

Amorphous, transparent, UV-stabilized sheet of a crystallizable thermoplastic

5 The invention relates to an amorphous, transparent, UV-stabilized sheet of a crystallizable thermoplastic whose thickness is in the range from 1 to 20 mm. The sheet contains at least one UV light stabilizer and is distinguished by very good optical and mechanical properties. The invention furthermore relates to a process for the production of this sheet, and to the use of the sheet.

10 Amorphous, transparent sheets having a thickness of from 1 to 20 mm are well known. These two-dimensional structures comprise amorphous, non-crystallizable thermoplastics. Typical examples of such thermoplastics which can be converted into sheets are, for example,
15 polyvinyl chloride (PVC), polycarbonate (PC) and polymethyl methacrylate (PMMA). These semifinished products are produced on so-called extrusion lines (cf. Polymer Werkstoffe, Volume II, Technologie 1, p. 136, Georg Thieme Verlag, Stuttgart, 1984). The pulverulent or
20 granular raw material is melted in an extruder. After extrusion, the amorphous thermoplastics can easily be shaped via polishing stacks or other shaping tools as a consequence of their viscosity, which continuously increases with decreasing temperature. After shaping,
25 amorphous thermoplastics then have adequate stability, i.e. a high viscosity, in order to be self-supporting in the calibration die. However, they are still sufficiently soft to be shaped by the die. The melt viscosity and inherent rigidity of amorphous thermoplastics is so high
30 in the calibration die that the semifinished product does not collapse in the calibration die before cooling. In the case of easily decomposed materials, for example PVC, special processing aids, for example processing stabilizers against decomposition and lubricants against
35 excessive internal friction and thus uncontrollable warming, are necessary during extrusion. External lubricants are necessary to prevent sticking to walls and

rolls.

The processing of PMMA is carried out using, for example, a vented extruder to enable removal of moisture.

5 The production of transparent sheets from amorphous thermoplastics sometimes requires expensive additives, which can migrate and can cause production problems owing to evaporations and surface coatings on the semifinished product. PVC sheets can be recycled only with difficulty or using special neutralization or electrolysis processes. 10 PC and PMMA sheets can likewise only be recycled with difficulty and only with loss or extreme impairment of the mechanical properties.

In addition to these disadvantages, PMMA sheets also have extremely poor impact strength and splinter on fracture 15 or mechanical loading. Furthermore, PMMA sheets are readily combustible, which means that they cannot be employed, for example, for internal applications and in exhibitions.

PMMA and PC sheets furthermore cannot be shaped when 20 cold; PMMA sheets disintegrate to form dangerous splinters, while PC sheets undergo hairline cracking and stress whitening.

DE-A-3 531 878 describes plastic films made from thermoplastic polyesters and containing a UV stabilizer and 25 having a thickness of 0.5 - 0.03 mm.

These films are obtained by extrusion blow molding and are thus partially crystalline. Consequently, the process described in this specification cannot give an amorphous film having a thickness of 1 mm or greater.

30 JP-A-5 320 528 describes a thermoplastic resin composition containing an epoxidized polyester. According to a preferred embodiment, this composition contains PVC as

principal constituent. The sheets obtained therefrom by compounding are transparent and have a thickness of 1 mm.

5 EP-A-0 471 528 describes a process for shaping an article from a polyethylene terephthalate (PET) sheet. The PET sheet is heat-treated on both sides in the thermofilming mold in a temperature range between the glass transition temperature and the melting point. The shaped PET sheet is removed from the mold when the degree of crystallization of the shaped PET sheet is in the region of 25 to 10 50%. The PET sheets disclosed in EP-A-0 471 528 have a thickness of from 1 to 10 mm. Since the thermoformed molding produced from the PET sheet is partially crystalline and thus no longer transparent and the surface properties of the molding are determined by the thermoforming process and by the thermoforming temperature and 15 mold, it is unimportant what optical properties (for example gloss, haze and light transmission) the PET sheets employed have. In general, the optical properties of these sheets are poor and in need of optimization.

