

Composition for polyester hydrolytic stabilization

The present invention relates to hydrolysis-resistant polyester films.

- 5 Polyester films are well known. However, a disadvantage of unstabilized polyester films is their susceptibility to hydrolysis, especially at temperatures above the glass transition temperature of the particular polyester. Susceptibility to hydrolysis is the property of the polyester to hydrolytically degrade under moisture conditions, which can be seen for example in a reduction in the IV (intrinsic viscosity) value.
- 10 This is a limiting factor for the use of polyester films, particularly in applications with high temperature stress, such as in film capacitors, cable sheathing, ribbon cables, motor protection films, battery films, flooring films, window films, photovoltaic back sheets, but also in long-term applications such as in glazing and outdoor applications.
- 15 Particularly pronounced susceptibility to hydrolysis is observed in aliphatic polyesters, but also with aromatic polyesters such as PBT and PET. When the hydrolysis tendency of PET is too large for the application, one has to resort to hydrolysis-stable PEN or even to other polymers such as polyethers or polyimides.
- 20 However, these polymers are significantly more expensive than PET and therefore disadvantageous for economic reasons.

Therefore, it has been proposed to improve the hydrolytic stability of polyester films by incorporating hydrolysis stabilizers.

- 25 Hydrolysis resistant polyester raw materials, which are obtained by using carbodiimides, are known (US-A-5,885,709, EP-A-0838500, CH-A-621 135). Films prepared from such polymers tend, however, both in manufacturing and in the later use to outgas isocyanates which are irritant to the mucous membrane, or set
- 30 free other harmful byproducts and degradation products. Hydrolysis stabilizers based on epoxy groups also give hydrolysis stabilization and are described for example in EP-A-0 292 251 or US-A-3,657,191. However, these compounds are based on the generation of oxirane rings by means of epichlorohydrin, and display

a tendency for cleaving low molecular weight toxic compounds, so that similar problems as associated with the use of carbodiimides arise. Furthermore, their incorporation into the polyester matrix is insufficient, leading to long reaction times and oriented polyester films in high clouding.

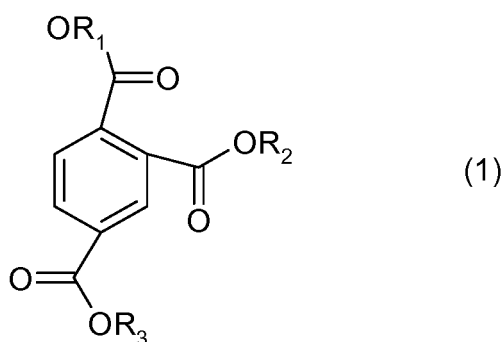
5

Moreover, known hydrolysis stabilizers such as carbodiimides and other substances such as those described in EP-A-0 292 251 have the disadvantage that they sometimes lead to strong increase in molecular weight (viscosity increase) in the polymer during extrusion and thus make the extrusion process

10 unstable and difficult to control.

It is therefore an object of the present invention to provide a hydrolysis-resistant polyester raw material which avoids the disadvantages of the prior art described.

- 15 The object is surprisingly achieved by a polyester article, preferably a film, which contains a hydrolysis stabilizer based on an alkoxy-functionalized trimellitate. The present invention is directed to the use of at least one compound of the formula (1)



20

wherein

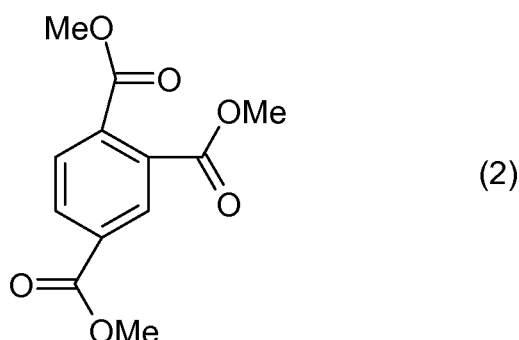
R₁, R₂ and R₃ are the same or different and denote a C₁-C₁₀-alkyl, preferably C₁-C₆-alkyl, more preferably C₁-C₄-alkyl, most preferably C₁-C₂-alkyl,

25 as a hydrolysis stabilizer in polyester materials.

Examples for compounds of the formula (I) are trimethyltrimellitate, triethyltrimellitate, tripropyltrimellitate, tributyltrimellitate, tripentyltrimellitate, trihexyltrimellitate, triheptyltrimellitate, trioctyltrimellitate, trinonyltrimellitate and tridecyltrimellitate.

