(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
2 October 2014 (02.10.2014)

(10) International Publication Number
WO 2014/154745 A1

(51) International Patent Classification:
C08J 11/24 (2006.01) *C08J 11/08* (2006.01)

(21) International Application Number:
PCT/EP2014/056053

(22) International Filing Date:
26 March 2014 (26.03.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
13161194.9 26 March 2013 (26.03.2013) EP
13171754.8 12 June 2013 (12.06.2013) EP

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

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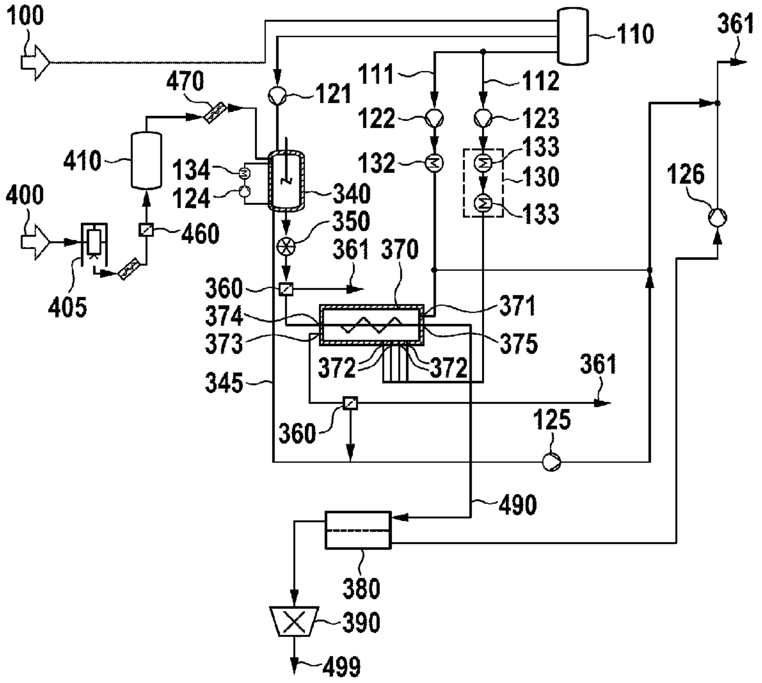
(54) Title: METHOD AND APPARATUS FOR COLOUR REMOVAL FROM PET-FLAKE (SHREDDED PET)

Fig. 1



(57) Abstract: Organic colourants incorporated in coloured PET-flake, as being obtained by shredding PET bottles, can be extracted from the PET-flake by extracting the PET-flake with ethylene glycol (EG) at ambient pressure and at the boiling temperature of EG. Pre-treating of PET-flake in EG or other suitable organic compounds prior to extraction enhances the discolouration.

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

Method and Apparatus for Colour Removal from PET-flake (shredded PET)

Field of the invention

The invention relates to a method and an apparatus for removing colorants from PET-flake which can be obtained by shredding commercially available used PET bottles.

Description of the related art

PET is the common abbreviation for "polyethylene terephthalate" or more precisely "poly(ethylene terephthalate)" (CAS: 25038-59-9). PET is a thermoplastic polyester and widely used for food containers and bottles, e.g. for water, carbonated soft drinks, beer or the like. Pure PET is transparent for visible light with wavelengths between 380 nm and 780 nm and thus colourless. For aesthetic reasons and as well as to protect the liquids to be handled by PET bottles from degrading when subjected to light, the bottles are often coloured by organic colorants and/or pigments.

Large amounts of used bottles are to be recycled. Various chemical recycling techniques are known, in particular glycolysis, methanolysis, hydrolysis, and saponification. However, according to the Petcore PET knowledge centre these methods are unable to remove colours from the PET feedstreams (www.petcore.org/content/processing 02.05.2013).

EP 1 153 070 B1 suggests to contact PET with a glycol, e.g. ethylene glycol (briefly "EG") to thereby obtain oligomers and monomers of the PET, in particular bis- (2-hydroxyethyl) terephthalate (briefly "BHET", CAS: 959-26-2) in an agitated reactor vessel at a temperature of about 150°C to 300°C and an absolute pressure of 0.5 to 3.0 bars. The ratio of EG to dicarboxylic acid is greater than 1 to 5 total glycol units to total dicarboxylic acid units. Lower density contaminants form a distinct top layer in the reactor vessel and are separated from a lower layer containing a remainder of a glycolysis reaction mixture. Remaining immiscible contaminants are removed by filtration or straining.

PET bottle recycling is addressed by the European Patent EP 1 437 377 B1. First PET bottles are unpacked, steel and aluminium residues are removed and the bottles are shredded. Subsequently, non PET polymers are separated by winnowing and float-sink separation. The such obtained PET-flake are depolymerized by charging them into EG at 175-190°C at 0.1- 0.5 MPa to thereby obtain BHET which is later subjected to an ester interchange reaction for forming crude dimethyl terephthalate (briefly “DMT”, CAS: 120-61-6) and EG. DMT and EG can be separated, purified and again used as monomers in the polymer industry.

EP 1 914 270 suggest to recover colorants from dyed polyester fiber as used in PET-fabric by a dye extraction using ethylene glycol.

Summary of the invention

The invention is based on the observation, that the prior art methods for PET-recycling require transparent PET-flake or PET-flake of the same colour i.e. include a colour sorting step to obtain high quality recycling products.