20 In addition, these sheets contain no UV light stabilizers, so that neither the sheets nor the moldings produced therefrom are suitable for external applications. If used externally, these sheets or moldings exhibit, after only a short time, yellowing and an impairment in the mechanical properties as a consequence of photooxidative degradation by sunlight. 25

US-A-3,496,143 describes the vacuum thermoforming of a 3 mm thick PET sheet whose degree of crystallization is said to be in the range from 5 to 25%. However, the 30 crystallinity of the thermoformed molding is greater than 25%. Again, no requirements regarding optical properties are made of these PET sheets. Since the crystallinity of the sheets employed is already between 5 and 25%, these sheets are hazy and non-transparent. These sheets again 35 contain no light stabilizer and consequently are unsuitable for external applications.

The processes known hitherto do not allow the production of amorphous sheets containing a crystallizable thermoplastic as principal constituent in a thickness of 1 mm or greater in adequate quality.

5 The object of the present invention was to provide an amorphous, transparent sheet having a thickness of from 1 to 20 mm which, in addition to good mechanical and optical properties, also has, in particular, high UV stability.

10 High UV stability means that the sheets experience extremely little damage, or none at all, due to sunlight or other UV radiation, so that the sheets are suitable for outdoor applications and/or critical indoor applications. In particular, after several years of use outside,
15 the sheets do not yellow or exhibit embrittlement or cracking of the surface or impairment of the mechanical properties.

The good optical properties include, for example, high light transmission, high surface gloss, extremely low
20 haze and high clarity.

The good mechanical properties include, inter alia, high impact strength and high breaking strength.

In addition, the novel sheet should be recyclable, in particular without loss of the mechanical properties, and
25 have low combustibility so that it can also be employed, for example, for indoor applications and in exhibitions.

This object is achieved by a transparent, amorphous sheet having a thickness in the range from 1 to 20 mm which contains, as principal constituent, a crystallizable
30 thermoplastic, wherein the sheet contains at least one UV light stabilizer.

The transparent, amorphous sheet contains, as principal

constituent, a crystallizable thermoplastic. Suitable crystallizable or partially crystalline thermoplastics are, for example, polyethylene terephthalate, polybutylene terephthalate, cycloolefin polymers and cycloolefin copolymers, preference being given to polyethylene terephthalate.

For the purposes of the invention, the term crystallizable thermoplastics is taken to mean

- crystallizable homopolymers,
- 10 - crystallizable copolymers,
- crystallizable compounds,
- crystallizable recycle and
- other variations of crystallizable thermoplastics.

For the purposes of the present invention, the term
15 amorphous sheet is taken to mean a sheet which is non-crystalline, although the crystallizable thermoplastic employed preferably has a crystallinity of from 5 to 65%, particularly preferably from 25 to 65%. Non-crystalline or amorphous means that the degree of crystallinity is
20 generally less than 5%, preferably less than 2%, particularly preferably 0%. The novel amorphous sheet is essentially unoriented.

The transparent, amorphous sheet furthermore contains at least one UV light stabilizer, of which the concentration
25 is preferably from 0.01 to 5% by weight, based on the weight of the crystallizable thermoplastic.

Light, in particular the ultra-violet part of sunlight, i.e. having a wavelength in the range of 280 to 400 nm, initiates degradation processes in thermoplastics,
30 resulting not only in a change in the visual appearance as a consequence of color change or yellowing, but also adversely affecting the mechanical-physical properties.

The inhibition of these photooxidative degradation processes is of considerable industrial and economic

importance, since otherwise the potential uses of numerous thermoplastics are drastically limited.

Polyethylene terephthalates begin to absorb UV light, for example, even at below 360 nm, their absorption increases considerably below 320 nm and is very pronounced at below 300 nm. The maximum absorption is between 280 and 300 nm.

In the presence of oxygen, principally chain cleavage, but no crosslinking is observed. Carbon monoxide, carbon dioxide and carboxylic acids represent the predominant photooxidation products in terms of amount. Besides direct photolysis of the ester groups, consideration must also be given to oxidation reactions, which likewise result in the formation of carbon dioxide via peroxide free radicals.

The photooxidation of polyethylene terephthalates can also result, by elimination of hydrogen in the α -position of the ester groups, in hydroperoxides and decomposition products thereof, and associated chain cleavage (H. Day, D. M. Wiles: J. Appl. Polym. Sci 16, 1972, page 203).

UV stabilizers and UV absorbers as light stabilizers are chemical compounds which can engage in the physical and chemical processes of photoinduced degradation. Carbon black and other pigments can provide partial protection from light. However, the substances are unsuitable for transparent sheets since they result in discoloration or a color change. For transparent, amorphous sheets, the only suitable compounds are organic and organometallic compounds which impart only an extremely weak color or color change, or none at all, in the thermoplastics to be stabilized.