5

The most preferred compound of formula (I) is trimethyl trimellitate (TMTM) of formula (2)



10

This molecule is manufactured by esterification of trimellitic anhydride with methyl alcohol.

The proportion of the hydrolysis stabilizer is preferably in the range from 0.1 to 20.0 wt.-%, more preferably from 1.0 to 10.0 wt.-%, and particularly preferably 1.5 to 5.0 wt.-%, based on the weight of the polyester. If incorporated in a masterbatch, the proportion of the hydrolysis stabilizer is generally from 0.1 to 80.0 wt.-%, preferably 1.0 to 50.0 wt.-%, more preferred 2.0 to 30 wt.-%, even more preferred 2.5 to 25 wt.-%, each based on the total weight of the masterbatch.

20

Suitable polyesters are, for example, aromatic polyesters, such as polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polybutylene terephthalate (PBT), polytrimethylene terephthalate (PTT), dibenzoyl polyethylene terephthalate (PETBB), dibenzoyl polybutylene terephthalate (PBTBB), dibenzoyl polyethylene naphthalate (PENBB) or mixtures thereof. Preferred are PET, PBT, PEN and PTT, and mixtures and co-polyesters thereof.

25

For the preparation of polyesters, in addition to the main monomers, dimethyl terephthalate (DMT), ethylene glycol (EG), propylene glycol (PG), 1,4-butanediol, terephthalic acid (TA), benzene dicarboxylic acid and / or

2,6-naphthalenedicarboxylic acid (NDA) and isophthalic acid (IPA), trans- and / or
5 cis-1,4-cyclohexanedimethanol (CHDM-c, t-CHDM or c / t-CHDM) and other suitable dicarboxylic acids or dicarboxylic acid esters and diol components may be used.

Suitable polyesters are also aliphatic polyesters such as polyhydroxybutyrate
10 (PHB) and its copolymer with polyhydroxyvalerate (PHV), polyhydroxybutyrate-valerate (PHBV), poly (ϵ -caprolactone) (PCL), SP 3/6, 4/6 SP (consisting of 1,3-propanediol / adipate or 1,4-butanediol / adipate), polycaprolactam or generally adipic-acid polyester and the esters of other aliphatic carboxylic acids.

15 The polyester used in the invention may further contain inorganic or organic particles, which are useful for adjusting the surface topography or optical properties and are called polyester composition hereinafter. The amount of the particles is dependent on the use and their particle size. The latter is generally in the range of 0.01 to 30.0, preferably 0.1 to 5.0, and especially 0.3 to 3.0 microns.

20

Suitable compounds for obtaining roughness are e.g. calcium carbonate, barium sulphate, apatite, silicon dioxide, titanium dioxide, aluminum oxide, crosslinked polystyrene, crosslinked PMMA, zeolites, and other silicates such as aluminum silicates. These compounds are generally used in amounts of 0.05 to 5 wt.-%,
25 preferably 0.1 to 0.6 wt.-%, (based on the total weight of the polyester composition).

Apart from the before mentioned additives, the polyester composition may additionally contain other components such as flame retardants and / or radical
30 scavengers and / or other polymers, such as polyetherimides, pigments and dyes, stabilizers, antioxidants, antibacterial agents, thermostabilizers, light stabilizers, neutralizers, antistatic agents, antiblocking agents, optical brighteners, heavy metal inactivation agents, hydrophobic agents, peroxides, water scavengers, acid

scavengers, hydrotalcites, elastomers, impact modifiers, laser marking additives, processing aids , and mixtures thereof.

5 The hydrolysis stabilizer of formula (1) is preferably added to the polyester by way of masterbatch technology. For this purpose, the hydrolysis stabilizer is first dispersed in a carrier material. Suitable support materials can be the polyester itself, e.g. polyethylene terephthalate, or other polymers which are compatible with the respective polyester. Depending on the carrier resin the masterbatch can be solid or liquid, a solid being preferred. After the addition of the masterbatch into the
10 polyester material, the components of the masterbatch melt during extrusion and are dissolved or finely dispersed in the polyester. As the hydrolysis stabilizer is physically homogeneously dispersed in the carrier, while the masterbatch is mixed with the polyester, the potential for localized higher concentrations of hydrolysis stabilizer is minimized. Furthermore, when introduced into a molding apparatus, a
15 premature reaction of the alkyloxy-functionalized trimellitic acid hydrolysis stabilizer within the let down polymer is prevented by increasing the time required to melt the concentrate. This delayed reaction time permits the hydrolysis stabilizer to be fully dispersed throughout the polymer.