The problem to be solved by the invention is to provide a method and apparatuses for the recycling of PET-flake without colour sorting.

Solutions of the problem are described in the independent claims. The dependent claims relate to further improvements of the invention.

The method of the invention can be used for pre-processing PET-flake in particular prior to depolymerisation. The PET-flake can be obtained for example by shredding PET bottles. PET-flake are preferably devoid of metal, paper and residues of beverages and other compounds previously stored in the bottles. This can be obtained by known prior art sorting and washing techniques, which are commercially available. The PET-flake may be of any colour and may comprise a mixture of colours, e.g. brown PET-flake as well as blue, green, red, or black PET-flake.

The colour removal process preferably comprises at least two process steps.
1) PET-flake are pre-treated in a hot organic liquid and (optional) and
2) Organic colorants are extracted from the PET-flake and the PET-flake are simultaneously embritteled using hot ethylene glycol (EG; IUPAC name: ethane-1,2-diol, CAS: 107-21-1).

Colorant extraction and simultaneous embrittlement of the PET-flake is obtained by contacting the PET-flake with hot EG in a contacting vessel (step 2). Only for brevity this is subsequently summarized by referring only to “extraction”. Extraction (and thus simultaneous embrittlement) is performed preferably at or slightly below the boiling temperature of EG (satp) at about ambient pressure. The extraction temperature T_{ext} is preferably about 197.5°C ($192°C \leq T_{ext} \leq 205°C$, preferably $195°C \leq T_{ext} \leq 200°C$, more preferably $196°C \leq T_{ext} \leq 199°C$, particularly preferred $197.0° \leq T_{ext} \leq 197.6°C$) at preferably ambient pressure p_a (typically $850\ hPa \leq p_a \leq 1100\ hPa$). The EG extracts the organic colorants and embrittles the PET-flake, however without significant depolymerisation. There is no need to add a catalyst to embrittle the PET, because in commercially produced PET, as used for the bottles from which the PET-flake preferably origin, catalysts used for polycondensation of the PET are embedded in the polymer matrix.

Below the 194.5 °C ($T_{ext}<194.5°C$) the colour removal slows down significantly. Above 200°C ($T_{ext}>200°C$) the PET-flake lose their form, get sticky and tend to form a mush with the EG, being is difficult to handle.

Preferably, the extraction step and as well the optional pre-treatment step are performed at least approximately at ambient pressure (+-200hPa).

Preferably, used EG, i.e. EG loaded with organic colorants is preferably continuously removed from the PET-flake and/or at least from the extraction vessel, i.e. the contacting vessel, containing the PET-flake. Fresh, i.e. colourless or at least less loaded EG is added to the PET-flake, preferably continuously.

Extraction of the PET-flake is preferably completed once the PET-flake are colourless. "Colourless" or the degree of decolourization can be defined using a colour analysis in the CIE L*, a*, b* colour space (1976) defining a CIE LAB colour difference ΔE being the Euklidic Norm of a vector defined by the triple (L*, a*, b*), i.e. $\Delta E^2=(L^*)^2+(a^*)^2+(b^*)^2$. The mean colour distance ΔE of the PET-flake when removing from the EG is preferably less or equal to 20, more preferably less or equal to 10.

Total depolymerisation of the PET to BHET is avoided by the preferred temperature and pressure range and by limiting the contact time between PET and EG, respectively the residence time of PET under extraction conditions. The extraction process removes organic colorants from PET-flake. However, pigments like titanium dioxide (TiO_2, CAS: 13463-67-7) remain in the solid PET. These pigments migrate very slowly in the amorphous phase of solid-state PET and can be removed by an optional downstream depolymerisation process of PET to DMT or any other PET monomer. The mechanism of organic colorants removal is still not fully understood. The working hypothesis is that the organic colorants are extracted from a preferably pre-treated amorphous polymer matrix by molecular diffusion and film diffusion.

PET-flake embrittle in the course of the extraction process. This could be explained by a reduction of the degree of polymerisation of PET-flake. However, PET-flake are not fully depolymerized to PET monomers during the extraction step. The degree of polymerizations (Pn) is solely reduced from initially typically 134 to a Pn of about 50 to 25. For example, treatment of bottle grade PET-flake in an EG counter-current flow for about 30 min at about 196°C yielded embrittled PET-flake with an intrinsic viscosity of IV=0.30 dL/g, a molar mass of Mn =7300 g/mol, and a degree of polymerization of Pn=38. Further extraction treatment for another 30 min yielded PET-flake with an intrinsic viscosity of IV=0.25 dL/g, a molar mass of Mn = 5800 g/mol, and a degree of polymerisation of Pn=30.

The extraction is preferably completed as soon as the PET-flake are sufficiently decolourized as explained above. The time to obtain sufficient colorant extraction depends on the residence time, i.e. the time the PET-flake are in contact with EG, the flow velocity of the liquid EG, the flake particle size, flake particle shape and the temperature. Apart from sufficient colorant extraction, the process should preferably be completed before the flake soften. Criteria for completing the extraction step can in addition or alternatively to the degree of decolourization as defined above be an intrinsic viscosity of IV ≤ 0.20 dL/g and/or a molar mass Mn ≤ 4000 g/mol and/or a degree of polymerization Pn ≤ 20 (±5).

