkylene terephthalate is a polyethylene terephthalate (PET).
12. A process according to one of Claims 1 to 11, characterised in that the initial polyalkylene terephthalate is constituted by packaging, film, fibre or bottle waste.
13. The powdery alkali metal or alkaline earth metal product obtained at the end of a process according to one of Claims 1 to 12.
14. Use of the product defined in Claim 13 or obtained at the end of a process according to one of Claims 1 to 12, for the manufacture of terephthalic acid or terephthalic ester of polymeric quality.

ABSTRACT

A description is given of an improved process for the recovery of alkali metal or alkaline earth metal terephthalate and of alkylene glycol, from polyalkylene terephthalate, in particular from polyethylene terephthalate (P.E.T.), the alkylene glycol, in particular the ethylene glycol, being produced in the form of vapour during the saponification reaction initiated by the action of intensive kneading of the polyalkylene terephthalate and alkali metal reagent mixture at a temperature of between 100° and 200°C. The alkylene glycol is recovered in gaseous form by entrainment by an inert gas or by extraction at reduced pressure. The alkali metal terephthalate or alkaline earth metal terephthalate is obtained in solid and powdery form; it can be easily stored, transported and re-dissolved in order to be purified and then possibly converted into terephthalic acid or ester.

THIS SHEET HAS BEEN
REPLACED

This Sheet Has Been Replaced



30 OCT 1998

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PROCESS FOR RECOVERY OF ALKALI METAL OR ALKALI EARTH METAL
TEREPHTHALATE AND ALKYLENE GLYCOL FROM ALKYLENE
POLYTEREPHTHALATES

The invention is concerned with an improved process for the recovery of terephthalates of alkali metals or alkaline earth metals or of terephthalic acid and of alkylene glycol by saponification of a polyalkylene terephthalate. The invention is concerned, more particularly, with the continuous production of terephthalates of alkali metals or alkaline earth metals from polyalkylene terephthalates.

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It has now been discovered that it is possible to carry out saponification, by means of an alkali metal hydroxide or an alkaline earth metal hydroxide, of polyalkylene terephthalate, with neither solvent nor diluent, in the molten state, whilst removing all the alkylene glycol formed, the alkali metal or alkaline earth metal terephthalate recovered being obtained in powder form.

Unexpectedly, it has been discovered that the saponification reaction between a polyalkylene terephthalate and an alkali metal or an alkaline earth metal hydroxide initiated by heating the mixture of reagents beforehand to a temperature of between 60 and 250°C happened by itself, without additional heating. The polyterephthalate continues to react until the end of the reaction, without even stirring, in order to form a product which is soluble in water, without any trace of the initial polymer.

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REPLACEMENT SHEET

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