20 The hydrolysis stabilizer of formula (1) can be incorporated into the polyester material to be stabilized as follows:

The carrier material of the masterbatch to be produced and the hydrolysis stabilizer are fed into an extruder, preferably a twin-screw extruder, melted, mixed
25 and then extruded through a perforated die, quenched and granulated. Preferred is a method in which the polymer is first melted in an extruder and after degassing the hydrolysis stabilizer is metered directly into the melt.

Thus, another subject of the invention is a method for stabilizing a polyester
30 material comprising the step of incorporating at least one hydrolysis stabilizer of formula (1) into the polyester material to be stabilized.

The hydrolysis stabilized polyester material is expediently processed into a polymeric article, e.g. sheets, films, containers or fibers. Sheets and films are particularly preferred.

- 5 Advantageously, the hydrolysis stabilized polyester articles, e.g. films, contain further customary polymer stabilizers such as radical scavengers, light stabilizers or heat stabilizers, advantageously in amounts of from 50 to 15,000 ppm, preferably 100 to 5,000 ppm, more preferably 300 to 1000 ppm, based on the total weight of the article. The customary polymer stabilizers can be selected from the
- 10 group of the primary stabilizers, such as sterically hindered phenols or secondary aromatic amines, or from the group of secondary stabilizers such as thioethers, phosphonites, and zinc dibutyl-dithio-carbamate or mixtures of primary and secondary stabilizers. Preferred are phenolic stabilizers. Particularly preferred among the phenolic stabilizers are sterically hindered phenols, thiobisphenols,
- 15 alkylidenebisphenols, alkyl phenols, hydroxybenzyl compounds, acyl-amino and hydroxyphenylpropionates.

- Also UV-absorbers, based on benzotriazoles, like Tinuvin 1577, Tinuvin 1600, Tinuvin 360, Tinuvin 234, Cyasob 3638, Cyasorb 1164, are advantageously used
- 20 in films for outdoor applications. These additives might be added in the range from 0.1 to 20.0 wt.-%, preferably from 1.0 to 10.0 wt.-%, and particularly preferably 1.5 to 5 wt.-%, based on the total weight of the film.

- Apart from the addition of the hydrolysis stabilizer in form of a masterbatch, the
- 25 hydrolysis stabilizer may be added directly during the production of the polyester article, e.g. film. Particularly good results are obtained when twin-screw extruders are used and the hydrolysis stabilizer is metered directly into the melt of the respective extruder.

- 30 Films can be prepared by conventional extrusion processes for producing monolayer and multilayer films. The hydrolysis stabilizer is preferably present in all layers, embodiments are also possible, in which not all layers are modified with the hydrolysis stabilizer.

Commonly, the respective melts are extruded through a flat-film die, the resultant film for solidification on one or more roller/s (cooling roll) is withdrawn as a substantially amorphous prefilm, and quenched, the film is then reheated and

5 biaxially stretched (oriented) and the biaxially stretched film is heat-set. The biaxial stretching is performed sequentially in machine direction (= MD) and then transversely, perpendicular to the machine direction (= TD). This leads to an orientation of the molecular chains.

10 The temperature at which the orientation is carried out can vary over a relatively wide range and depends on the desired properties of the film. The first longitudinal stretching can optionally be carried out simultaneously with the transverse stretching (simultaneous stretching).

15 Film produced in this manner has a much lower tendency to hydrolyze from room temperature up to 210 °C than an unmodified polyester film. The stabilization is largely independent of the film thickness and the temperature.

It was particularly surprising that no undesired viscosity increase in the extruder
20 during film production occurs and no increased gel or speck level was observed.

Films, which are stabilized by means of the hydrolysis stabilizer of formula (1) are ideal for the production of products containing polyester films which should have a long life (greater than 1 year), and are employed in applications where higher
25 temperatures (above 80 °C) and high humidity are present.

The stabilizers of formula (1) are especially useful for the production of film capacitors (preferred thickness range from 0.3 to 12 microns). For the manufacture of capacitors, it has proved to be advantageous when the films have
30 a longitudinal shrinkage of less than 4 % and a transverse shrinkage of less than 1 % at 200 °C, as it particularly well suited for the production of SMD capacitors. Another application is for ribbon cables in automobiles.

In the following embodiments, the measurement of individual properties are in accordance with approved standard methods. Percentages are weight percent unless indicated otherwise.

5 Measurement methods

Pressure Cooker Test PCT

This kind of test provides information about hydrolysis resistivity as fast track.

10 Samples were cut before autoclaving and stored at 120 °C and 2 bar (abs) for 0, 40, 50 h. For each test, five test samples were measured.