Extracting the organic colourants is preferably obtained by conveying the PET-flake in a conveying direction and simultaneously contacting the PET-flake with liquid EG. In a preferred embodiment extraction is obtained by establishing a counter-current flow of EG directed against the PET conveying direction.

Such counter-current flow can be realized by conveying the PET-flake in a conveyor, e.g. a screw-conveyor, in a PET conveying or flow direction. Extraction liquid, i.e. liquid EG can be fed to the screw conveyor via an EG inlet downstream of the PET-flake inlet. The EG is removed from the screw conveyor upstream of the EG inlet. Thus, the EG flows in the opposite direction of the PET-flake flow, to which upstream and downstream refers. The EG flows through the voids of the PET-flake bulk. Such, the PET-flake and the EG are in close contact and the PET-flake are extracted by a counter-current flow of EG.

Preferably, the PET-flake are heated by heat transfer from condensing EG vapour while being extracted. In other words, at least a part of the EG being used for extraction of colorants from the PET-flake condenses from a gaseous phase into a liquid phase on the PET-flake and/or in already liquid EG. Such, the optimum temperature for colorant extraction can be obtained easily, which turned out to be only slightly below the boiling temperature of EG (197.3°C at 1013 hPa). In other words, EG provided to the EG inlet or at least one of multiple EG inlets of the conveyor is at least partially in vapour phase and condenses in the conveyor. Additional heat can also be provided to the conveyor by heat transfer media at its shell or by electric heating devices via the shell or any other means.

Prior to extracting organic colorants from the PET-flake by contacting them with hot EG, the PET-flake are preferably pre-treated in a pre-treating liquid, referred to as pre-processing by pre-treatment. The pre-treatment liquid may at least comprise one of the following compounds: benzophenone ($C_{13}H_{10}O$, CAS: 119-61-9) and/or polyethylene glycol 600 (“PEG”, $HO(C_2H_4O)_n$, CAS: 25322-68-3) and/or 1,2-dichlorobenzene ($C_6H_4Cl_2$, CAS: 95-50-1) and/or limonene ($C_{10}H_{16}$, CAS: 5989-27-5) and/or 1,4-dioxane ($C_4H_8O_2$, CAS: 123-91-1) and/or ethylene glycol ($C_2H_6O_2$, CAS: 107-21-1) and/or triethylene glycol (“TEG”, $C_6H_{14}O_4$, CAS: 112-27-6) and/or tetraethylene glycol ($C_8H_{18}O_5$, CAS: 112-60-7) and/or methanol (CH_4O, CAS: 67-56-1). In a particular preferred embodiment the pre-treatment liquid is ethylene glycol (“EG”).

During the pre-treatment step the PET-flake are brought in close contact with the pre-treatment liquid. For example, the PET-flake can be immersed in a pre-treatment vessel containing the pre-treatment liquid

The pre-treatment temperature T_{pre} should be above the glass transition temperature (T_{gl}) of the PET-flake and below the melting temperature (T_{melt}) of the PET-flake. The glass transition temperature together with the melting point of the bottle grade PET-flake differs with the PET-flake and depends on the PET specification (i.e. the kind and amount of PET co-monomers). A typical glass transition temperature of “bottle grade PET” is about 80°C (± 5 K). The melting temperature of “bottle grade PET” is about 240°C to 255°C. More preferably, the pre-treatment temperature T_{pre} is below the temperature where significant softening of the PET-flake can be observed (T_{soft}), to thereby avoid that the PET-flake get “sticky” and agglomerate while pre-treated. This happens typically above 220°C (± 5 K). Briefly summarizing, the pre-treatment temperature interval can be chosen as $T_{gl} \leq T_{pre} \leq T_{melt}$, more preferred $T_{gl} \leq T_{pre} \leq T_{soft}$. Typical values for T_{pre} are between 120°C and 180°C. It has been observed that the PET-flake shrink and the wall thickness increases while pre-treated. It was shown experimentally that the PET relaxes above the glass transition temperature. However, almost no or at least no significant depolymerisation has been observed while pre-treating the PET-flake. As well no or at least no significant colour extraction and no measureable embrittlement can be observed during the pre-treatment step (step 1). However, surprisingly the pre-treatment step enhances subsequent colour extraction in step 2.

The mass ratio of PET-flake to liquid for pre-treating PET-flake in e.g. EG is preferably at least about 1:2 (possible 1:1 to 1:5). A pre-treatment vessel may be used to immerse the PET-flake in the pre-treatment liquid, e.g. EG. The pre-treatment vessel may be heated to T_{pre} with $T_g \leq T_{pre} \leq T_{melt}$, and may preferably have a thermal insulation layer. A blanket of gaseous nitrogen (N_2) may be used on top of the pre-treatment liquid/PET-flake slurry to avoid contamination of the PET-flake with moisture and/or oxygen. Agitation, e.g. by stirring is preferred. A condenser e.g. on top of and/or above the pre-treatment vessel may be used to recover condensable components (e.g. EG and water from moist PET). Non-condensable components may be removed and e.g. burnt. The pre-treatment liquid can be provided, preferably continuously to the pre-treatment vessel, e.g. via a tube. The tube’s outlet is preferably below the fluid level in the pre-treatment vessel. The pre-treatment liquid can be removed, preferably continuously from the pre-treatment vessel for example by an overflow. A mesh may ensure that the PET-flake remain in the pre-treatment vessel. The PET-flake can be removed using a conveyor means, e.g. a screw conveyor with its lower end inside the pre-treatment vessel.

