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(54) PROCESS FOR DRYING POLYESTERS

(71) We, HOECHST AKTIENGESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a process and an apparatus for crystallizing and drying polyethylene terephthalate.

Prior to being processed into fibers, sheets or other shaped structures, polyethylene terephthalate, which is generally obtained in the form of amorphous granules, must be dried very carefully. If it is not so dried, the sensitivity of the polyester to hydrolyze at elevated temperature, especially in the molten state gives rise to degradation reactions whereby the mechanical properties are deterimentally affected.

In industry, polyethylene terephthalate is customarily dried by heating the granules and the emerging moisture is carried off by a gas current as rapidly as possible. In such a process the drying temperature is necessarily above the second order transition temperature of the polyester (about 80°C) and therefore the amorphous polyethylene terephthalate is transformed into the crystalline state. When, however the amorphous material is heated above the second transition temperature, it tends to become sticky and agglomerates are formed and, therefore, special measures are required to overcome this agglomeration problem.

Many proposals have been made to overcome the difficulties arising from the agglomeration of the polyester granules. According to the process described in US Patent 3,014,011, crystallization is brought about prior to drying by the action of swelling agents, steam or hot water. This process has the drawback that the removal of the solvents used as swelling agent is rather problematical or, in the case of hot water or steam being used, the subsequent drying becomes more expensive because of the necessity to remove the additional absorbed water. According to German Offenlegungsschrift 1,770,410, the polyester is crystallized while kept in constant motion in an oscilliating apparatus or in the crystallization zone of a reactor, which is not described in detail, whereby the molecular weight is increased. In another process the polyester is crystallized in a fluidized bed and agglomeration is avoided by adding 50% of crystallized material (German Auslegungschrift 1,454,834 and U.S. Patent 3,305,532). In German Patent 1,182,153 the flow properties of the granules is maintained by strong fluidization, while in the process of U.S. Patent 3,547,890, agglomeration is avoided by effecting crystallization in a crystallization zone while stirring and drying in a continuously operating apparatus in a series of zones. The main disadvantage resides, however, in the fact that the granules are deformed by the mechanical strain in the plastic state. It has also been proposed to dry polyethylene terephthalate granules with the addition of anti-blocking agents, optionally with simultaneous mechanical agitation. In German Offenlegungsschrift 1,694,456, the chips are prevented from agglomerating by adding from 100 to 1,000 ppm of magnesium stearate with slow temperature increase and according to German Offenlegungsschrift 2,124,203 agglomeration is prevented by adding TiO_2. A similar process is described in German Offenlegungsschrift 2,352,426 in which drying is performed in a weakly agitated fluidized bed in the presence of magnesium or aluminium stearate.

Hence, the known processes allow drying

of polyethylene terephthalate granules but they are affected with disadvantages in that large apparatuses and the expenditure of large amounts of energy are required or substances are added which are sometimes little suitable for the intended use of the polyester and in many cases an additional deformation use of the granules by the action of mechanical forces in the plastic state cannot be avoided.

It has now been found that certain amorphous polyester granules can be crystallized and dried in one process step.

The present invention provides a process for crystallizing and drying granules of amorphous polyethylene terephthalate by treating the granules of the said polyester material with hot gases at a temperature of from 120 to 190°C, the hot gases passing through a cylindrical layer of loose polyester granules, which process comprises crystallizing and drying the polyethylene terephthalate in a single process step in such a manner that a fluidised bed is not formed, that the said layer is not moved and that, under the action of the hot gases, the cylindrical layer of loose polyester granules agglomerates to a cylindrical block, destroying the said cylindrical block from the bottom thereof by scratching polyester material off by means of stripping edges provided on a perforated tray that is rotated about its vertical axis and discharging the disintegrated polyester material through discharge slots.

It is surprising and could not have been foreseen that in the process of the invention, in contrast with general knowledge, it is not only unnecessary but even disadvantageous to keep the polyester granules in motion when heated to a temperature above the second order transition temperature in order to obtain a freely flowing crystalline product and that the best results are obtained when a loose layer of granules, as formed by freely pouring the material into a container, is subjected to the action of the hot gases and allowed to agglomerate without interference. It is also surprising that in spite of considerable layer thicknesses, which may be 1 to 4 times diameter of the reactor vessel, the formed agglomerate is not very strong and, therefore, can be disintegrated in the crystallized state and readily discharged.

The measures in accordance with the invention mean that there are fewer points of contact between the individual granules than in the "ideal" packing produced by vibration or agitation and that the strength of agglomeration is only determined by the pressure exerted by the weight of the polymer lying above it. Since there is no additional local compression in the zone of crystallization which would necessarily result from stirring, and since the heating and drying gas is passed through the material at a velocity which is not sufficient for fluidization of the granules, the product is not subjected to great mechanical strain before crystallization is terminated, i.e. the process step in which the polyester granules lose their stickiness. Hence, the granules are not substantially deformed by strain in the plastic state.