Damp Heat Test DHT

This kind of test provides information about hydrolysis resistivity as long-term process. Samples were cut before autoclaving and stored at 85 °C and normal
15 pressure up to 5000 h, after each 500 h test results were measured.

Tensile Testing

The tensile test was processed with an aluminum clamp of 100 mm compliant with ISO 527-1/2 to obtain elongation at break and tensile strength. The results are the
20 averaged values of five measurements.

- Testing speed:

- $\epsilon < 0.25 \%$: 1 mm/min
- $\epsilon > 0.25 \%$: 100 mm/min

25

- Elongation at break retention is measured to receive an indication of embrittlement of the film, after x h autoclaving:

$$= \frac{\text{Elongation at break after } x \text{ h autoclaving}}{\text{Elongation at break after } 0 \text{ h autoclaving}}$$

30

Intrinsic Viscosity (I.V.)

The measurement of the intrinsic viscosity (I.V.) was used to measure the molecular weight of the polymer, as the intrinsic viscosity is a unique function of the molecular weight of a polymer. The I.V. was detected by using a Davenport viscosimeter for melt viscosity measurements, e.g. for PET, in the molten state
 5 extruded through a calibrated die using high pressure nitrogen gas.

Standard viscosity (S.V.)

The standard viscosity S.V. is – based on DIN 53726. By measuring the relative viscosity η_{rel} of a 1 % solution in dichloroacetic acid (DCA) in an Ubbelohde
 10 viscometer at 25 °C. The S.V. value is defined as follows:

$$S.V. = (\eta_{rel} - 1) \cdot 1000 \quad S.V. = (\eta_{rel} - 1) \times 1000$$

In the following Examples the following materials are used:

- | | | |
|----|--------------------------|--|
| 15 | PET1: | (XPURE 4004, Invista, I.V. 0.63) |
| | PET2: | regranulat RT4027 (Invista / Erema) |
| | PET3: | RAMAPET R 180 GR BB (Indorama Plastics) |
| | PC (Polycarbonate): | Trirex 3022PJ(01) Entec |
| | Hydrolysis stabilizator: | TMTM (Trimethyltrimellitate) |
| 20 | UV-Absorber: | 2-(4,6-Diphenyl-1,3,5-triazin-2-yl)-5-hexyloxy-phenol
(TINUVIN 1577 ED, BASF) |

Two Masterbatches (MBHS and MBUV) were produced by using a twin-screw extruder Leistritz MASS technology (27 mm/ 40D). MBHS contains 10 % of TMTM
 25 on PC for the hydrolysis stabilization. MBUV contains 15 % of the UV-absorber Tinuvin 1577 on PET3.

Example 1

A three layer film was produced with a structure of ABA. The composition of the
 30 core layer B consists of 52 % PET1, 15 % PET 2, 3 % MBHS, 30 % MBUV. The outer layers A consists of 67 % PET1, 3 % MBHS, 30 % MBUV. The used PET was predried at 100 - 170 °C. The main extruder was equipped with vacuum ~10 mbar. The coextruder was equipped with vacuum ~ 20 mbar.

The extrusion temperatures of the different zones are displayed in Table 1.

Table 1: Extrusion Temperatures in °C:

Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Zone 8	Zone 9
100	102	104/105	106	120/130	210	210/215	220	200/190

5

The molten polymer was discharged from a nozzle of a draw roller. The film was stretched by a factor of 3.0 in the machine direction and stretched in a cross-stretching by a factor of 3.4. Subsequently, the film was heat set at 225 °C and relaxed in the transverse direction by 3 % at temperatures of 220 - 180 °C. The final film thickness was 50 microns.

10

Example 2 (comparative)

A three layer film was produced with a structure of ABA. The composition of the core layer B consists of 45 % PET1, 25 % PET 2, 30 % MBUV. The outer layers A consists of 70 % PET1, 30 % MBUV. The used PET was predried at 100 - 170 °C. The main extruder was equipped with vacuum ~10 mbar. The coextruder was equipped with vacuum ~ 20 mbar.

15

The extrusion temperatures of the different zones are displayed in Table 2.

20

Table 2: Extrusion Temperatures in °C:

Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Zone 8	Zone 9
100	102	104/105	106	120/130	210	210/215	220	200/190

The molten polymer was discharged from a nozzle of a draw roller. The film was stretched by a factor of 3.0 in the machine direction and stretched in a cross-stretching by a factor of 3.4. Subsequently, the film was heat set at 225 °C and relaxed in the transverse direction by 3 % at temperatures of 220 - 180 °C. The final film thickness was 50 microns.