The pre-treatment has two advantages: firstly, the PET is dried. PET is hygroscopic and PET-flake being subjected to ambient air have typical moisture (water, H_2O) content of up to 10,000 ppm by weight (typically 3000 ppm to 6000 ppm) and already small amounts of water may affect the boiling temperature of the extracting liquid and thus have an impact on extracting temperature T_{ext}. Secondly, the subsequent colourant extraction is enhanced. It is assumed that pre-treating the PET-flake somehow affects the amorphous part of the solid PET matrix by a kind of “swelling” effect. However, a profound microscopic understanding is still missing. During the pre-treatment step only minor colour extraction is noticed.

The pre-treatment time t_{pre} depends on the pre-treatment liquid and the pre-treatment temperature T_{pre}. In case of pre-treatment in EG with, e.g. T_{pre}=130°C, good results have been obtained with a residence time of t_{pre} = 60 min (± 15 min). A higher pre-treatment temperature requires a lower residence time, but a non-linear relation between temperature and time is noticed.

An apparatus for extracting organic colorants from PET-flake preferably comprises a conveyor as extracting vessel for conveying a flow of PET-flake from a PET-flake inlet in a conveying direction to a PET-flake outlet. The conveyor can be for example a screw-conveyor with a screw housing and a conveyor screw for conveying PET-flake via the screw housing from at least one PET-flake inlet in a PET conveying direction to at least one PET-flake out-let. The conveyor has at least one EG inlet, i.e. an extraction liquid inlet in the screw housing. The EG inlet is downstream of said PET-flake inlet. At least one EG outlet, i.e. an extraction fluid outlet is upstream of the EG inlet for providing a counter-current flow. “Upstream” and “downstream” refer to the PET flow, i.e. the PET conveying direction. The apparatus may be used in particular for pre-processing PET-flake prior to depolymerization of PET-flake with an extraction fluid, in particular EG.

For example, the counter-current EG flow in opposite direction to the PET-flake flow can be obtained if the PET conveying direction is inclined against the horizontal or in other words sloped (including a vertical PET-flake conveying direction). In this case the extraction fluid pours or flows downwards in the conveyor through voids between the PET-flake, whereas the PET-flake are conveyed upwards. In the above example of the screw-conveyor, the screw axis may be sloped. However, the invention is not restricted to this possible arrangement. The EG can of course be provided to the extraction vessel at its lower end and removed at the top, while the PET-flake are conveyed in the opposite direction.

The apparatus may further comprise at least one EG vapour source being connected to the screw housing for providing gaseous EG, i.e. EG vapour, to the screw housing.

The conveyor housing may comprise at least one condenser, for example being attached to its screw housing. This arrangement ensures that vapour from the extraction apparatus (which consists at least mainly of EG) is condensed, thus ensuring ambient (or slightly above ambient) pressure in the extraction apparatus.

Preferably, the condensing chamber has at least one drain for removing condensed EG vapour, i.e. liquid EG. The drain may be connected to at least one extraction fluid-inlet of the screw housing and/or at least one vapour generator for providing a liquid to said at least one vapour generator.

Preferably, the apparatus further comprises at least a pre-treatment vessel for immersing PET-flake in one of the above specified a pre-treatment liquids at a temperature T_{pre} of $T_g \leq T_{pre} \leq T_{soft}$. Such immersing is subsequently referred to as pre-treatment (optional step 1). Thus, the pre-treatment vessel and/or pre-treatment liquid (e.g. EG) is preferably heated. The pre-treatment vessel contains the pre-treatment liquid. By pre-treating the PET-flake e.g. in liquid EG, water can be removed from the PET. Further, pre-treatment enhances colour extraction in the second step as explained above. In the pre-treatment step no significant colour extraction or embrittlement is observed. The colour of the pre-treatment liquid remains almost unchanged.

If the pre-treatment vessel comprises a PET strainer for removing PET from the pre-treatment vessel and feeding the PET-flake inlet of the screw conveyor, handling of large amounts of PET-flake is facilitated.

The pre-treatment vessel has been explained above with respect to EG as pre-treatment liquid. However, the other above cited pre-treatment liquids may as well be used for pre-treatment of PET-flake, e.g. in said pre-treatment vessel.

Preferably, the apparatus further comprises a rectification apparatus for rectifying liquid EG drained at the screw-conveyor’s EG outlet to thereby obtain a colourless fraction and an a fraction comprising organic colorants and other high boiling residues. The colourless fraction may be reused for pre-treating and extracting PET-flake.

Only for clarity, the term “PET-flake” denotes the singular and the plural, i.e. a single PET-flake as well as a multitude of PET-flake. In an industrial scale process, only the plural is relevant. The terms extractions vessel and contacting vessel are used interchangeably throughout this application, as the colour extraction and PET-flake embrittlement is obtained by contacting the PET-flake with hot EG. The pre-treatment vessel for immersing the PET-flake prior to the extraction step could thus as well be referred to as immersing vessel.