Examples of suitable UV light stabilizers are 2-hydroxybenzophenones, 2-hydroxybenzotriazoles, organonickel compounds, salicylic esters, cinnamic ester derivatives, resorcinol monobenzoates, oxanilides, hydroxybenzoic

esters, sterically hindered amines and triazines, preference being given to 2-hydroxybenzotriazoles and triazines.

5 In a particularly preferred embodiment, the novel transparent, amorphous sheet contains, as principle constituents, a crystallizable polyethylene terephthalate and from 0.01 to 5.0% by weight of 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyl)oxyphenol (structure in Fig. 1a) or from 0.01 to 5.0% by weight of 2,2'-methylene-bis(6-10 (2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol (structure in Fig. 1b). In a preferred embodiment, it is also possible to employ mixtures of these two UV stabilizers or mixtures of at least one of these two UV stabilizers with other UV stabilizers, with a total 15 concentration of light stabilizers, preferably from 0.01 to 5.0% by weight, based on the weight of crystallizable polyethylene terephthalate.

The surface gloss, measured in accordance with DIN 67530 (measurement angle 20°), is greater than 120, preferably 20 greater than 140, the light transmission, measured in accordance with ASTM D 1003, being greater than 84%, preferably greater than 86%, and the haze of the sheet, measured in accordance with ASTM D 1003, being less than 15%, preferably less than 11%.

25 The clarity of the sheet measured at an angle of less than 2.5° (ASTM D 1003) is preferably greater than 96%, particularly preferably greater than 97%.

In the case of polyethylene terephthalate, measurement of the Charpy impact strength a_n (measured in accordance 30 with ISO 179/1D) of the sheet is preferably not accompanied by a fracture. In addition, the Izod notched impact strength a_k (measured in accordance with ISO 180/1A) of the sheet is in the range from 2.0 to 8.0 kJ/m², preferably from 3.0 to 8.0 kJ/m², particularly preferably in 35 the range from 4.0 to 6.0 kJ/m².

Polyethylene terephthalate polymers having a crystalline melting point T_m , as measured by DSC (differential scanning calorimetry) at a heating rate of $10^\circ\text{C}/\text{min}$, of from 220° to 280°C , preferably from 250°C to 270°C , a crystallization temperature range T_c from 75°C to 280°C , preferably from 75°C to 260°C , a glass transition temperature T_g of from 65°C to 90°C and a density, measured in accordance with DIN 53479, of from 1.30 to 1.45 g/cm^3 and a crystallinity of from 5 to 65% , preferably from 25% to 65% , are preferred polymers as starting materials for production of the novel sheet.

The standard viscosity SV (DCA) of the polyethylene terephthalate, measured in dichloroacetic acid in accordance with DIN 53728, is from 800 to 1800 , preferably from 950 to 1250 , particularly preferably from 1000 to 1200 .

The intrinsic viscosity IV (DCA) is calculated from the standard viscosity SV (DCA) as follows:

$$\text{IV (DCA)} = 6.67 \cdot 10^{-4} \text{ SV (DCA)} + 0.118$$

The bulk density, measured in accordance with DIN 53466, is preferably from 0.75 to 1.0 kg/dm^3 , particularly preferably from 0.80 to 0.90 kg/dm^3 .

The polydispersity of the polyethylene terephthalate M_w/M_n , measured by gel permeation chromatography, is preferably from 1.5 to 6.0 , particularly preferably from 2.0 to 3.5 .

Weathering tests have shown that the novel UV-stabilized sheets exhibit no yellowing, no embrittlement, no loss in gloss on the surface, no cracking on the surface and no impairment of the mechanical properties even after use outside for from five to seven years.

Besides excellent UV stability, entirely unexpectedly,

good cold formability without fracture, hairline cracking and/or stress whitening was observed, meaning that the novel sheet can be shaped and bent without the action of heat.

- 5 In addition, measurements showed that the novel PET sheet has low combustibility and low flammability, so that it is suitable, for example, for internal applications and in exhibitions.

10 Furthermore, the novel sheet can easily be recycled without environmental pollution and without loss of the mechanical properties, meaning that it is suitable, for example, for use as short-term advertising hoardings or other advertising articles.

15 The novel transparent, amorphous, UV-stabilized sheet can be produced, for example, by extrusion in an extrusion line.