The perforated tray may be flat, conical or frusto conical.

The or each stripping edge mounted on the tray is advantageously part of an upwardly extending cantilever arm, and the polyester material may be discharged through slots which are formed below the above mentioned cantilever arms. In any case, the or each cantilever arm is preferably inclined backwardly with respect to the direction of rotation of the tray.

The process may be carried out continuously, in which case it will be appreciated that undried polyester material is preferably fed into the drying zone at substantially the same rate (based on volume) as the dried polymer is discharged. There may be maintained a layer of polyester material which has a height in the range of from 1 to 4 times the diameter of the tray.

After it has been discharged through the discharge slots, the crystallised material may be subjected to a further heating treatment which may take place in a chamber through which the heated gas is passed prior to its entering the drying zone. If the chamber is situated below the perforated tray, heating gas passes into the drying zone through the perforations in the support member.

An agglomerate should not be disintegrated until the granules have lost their tendency to agglomerate, i.e. they have been transformed into the crystallized state. For the breaking up of the agglomerate block, the stripping edges mounted on the tray raise and lower the agglomerate resting on the tray, thereby reducing it as its lower side in to particles which are freely flowing, and may be discharged through slots in the tray.

In addition to the specified advantages, the process of the invention requires relatively little energy and expenditure to run the apparatus, the particles are not abraded and very short residence times are sufficient as only a plug flow occurs due to the agglomeration.

It is further object of the invention to provide an apparatus suitable for drying amorphous granules of polyethylene terephthalate which comprises a cylindrical drying zone, the lowest extent of which is defined by a rotatable perforated tray having stripping edges on the upper surface thereof and having a circular cross-section, an inlet orifice for heated gas that is so located that the gas, in operation, passes into the drying zone through the perforations in the tray, an outlet orifice for gas and one or more discharge slots for discharging material from the drying zone.

The discharging slots may be formed in the tray. The or each stripping edge is preferably part of an upwardly extending cantilever arm, having a discharge slot located below it, and the arm is advantageously inclined backwardly with respect to the direction of rotation of the tray.

The axes of the tray and the drying zone are preferably co-linear, and the tray advantageously nearly abuts the walls which define the sides of the drying zone.

In one advantageous embodiment, an inlet for heated gas is situated in a chamber below the tray, and the discharge slots, in operation, discharge crystallised material from the zone into the chamber and the chamber includes means for discharging the material therefrom.

An apparatus according to the invention will now be described by way of example with reference to the accompanying drawings in which:

Figure 1 is a longitudinal view partly in section of the apparatus; and

Figure 2 represents a sectional view along line II - II of Figure 1.

The figures are not drawn to scale.

Referring to Figure 1, the apparatus comprises in a container (5), a cylindrical drying zone (1) which is closed at its lower end by a plane or conical perforated tray (2) with stripping edges (3) and discharge slots (4). The perforated tray is fixed on a vertical axis around which it slowly rotates during operation. The diameter of the tray is only a little smaller than the diameter of the drying zone, that is to say it nearly abuts the wall of the drying zone. The perforated tray is driven by an axle which protrudes out of the apparatus at the upper or optionally the lower end and which, according to these possible constructional features, can be supported below the perforated tray or above the layer of material. To achieve the desired effect, i.e. alternately to lift and to lower the product layer and thereby to disintegrate the lower portion of the agglomerate of granules so that the granules can be discharged, different modes of construction of the perforated tray are possible. According to one embodiment, the support is provided with one or several radial cuts and each edge is bent upwardly, that is towards the agglomerate, to form the stripping edge as illustrated in Figure 2. In the case of possible discharge troubles, the direction of rotation of the tray can be reversed for a short period of time. In general, the stripping edge is straight although edges with teeth are also possible.

Below the perforated tray a chamber (6) is provided in which the dried product accumulates and through which the hot gas is fed to the perforated tray. The chamber is optionally dimensioned in such a manner that the accumulated granules can be after-dried or drying is finished by passing the drying gas through the material in the chamber (6) before it passes through the perforated tray. The crystallized and dried polyethylene terephthalate is discharged through discharge means, in the present case a rotary valve (7). The used hot gas (8), escapes through pipe (11) while the polyester material is introduced through inlet (10).

The drying gases have a temperature of from 120 to 190°C, preferably 140 to 170°C. They are fed to the drying apparatus in such an amount that the material does not form a fluidised bed. Air has proved to be an especially suitable gas.

The process of the invention is preferably operated in continuous manner. The polyester layer in the drying zone above the perforated tray may have a height which is equal to 1 to 4 times the reactor diameter. When the process is carried out continuously a distributor (9), which rotates together with the perforated tray, levels the upper surface of the layer of loose granules of polyester material.