25

Test results

Table 3: Results of testing

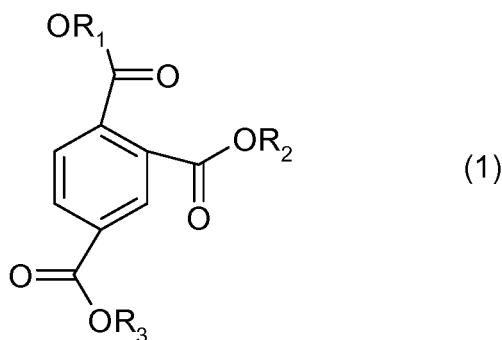
Test	Example 1	Example 2 comp.
Pressure Cooker Test = Elongation at break retention after autoclavation (120 °C / 2 bar abs)	87 % after 40 h 81 % after 50 h	76 % after 40 h 42 % after 50 h
Damp Heat Test = Elongation at break retention after conditioning (85 % rH / 85 °C)	58 % after 2000 h 22 % after 2500 h	43 % after 2000 h 1 % after 2500 h
Intrinsic melt Viscosity (I.V.)	0.639	0.527
Standard Viscosity (S.V.)	0.638	0.608

- 5 The test results of example 1, which contain the anti-hydrolysis-additive convinces in all tests, which simulate hydrolysis degradation of polymer. In the pressure cooker test the film stayed significantly longer stabile than the film without anti-hydrolysis-additive. Also in the damp heat test the material equipped with anti-hydrolysis-additive resisted significantly longer than the non-equipped film. Also
- 10 the measurement of the melt viscosity and the standard viscosity show the more stabilized material is the one which was equipped with the anti-hydrolysis-additive.

All films of Example 1 also display a high UV stability.

Patent claims

1. Use of at least one compound of the formula (1)



wherein

R₁, R₂ and R₃ are the same or different and denote a C₁-C₁₀-alkyl,
as a hydrolysis stabilizer in polyester materials.

2. The use as claimed in claim 1, wherein the compounds of the formula (I) are trimethyltrimellitate, triethyltrimellitate, tripropyltrimellitate, tributyltrimellitate, tripentyltrimellitate, trihexyltrimellitate, triheptyltrimellitate, trioctyltrimellitate, trinonyltrimellitate or tridecyltrimellitate.

3. The use as claimed in claims 1 or 2, wherein the compound of formula (1) is trimethyltrimellitate.

4. The use as claimed in any of the preceding claims, wherein the polyester in the polyester materials is polyethylene terephthalate, polyethylene naphthalate, polybutylene terephthalate, polytrimethylene terephthalate, dibenzoyl polyethylene terephthalate, dibenzoyl polybutylene terephthalate, dibenzoyl polyethylene naphthalate or mixtures thereof.

5. The use as claimed in any of the preceding claims, wherein the polyester in the polyester materials is polyethylene terephthalate, polybutylene terephthalate,

polyethylene naphthalate, polytrimethylene terephthalate or mixtures or co-polyesters thereof.

6. The use as claimed in any of the preceding claims, wherein the polyester in the polyester materials are aliphatic polyesters selected from the group consisting of polyhydroxybutyrate and its copolymer with polyhydroxyvalerate, polyhydroxybutyrate-valerate, and poly (ϵ -caprolactone).

7. The use as claimed in any of the preceding claims, wherein the proportion of the compound of formula (1) is from 0.1 to 20.0 wt.-%, based on the weight of the stabilized polyester material.

8. The use as claimed in any of the preceding claims, wherein the proportion of the compound of formula (1) is from 1.0 to 10.0 wt.-%, based on the weight of the stabilized polyester material.

9. The use as claimed in any of the preceding claims, wherein the proportion of the compound of formula (1) is from 1.5 to 5.0 wt.-%, based on the weight of the stabilized polyester material.

10. The use as claimed in any of the preceding claims, wherein the compound of formula (1) is used in combination with further additives selected from the group consisting of radical scavengers, light stabilizers, heat stabilizers, flame retardants, pigments, dyes, antioxidants, antibacterial agents, neutralizers, antistatic agents, antiblocking agents, optical brighteners, heavy metal inactivation agents, hydrophobic agents, peroxides, water scavengers, acid scavengers, hydrotalcites, elastomers, impact modifiers, laser marking additives, processing aids, and mixtures thereof.

11. The use as claimed in any of the preceding claims, wherein the compound of formula (1) is used in combination with UV-absorbers.

12. The use as claimed in any of the preceding claims, wherein the compound of formula (1) is used in form of a masterbatch.

13. The use as claimed in any of the preceding claims, wherein the polyester
5 material is in the form of a film or a sheet.