Description of Drawings

In the following, the invention will be described by way of example, without limitation of the general inventive concept, on examples of embodiment with reference to the drawings.

Figure 1 shows a process flow diagram of a method for extracting organic colorants from coloured PET-flake.

Figure 2 shows an apparatus for extracting PET-flake with hot EG.

According to Fig. 1, PET-flake are supplied by PET-flake supply 400. The PET-flake are typically provided in so called bigbags and thus unpacked as indicated by Symbol 405. Subsequently, the PET-flake may pass an optional separator 460 for removing foreign material or PET-flake with a size out of a given specification and stored in a PET-flake reservoir 410. The PET-flake reservoir 410 is a PET-flake source for the pre-processing PET-flake. Other bulk transport means can as well be used for providing the PET-flake. Required is only a preferable continuous PET-flake stream to the pre-treatment vessel 340.

In this example, PET-flake from a PET-flake source, i.e. reservoir 410, are supplied to a pre-treatment vessel 340. In the pre-treatment vessel 340 the PET-flake are immersed in EG. EG is preferably continuously provided from an EG-source, in this case an EG-reservoir 110. The EG is heated to a pre-treatment temperature T_{pre} of typically 150°C (preferred: $T_g \leq T_{pre} \leq T_{soft}$). For heating the EG, EG is pumped from the pre-treatment vessel 340 by pump 124, fed to a heater 134 and fed back to the pre-treatment vessel 340. Other possibilities for obtaining the required temperature are as well suitable, for example an electrical pre-treatment vessel heating. EG is preferably continuously removed from the pre-treatment vessel, e.g. via line 345 and may be provided to an EG treatment device, e.g. a filtration and/or rectification unit. Purified EG may be used again, e.g. by providing it to the EG reservoir 110.

Pre-treated PET-flake are drained from the pre-treatment vessel and transported via a separator 360 to an extraction vessel 370. Transporting may be obtained e.g. by use of a rotary feeder 350. Most EG may be removed from the PET-flake flow using the separator 360 and then fed to a PET-flake inlet 374 of a conveyor 370 used as extraction vessel. For example, a screw-conveyer as shown in Fig. 2 may be used as extraction vessel 370.

In the screw conveyor 370, the PET-flake are conveyed by rotation of the screw from the PET-flake inlet 374 to a PET-flake outlet 375. EG is provided in a counter-current flow (with respect to the PET-flake flow) to the conveyor. EG is provided from the reservoir 110 and may be split on two lines: In a first line 111 the EG is heated using a first heater 132 and fed as liquid EG to the downstream end of the conveyor. The temperature T_l of the liquid EG provided to the extraction vessel should be adjusted to the extraction temperature $T_{ext,}$i.e. to: $195°C \leq T_l = T_{ext} \leq T_{boil}$ preferably to $T_{ext} = 196 \pm 1°C$, where T_{boil} stands for the boiling temperature of the EG. In the second line 112, the EG is vaporized at least partially by an EG-vapour generator 130, symbolized by two heaters 133; the number of heaters 133 is of course not essential, nor the energy source for heating the EG. The vapourized EG, i.e. gaseous EG is as well fed downstream of the PET-flake inlet to the conveyor. The gaseous EG thereby heats the PET-flake by condensation preferably to about 197°C, i.e. just below the boiling temperature of EG at ambient pressure. At the upstream end of the conveyor is an EG outlet from which EG is removed to thereby obtain a counter-current flow of EG and PET-flake. The removed EG can be provided to an EG treatment (indicated by arrow 361) for purification and reuse.

Organic colorants are extracted from the PET-flake in the conveyor 370 by contacting the PET-flake with a counter-current EG flow. The PET-flake are preferably at least almost colourless when leaving the conveyor 370 via the PET-flake outlet 375. The PET-flake are not only at least almost colourless but as well brittle after passing the conveyor 370. EG leaving the conveyor via the PET-flake outlet 375 can be separated using a strainer 380. PET-flake from the outlet 375 can be further processed, e.g. by milling. The colourless brittle PET-flake (line 490) can be subjected to depolymerisation, e.g. by methanolysis as indicated by arrow 499.

Fig. 2 shows a simplified screw-conveyor 500 for pre-processing PET-flake, in particular for extracting organic colorants from PET-flake. In other words, the screw conveyor is a possible extraction vessel for extracting organic colorants from PET-flake while simultaneously obtaining an embrittlement of the PET-flake, as referred to as step 2. In particular, the the screw-conveyor as shown in Fig. 2 can be used as conveyor 370 in the scheme of Fig. 1. The screw-conveyor 500 has a tubular screw housing 510, the latter housing a conveyor screw 520, briefly referred to as screw 520. The screw 520 is preferably motor driven. The longitudinal axis 515 of the screw 520 and accordingly as well of the screw housing 510 is sloped. The screw housing 510 has a PET-flake inlet 374, being connected to a down pipe 511 for feeding PET-flake to the PET-flake inlet 374. The down pipe 511 is optional. The screw 520 conveys the PET-flake to a PET-flake outlet 375 at the upper end of the screw housing 510. A further optional down pipe 519 is attached to PET-flake outlet. The screw housing 510 has nozzles 530 as EG inlets 372 for injecting vaporous EG into the screw housing and thereby heating the PET-flake to a temperature slightly below the boiling temperature of EG. The vaporous EG thus condenses inside the screw housing. The condensed, i.e. liquid, EG flows downwards through the voids in the PET-flake bulk to an EG outlet 373. At the EG outlet 373 the EG is removed from the screw-conveyor. In addition to the vaporous/gaseous EG, liquid EG may as well be injected into the screw housing 510 for example via EG inlet 371. The temperature in the conveyor can thus be adjusted by adjusting the amount of EG vapour provided to the extraction vessel. For better control of the temperature, the crew conveyor may have an additional shell for heat transfer by a heat transfer medium and/or other heating means like an electrical heater.