An extrusion line of this type is shown diagrammatically in Fig. 2. It essentially comprises

- an extruder (1) as plastication unit,
- 20 - a sheet die (2) as shaping tool,
- a polishing stack/calender (3) as calibration die,
- a cooling bed (4) and/or a roller conveyor (5) for aftercooling,
- a take-off roll (6),
- 25 - a separating saw (7),
- an edge trimming device (9), and, if desired,
- a stacking unit (8).

30 The process for the production of the novel sheet is described in detail below using the example of polyethylene terephthalate as thermoplastic.

The process comprises drying the crystallizable thermoplastic (e.g. polyethylene terephthalate) if necessary, then melting the dry polymer in the extruder, preferably

together with the UV stabilizer, extruding the melt through a die, calibrating, smoothing and cooling the sheet in the polishing stack and then cutting the sheet to size.

- 5 It is essential in the novel process that the first roll of the polishing stack has a temperature in the range from 50°C to 80°C, since it is otherwise difficult to obtain an amorphous transparent sheet containing a crystallizable thermoplastic in a thickness of 1 mm or
10 greater.

In accordance with the invention, it is possible for the light stabilizer already to have been added by the producer of the thermoplastic raw material or to be metered into the extruder during production of the sheet.

- 15 The light stabilizer is particularly preferably added via masterbatch technology, where the light stabilizer is fully dispersed in a solid carrier material. Suitable carrier materials are certain resins, the thermoplastic itself, such as for example, polyethylene terephthalate,
20 or alternatively other polymers which are sufficiently compatible with the thermoplastic.

- It is important that the particle size and bulk density of the masterbatch are similar to the particle size and bulk density of the thermoplastic, so that a homogeneous
25 distribution and thus homogeneous UV stabilization can take place.

The polyethylene terephthalate is preferably dried at from 160 to 180°C for from 4 to 6 hours before extrusion.

- The polyethylene terephthalate is then melted in the
30 extruder. The temperature of the PET melt is preferably in the range from 250 to 320°C, it being possible for the temperature of the melt to be adjusted essentially both through the temperature of the extruder and through the

residence time of the melt in the extruder.

The melt then leaves the extruder through a die. This die is preferably a sheet die.

5 The PET melted by the extruder and shaped by a sheet die is calibrated, i.e. intensively cooled and smoothed, by smoothing calender rolls. The calender rolls can be arranged, for example, in an I-, F-, L- or S-shape (see Fig. 3).

10 The PET material can then be cooled on a roller conveyor, cut to size in width, cut into appropriate lengths and finally stacked.

15 The thickness of the PET sheet is determined essentially by the take-off unit, which is arranged at the end of the cooling zone, the chill (smoothing) rolls, which are coupled to the take-off unit with respect to speed, and the conveying rate of the extruder on the one hand and the separation between the rolls on the other hand.

The extruders employed can be either single-screw or twin-screw extruders.

20 The sheet die preferably comprises a collapsible die body, the lips and the restrictor bar for flow regulation over the width. To this end, the restrictor bar can be bent by means of tension and pressure screws. The thickness is set by adjusting the lips. It is important to
25 ensure a uniform temperature of the PET and of the lip, since otherwise the PET melt flows out through the various flow channels in different thicknesses.

30 The calibration tool, ie. the smoothing calender, gives the PET melt shape and dimensions. This is achieved by freezing at below the glass transition temperature by cooling and smoothing. Shaping should not be carried out in this state, since otherwise surface defects would form

in this cooled state. For this reason, the calender rolls are preferably driven jointly. The temperature of the calender rolls must be lower than the crystalline melting point in order to avoid sticking of the PET melt. The PET melt leaves the sheet die at a temperature of from 240 to 300°C. The first smoothing/chill roll is at a temperature of from 50°C to 80°C, depending on the output rate and sheet thickness. The second, somewhat colder roll cools the second or other surface.

While the calibration unit freezes the PET surfaces as smoothly as possible and cools the profile until it is rigid in shape, the aftercooling device lowers the temperature of the PET sheet virtually to room temperature. The aftercooling can be carried out on a roller board. The take-off rate should be matched accurately to the calender roll speed in order to prevent defects and thickness variations.