The process of the invention can be used to crystallize and dry polyethylene terephthalate granules having a reduced specific viscosity of from about 0.4 to about 1.0 dl/g (measured in a 3:2 by weight mixture of phenol-tetrachloroethane) which is usual for further processing. The granules can be free from pigments or contain pigments. It is also possible to treat, according to the invention, polyethylene terephthalate modified by other acids or glycols provided that such a modification does not affect essentially the crystallization properties of the product.

The process is suitable for all types of granules usual with polyethylene terephthalate, such as obtained from ribbons or ropes or those obtained by underwater granulation.

The following example illustrates the invention.

Example:

A drier as shown in Figure 1 having a cylindrical drying zone with a diameter of 60 cm and a height of 150 cm, corresponding to a capacity of about 400 liters, and a chamber or discharge cone of a length of 40 cm is provided below the drying zone, cone and the drying zone being separated by a perforated tray which can be slowly rotated around its vertical axle. The drier is charged via a suction conveyor through an inlet (10) with about 250 kg of amorphous polyethylene terephthalate (bulk weight about 0.75 g per cm^3) while the tray is at a standstill. The layer above the tray has a height of about 125 cm. The tray through which the gas streams into the drying zone has a very flat conical shape; at the apex it is connected to the axle of rotation. The tray consists of a stainless steel frame carrying a perforated sheet with an orifice diameter of 2 mm. The perforated sheet is provided with two radial discharge slots having a length of 25 cm and a width of 2 cm and the front edge of each slot in the sense of rotation carries a radial stripping edge having a height of 1.5 cm and a width of 25 cm (cf. the letter h in Figure 2).

Without rotating the tray, air at a temperature of 170°C, which has not been predried specially, is forced by a blower in upward direction for about 1 hour through the perforated tray and the layer of loose material. The air current of 200 Nm^3/hr ensures that a fluidized bed is not formed. The polyester material crystallizes during the indicated perod of time which can be perceived by the opaque appearance up to the material inlet. The tray is then rotated slowly (1.5 revolutions per minute), whereby the crystallized and dried agglomerate is gradually broken up and discharged into the cone, from where it is removed through the rotary valve. During this period, the dried material uniformly sinks over the entire sectional area. To keep constant the height of the material layer in the drying zone undried granules from a container are introduced and the loose material is levelled by the distributor fixed on the axle of the tray.

From the drier about 100 kg/hr of dried and crystallized polyester granules are discharged.

WHAT WE CLAIM IS:

1. A process for crystallizing and drying granules of amorphous polyethylene terephthalate by treating the granules of the said polyester material with hot gases at a temperature of from 120 to 190°C, the hot gases passing through a cylindrical layer of loose polyester granules, which process comprises crystallizing and drying the polyethylene terephthalate in a single process step in such a manner that a fluidised bed is not formed, that the said layer is not moved and that, under the action of the hot gases, the cylindrical layer of loose polyester granules agglomerates to a cylindrical block, destroying the said cylindrical block from the bottom thereof by scratching polyester material off by means of stripping edges provided on a perforated tray that is rotated about its vertical axis and discharging the disintegrated polyester material through discharge slots.

2. A process as claimed in claim 1, wherein the temperature of the heated gas is in the range of 140°C to 170°C.

3. A process as claimed in claim 1 or claim 2, wherein the heated gas is air.

4. A process as claimed in any one of claims 1 to 3, wherein the tray is flat.

5. A process as claimed in any one of claims 1 to 4, wherein the tray is conical or frusto conical.

6. A process as claimed in any one of claims 1 to 5, wherein disintegrated polyester material is discharged through slots formed in the tray.

7. A process as claimed in claim 6, wherein the or each stripping edge is part of an upwardly extending cantilever arm and the or each arm has a discharge slot located below it.

8. A process as claimed in claim 7, wherein the or each arm is inclined backwardly with respect to the direction of rotation of the tray.

9. A process as claimed in any one of claims 1 to 8, wherein there is maintained a layer of polyester material which has a height in the range of from 1 to 4 times the diameter of the tray.

10. A process as claimed in any one of claims 1 to 9, which is performed continuously and the undried polyester material is fed into the drying zone at substantially the same rate (based on volume) as the dried polyester material is discharged.

11. A process as claimed in any one of claims 1 to 10, wherein material is subjected to a further heating treatment after it has been discharged.

12. A process as claimed in claim 11, wherein the material is subjected to the further treatment in a chamber through which the heated gas is passed prior to its passing through the said layer of loose polyester granules.