List of reference numerals

100	EG supply
110	EG reservoir / EG source
121	pump
122	pump
123	pump
124	pump
125	pump
126	pump
130	steam generator
132	heater
133	heater
134	heater
340	pre-treatment vessel / immersing vessel
350	feeder (e.g. star feeder)
360	separator
361	to EG treatment (e.g. filtration and/or rectification)
370	conveyor (screw conveyor) / contacting vessel /extraction vessel
371	liquid extraction fluid inlet / EG inlet (fluid)
372	EG inlet (gaseous)
373	extraction fluid outlet / EG oulet (liquid)
374	PET-flake inlet
375	PET-flake outlet
400	PET-flake supply
405	unpacking station
405	cleaning means

410	PET-flake reservoir / PET-flake source
460	separator
470	transport means
490	decolourized brittle PET-flake line
499	to depolymerization facility
500	screw conveyor / contacting vessel / extraction vessel
510	screw housing
511	downpipe, PET-flake feed
519	downpipe, brittle PET-flake outlet
515	longitudinal axis of the screw 520 and the screw housing 510
520	conveyor screw
530	nozzle

Claims

1. Method for preprocessing PET-flake in particular prior to depolymerisation by glycolysis and/or methanolysis and/or hydrolysis and/or saponification or any other combination of these PET depolymerisation processes, wherein the method comprises extracting organic colorants from the PET-flake and simultaneous embrittlement of the PET-flake by:

   – contacting PET-flake with ethylene glycol (EG, IUPAC name: ethane-1,2-diol, CAS: 107-21-1) in a contacting vessel (370) at preferably ambient pressure, and

   – removing used ethylene glycol and adding fresh ethylene glycol,

   characterized in, that

   prior to the extraction step the PET-flake are pre-treated by immersing the PET-flake in an organic solvent comprising at least one of the following compounds: benzophenone ($C_{13}H_{10}O$, CAS: 119-61-9) and/or polyethylene glycol 600 (“PEG”, $HO(C_2H_4O)_n$, CAS: 25322-68-3) and/or 1,2-dichlorobenzene ($C_6H_4Cl_2$, CAS: 95-50-1) and/or limonene ($C_{10}H_{16}$, CAS: 5989-27-5) and/or 1,4-dioxane ($C_4H_8O_2$, CAS: 123-91-1) and/or ethylene glycol (EG, $C_2H_6O_2$, CAS: 107-21-1) and/or triethylene glycol (“TEG”, $C_6H_{14}O_4$, CAS: 112-27-6) and/or tetraethylene glycol ($C_8H_{18}O_5$, CAS: 112-60-7).

2. Method of claim 1,

characterized in, that

extracting is stopped if the PET-flake show at least one of the following properties:

- an intrinsic viscosity IV < 0.20dL/g and/or
- a molar mass Mn with 3000g/mol ≤ Mn ≤ 8000 g/mol and/or
- a degree of polymerization Pn < 20.

3. Method of claim 1 or 2

characterized in, that

the method further comprises conveying PET-flake in a PET conveying direction and simultaneously contacting the PET-flake with ethylene glycol.

4. Method of claim 3,

characterized in, that

extracting is obtained by contacting the PET-flake with a counter flow of ethylene glycol being directed against the PET conveying direction.

5. Method of claim 3 or 4,

characterized in, that

the method further comprises

conveying the PET-flake in a screw-conveyor (370, 500) as contacting vessel and establishing a counter flow of ethylene glycol in the screw conveyor to thereby extract organic colorants form the PET-flake.

6. Method of one of the previous claims,

characterized in, that

the method includes providing ethylene glycol vapour to the PET-flake and/or an contacting vessel and/or liquid ethylene glycol in the contacting vessel for heating the PET-flake by heat transfer from condensing ethylene glycol vapour.

7. Method of one of claims 1 to 6,

characterized in, that

the extraction temperature T_{ext} is set between 192°C and 205°C ($192°C \leq T_{ext} \leq 205°C$), preferably $195°C \leq T_{ext} \leq 200°C$, more preferably $196°C \leq T_{ext} \leq 199°C$, particularly preferred $197.0° \leq T_{ext} \leq 197.6°C$ at preferably ambient pressure p_a (±200hPa)

8. Method of one of claims 1 to 7,

characterized in, that

the temperature T_{pre} of the organic solvent while immersing the PET-flake is above the glass transition temperature T_{gl} of the PET-flake and below the melting point temperature T_{melt} of the PET-flake ($T_{gl} \leq T_{pre} \leq T_{melt}$).