As additional equipment, the extrusion line for the production of PET sheets can also include a separating saw for cutting the sheet to length, a side trimmer, a stacking unit and a monitoring station. The side or edge trimmer is advantageous since the thickness in the edge region may under certain circumstances not be uniform. At the monitoring station, the thickness and optical properties of the sheet are measured.

The surprising multiplicity of excellent properties makes the novel, transparent, amorphous sheet highly suitable for a multiplicity of different uses, for example for interior room panels, for exhibitions and exhibition articles, as displays, for signs, for protective glazing of machines and vehicles, in the lighting sector, in shop fitting and shelf construction, as advertizing articles, as menu holders, as basketball backboards, as room dividers, for aquaria, as information panels and as brochure and newspaper stands.

Owing to the good UV stability, the novel transparent, amorphous sheet is likewise suitable for external applications, such as, for example, for greenhouses, roofing systems, glazing systems, safety glass, external cladding, covers, applications in the construction sector, illuminated advertising profiles, balcony cladding, roof exit doors and caravan windows.

The invention is described in greater detail below with reference to working examples without this representing a limitation.

The individual properties are measured in accordance with the following standards or by the following processes.

Measurement methods

Surface gloss:

The surface gloss is measured at a measurement angle of 20° in accordance with DIN 67530.

Light transmission:

The light transmission is taken to mean the ratio between the total amount of transmitted light and the amount of incident light.

The light transmission is measured using a "Hazegard plus" instrument in accordance with ASTM D 1003.

Haze and clarity:

Haze is the percentage of transmitted light deflected from the incident ray bundle by an average of more than 2.5°. The clarity is measured at an angle of less than 2.5°.

The haze and clarity are measured using a "Hazegard plus" instrument in accordance with ASTM D 1003.

Surface defects:

The surface defects are determined visually.

Charpy impact strength a_n :

5 This parameter is determined in accordance with ISO 179/1D.

Izod notched impact strength a_k :

The Izod notched impact strength a_k is measured in accordance with ISO 180/1A.

Density:

10 The density is determined in accordance with DIN 53479.

SV (DCA) and IV (DCA):

The standard viscosity SV (DCA) is measured in accordance with DIN 53726 in dichloroacetic acid.

15 The intrinsic viscosity (IV) is calculated as follows from the standard viscosity (SV):

$$IV (DCA) = 6.67 \times 10^{-4} SV (DCA) + 0.118.$$

Thermal properties:

20 The thermal properties, such as crystalline melting point T_m , crystallization temperature range T_c , after- or cold-crystallization temperature T_{CN} and glass transition temperature T_g are measured by differential scanning calorimetry (DSC) at a heating rate of 10°C/min.

Molecular weight and polydispersity:

25 The molecular weights M_w and M_n and the resultant polydispersity M_w/M_n are measured by gel permeation chromatography (GPC).

Weathering (on both sides), UV stability:

The UV stability is tested as follows in accordance with ISO 4892 test specification:

	Test instrument	:	Atlas Ci 65 Weather-O-meter
	Test conditions	:	ISO 4892, i.e. artificial weathering
	Exposure time	:	1000 hours, (per side)
5	Exposure	:	0.5 W/m ² , 340 nm
	Temperature	:	63°C
	Relative atmospheric humidity	:	50%
10	Xenon lamp	:	inner and outer filters made of borosilicate
	Exposure cycles	:	102 minutes UV light, then 18 minutes UV light with water spraying of the samples, then a further 102 minutes UV light, etc.
15			

Color change:

The color change of the samples after artificial weathering is measured in accordance with DIN 5033 using a spectrophotometer.

20 The following symbols are used:

ΔL : Difference in brightness

+ ΔL : The sample is brighter than the standard

- ΔL : The sample is darker than the standard

ΔA : Difference in the red-green region

25 + ΔA : The sample is redder than the standard

- ΔA : The sample is greener than the standard

ΔB : Difference in the blue-yellow region

+ ΔB : The sample is yellower than the standard

- ΔB : The sample is bluer than the standard

30 ΔE : Overall color change

$$\Delta E = \sqrt{\Delta L^2 + \Delta A^2 + \Delta B^2}$$

The larger the numerical deviation from the standard, the greater the color difference.

Numerical values of ≤ 0.3 can be neglected and mean that there is no significant color change.

Yellow value:

The yellow value G is a deviation from colorlessness toward "yellow" and is measured in accordance with DIN 6167. Yellow values of ≤ 5 are invisible.