13. A process for crystallizing and drying granules of amorphous polyethylene terephthalate by treating them with hot gases of from 120 to 190°C, which comprises passing, in the cylindrical drying zone of a cylindrical reactor, the hot gases in upward direction through a planar or conical perforated tray, which is rotated about its vertical axis and is provided with stripping edges and with discharge slots, and through a loose layer of the polyester granules resting on said tray, the gases being passed through the layer of granules at a velocity such that no fluidization occurs, alternately lifting slightly and lowering the agglomerates of granules forming on the tray under the action of the hot gases by the stripping edges of the rotating perforated tray, thereby disintegrating the agglomerates, and discharging the disintegrated polyester material through the discharge slots of the perforated tray.

14. The process of claim 13, wherein the crystallization and drying is performed continuously and the layer of the loose polyes-

ter material has a height which is equal to 1 to 4 times the reactor diameter.

15. Apparatus for drying amorphous granules of polyethylene terephthalate which comprises a cylindrical drying zone, the lowest extent of which is defined by a rotatable perforated tray having stripping edges on the upper surface thereof and having a circular cross-section, an inlet orifice for heated gas that is so located that the gas, in operation, passes into the drying zone through the perforations in the tray, an outlet orifice for gas, and one or more discharge slots for discharging material from the drying zone.

16. Apparatus as claimed in claim 15, wherein the tray is flat.

17. Apparatus as claimed in claim 15, wherein the tray is substantially conical or frusto conical.

18. Apparatus as claimed in any one of claims 15 to 17, wherein the or each stripping edge is part of an upwardly extending cantilever arm having a discharge slot located below it.

19. Apparatus as claimed in claim 18, wherein the or each arm is inclined backwardly with respect to the direction of rotation of the tray.

20. Apparatus as claimed in any one of claims 15 to 19, wherein the inlet for heated gas is situated in a chamber below the tray.

21. Apparatus as claimed in claim 20, wherein the arrangement is such that the or each discharging slot in operation, discharge material from the zone into the chamber, and the chamber includes means for discharging the material therefrom.

22. A process substantially as hereinbefore describd in the Example.

23. Polyester material whenever dried by a process as claimed in any one of claims 1 to 14 or 22.

24. A reactor for crystallizing and drying amorphous polyethylene terephthalate granules by treating same with hot gases of from 120 to 190°C, comprising a cylindrical drying zone closed at its lower end by a plane or conical perforated tray rotating about its vertical axis and provided with stripping edges and discharge slots, said tray being mounted in concentric position and nearly scrapes along the reactor wall, a chamber below the perforated tray into which the hot gas is introduced and from which the dried material is discharged.

25. The reactor as claimed in claim 24, wherein the dried and crystallized material is after-dried in the chamber below the perforated tray.

26. Apparatus substantially as hereinbefore described with reference to, and as shown in, Figure 1 of the accompanying drawings.

27. Apparatus as claimed in claim 15, wherein the stripping edges and slots are substantially as hereinbefore described with reference to and as shown in Figure 2 of the accompanying drawings.

28. Polyester material that has been dried in an apparatus as claimed in any one of claims 15 to 21 or 24 to 27.

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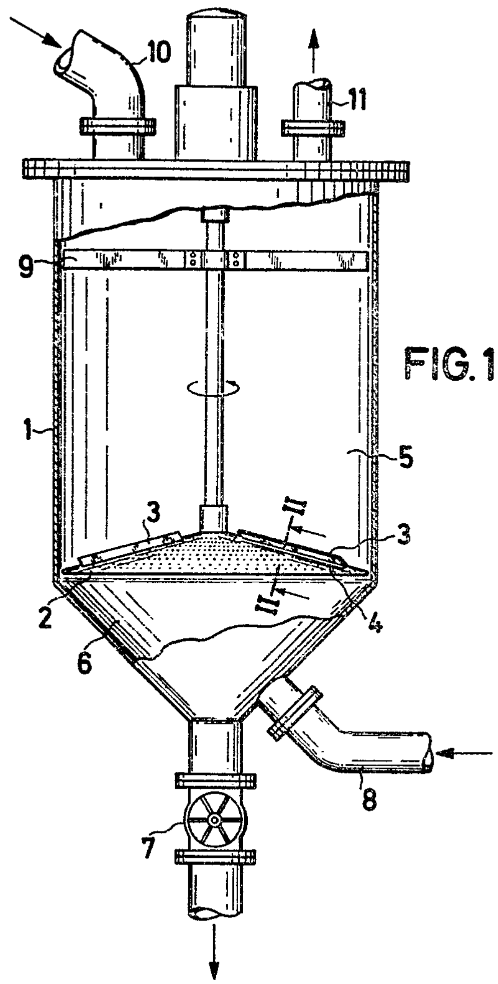

FIG.1

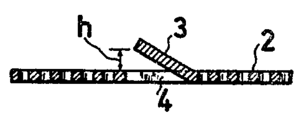

FIG.2