9. Apparatus, for extracting organic colorants from PET-flake in particular according to the method of claims 1 to 8, comprising at least

   – a screw-conveyor (370, 500) with a screw housing (510) and a conveyor screw (520) for conveying PET-flake via the screw housing (510) from at least one PET-flake inlet (374) in a PET conveying direction to at least one PET-flake outlet (375), and

   – at least one ethylene glycol inlet (371,372) in the screw housing (510), the ethylene glycol inlet (371,372) being downstream of the PET inlet (374) and an ethylene glycol outlet (373) upstream of the ethylene glycol inlet (371, 372) for contacting the PET-flake with a flow of ethylene glycol being counter-current to the PET-conveying direction.

   characterized in that

   the apparatus further comprises at least a pre-treatment vessel (340) for immersing PET-flake in a pre-treatment liquid at a temperature T_{pre} of $T_{gl} \leq T_{pre} \leq T_{melt}$, wherein T_{gl} is the glas transition temperature and T_{melt} the melting temperature; wherein the pre-treatment vessel (340) comprises a PET-strainer for removing PET from the pre-treatment vessel and feeding the PET-flake inlet of the screw conveyor (500).

10. Apparatus of claim 9

    characterized in that

    pre-treatment vessel comprises an inlet for the pre-treatment liquid, wherein the inlet for the for the pre-treatment liquid is connected with a source of an organic solvent, the organic solvent comprising at least one of the following compounds: benzophenone ($C_{13}H_{10}O$, CAS: 119-61-9) and/or polyethylene glycol 600 ("PEG", $HO(C_2H_4O)_n$, CAS: 25322-68-3) and/or 1,2-dichlorobenzene ($C_6H_4Cl_2$, CAS: 95-50-1) and/or limonene ($C_{10}H_{16}$, CAS: 5989-27-5) and/or 1,4-dioxane ($C_4H_8O_2$, CAS: 123-91-1) and/or ethylene glycol (EG, $C_2H_6O_2$, CAS: 107-21-1) and/or triethylene glycol ("TEG", $C_6H_{14}O_4$, CAS: 112-27-6) and/or tetraethylene glycol ($C_8H_{18}O_5$, CAS: 112-60-7).

11. Apparatus for of claim 9 or 10,

    characterized in that

    it further comprises at least one ethylene glycol vapour source (130) for providing gaseous ethylene glycol to the PET-flake in the screw housing (510), the ethylene glycol vapour source being connected to an ethylene glycol inlet (372).

12. Apparatus of claim 10 or 11

    characterized in that

    the screw housing (510) has at least one condensing chamber, the condensing chamber being in fluid communication with an ethylene glycol vapour source.

13. Apparatus of claim 12

characterized in that

the condensing chamber has a drain for removing condensed ethylene glycol vapour, the drain being connected to at least one ethylene glycol inlet (371) of the screw housing and/or at least one ethylene glycol vapour generator for providing liquid ethylene glycol to said at least one ethylene glycol vapour generator.

Fig. 1

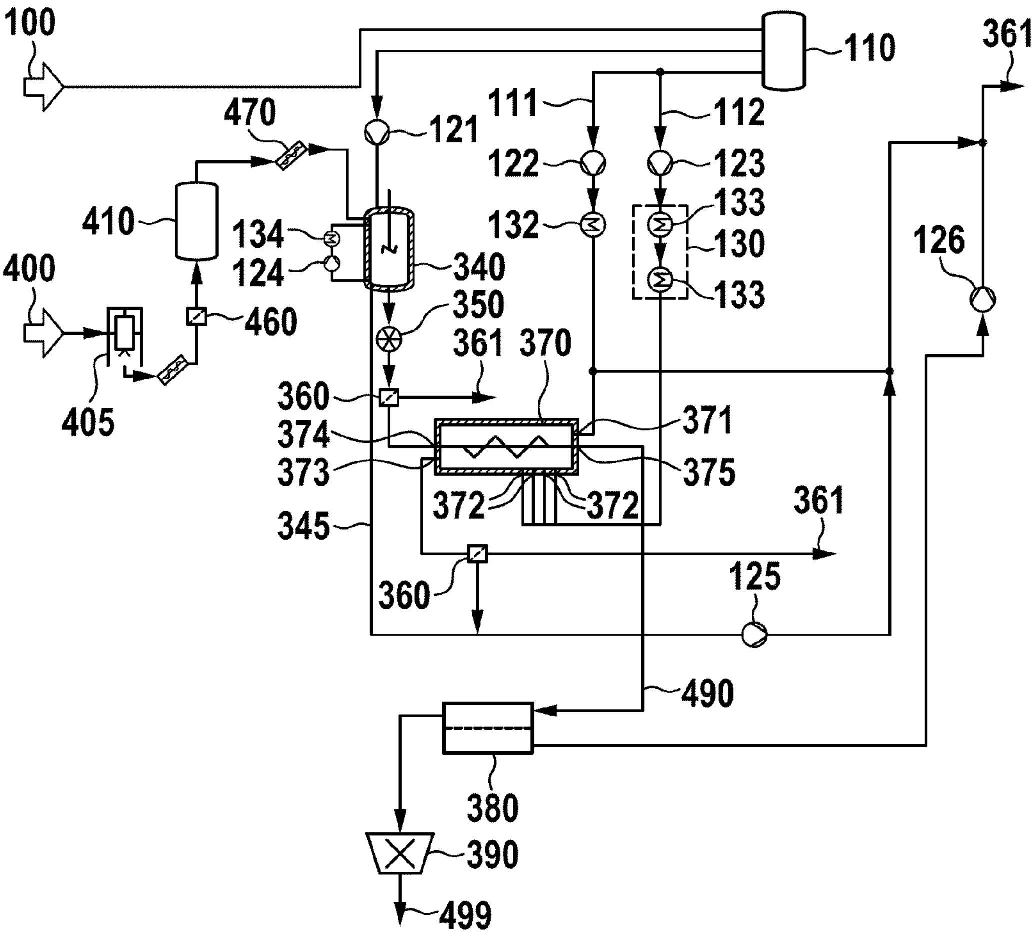

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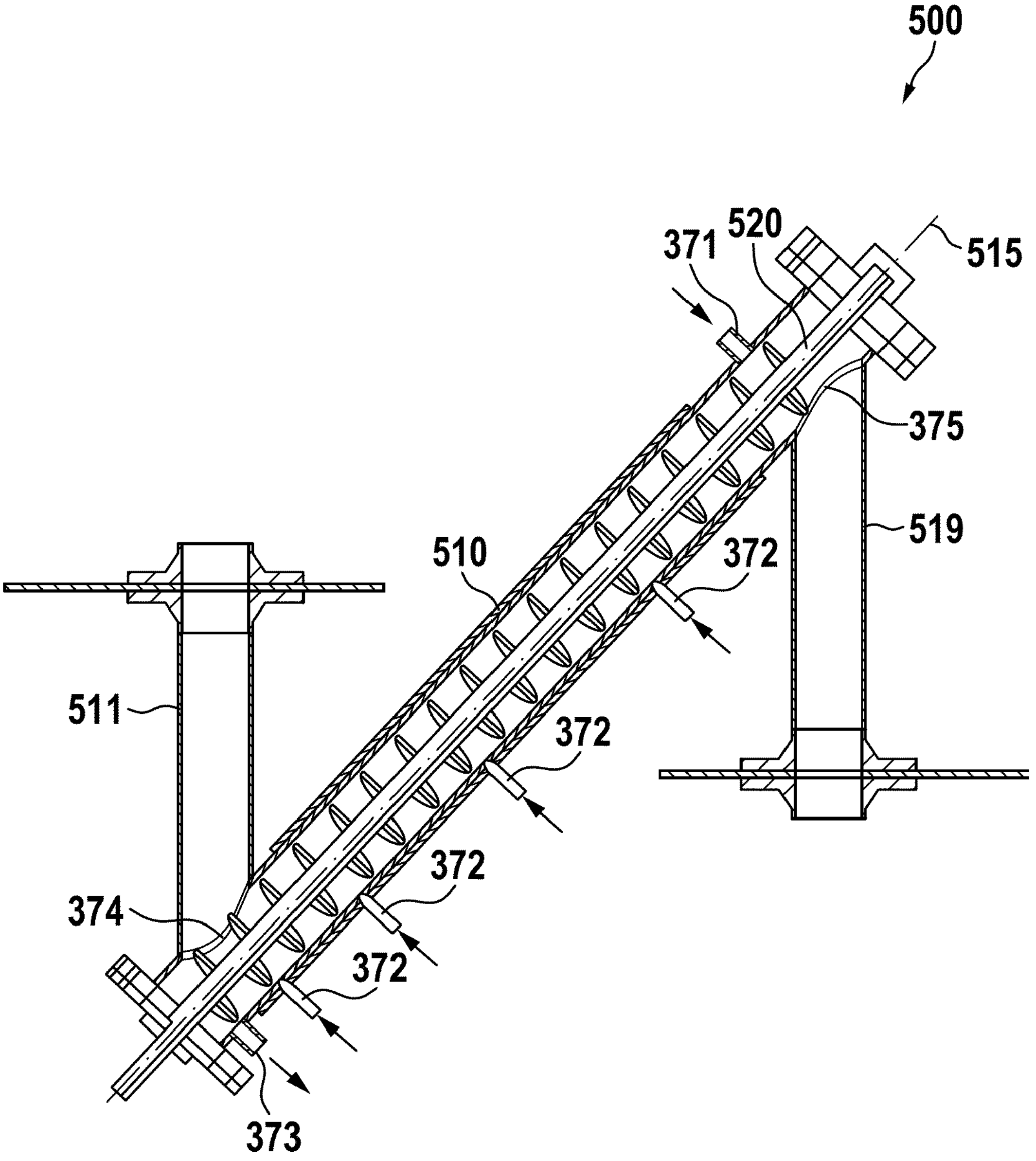
Fig. 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/056053

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J11/24 C08J11/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X Y	EP 1 914 270 A1 (TEIJIN FIBERS LTD [JP]) 23 April 2008 (2008-04-23) paragraphs [0001], [0017], [0019], [0032], [0035], [0037], [0059] - [0062] -----	9,11-13 1-8,10
X Y	JP 2007 045874 A (TEIJIN FIBERS LTD) 22 February 2007 (2007-02-22) paragraphs [0002], [0024], [0026], [3143] - [0046] -----	9,11-13 1-8,10
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search 4 April 2014	Date of mailing of the international search report 16/04/2014
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Magrizo, Simeon

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/056053

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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