The examples and comparative examples below each relate to single-layer transparent sheets of various thicknesses produced on the extrusion line described.

10 All sheets were weathered in accordance with ISO 4892 test specification on both sides for 1000 hours per side using the Atlas Ci 65 Weather-O-meter and subsequently tested for their mechanical properties discoloration, surface defects, haze and gloss.

15 Example 1:

A transparent, amorphous sheet with a thickness of 3 mm is produced which contains, as principal constituents, polyethylene terephthalate and 1.0% by weight of UV stabilizer 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyl)-oxyphenol ([®]Tinuvin 1577 from Ciba-Geigy).

Tinuvin 1577 has a melting point of 149°C and is thermally stable up to about 330°C.

In order to ensure homogeneous distribution, 1.0% by weight of the UV stabilizer are incorporated into the polyethylene terephthalate directly by the raw material producer. The polyethylene terephthalate from which the transparent sheet is produced has a standard viscosity SV (DCA) of 1010, which corresponds to an intrinsic viscosity IV (DCA) of 0.79 dl/g. The moisture content is < 0.2% and the density (DIN 53479) is 1.41 g/cm³. The crystallinity is 59%, and the crystalline melting point, according to DSC measurements, is 258°C. The crystal-

lization temperature range T_c is between 83°C and 258°C , and the after- crystallization temperature (also known as cold-crystallization temperature) T_{CN} is 144°C . The polydispersity M_w/M_n of the polyethylene terephthalate is 2.14. The glass transition temperature is 83°C .

Before extrusion, the polyethylene terephthalate with a crystallinity of 59% is dried in a drier for 5 hours at 170°C and then extruded in a single-screw extruder at an extrusion temperature of 286°C through a sheet die onto a smoothing calender whose rolls are arranged in an S-shape, and smoothed to give a sheet with a thickness of 3 mm. The first calender roll has a temperature of 73°C and the subsequent rolls each have a temperature of 67°C . The take-off rate and the calender roll speed are 6.5 m/min.

Following aftercooling, the transparent PET sheet with a thickness of 3 mm is trimmed at the edges using separating saws, cut to length and stacked.

The transparent, amorphous PET sheet produced has the following property profile:

	- thickness	: 3 mm
	- surface gloss, 1st side	: 198
	(measurement angle 20°) 2nd side	: 196
	- light transmission	: 91%
25	- clarity	: 100%
	- haze	: 1.5%
	- surface defects per m^2	: none
	(fisheyes, orange peel, bubbles, etc)	
30	- Charpy impact strength a_n	: no fracture
	- Izod notched impact strength a_k	: 4.2 kJ/m^2

- cold formability : good, no defects
- crystallinity : 0%
- density : 1.33 g/cm³

5 After weathering for 1000 hours per side using the Atlas Ci 65 Weather-O-meter, the PET sheet exhibits the following properties:

- thickness : 3 mm
- surface gloss, 1st side : 196
- (measurement angle 20°) 2nd side : 195
- 10 - light transmission : 91.1%
- clarity : 100%
- haze : 1.6%
- overall discoloration ΔE : 0.22
- dark discoloration ΔL : -0.18
- 15 - red-green discoloration ΔA : -0.08
- blue-yellow discoloration ΔB : 0.10
- surface defects
(cracks, embrittlement) : none
- yellow value G : 4
- 20 - Charpy impact strength a_n : no fracture
- Izod notched impact strength a_k : 4.1 kJ/m²
- cold formability : good

Example 2:

25 A transparent, amorphous sheet is produced analogously to Example 1, with the UV stabilizer 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyl)-oxyphenol ([®]Tinuvin 1577) being metered in in the form of a masterbatch. The masterbatch consists of 5% by weight of [®]Tinuvin 1577 as active ingredient and 95% by weight of the polyethylene tere-

phthalate from Example 1.

Before extrusion, 80% by weight of the polyethylene terephthalate from Example 1 are dried at 170°C for 5 hours with 20% by weight of the masterbatch. The extrusion and sheet production are carried out analogously to Example 1.

The transparent, amorphous PET sheet produced has the following property profile:

	- thickness	: 3 mm
10	- surface gloss, 1st side	: 194
	(measurement angle 20°) 2nd side	: 193
	- light transmission	: 91.3%
	- clarity	: 100%
	- haze	: 1.4%
15	- surface defects	: none
	(fisheyes, orange peel, bubbles, etc)	
	- Charpy impact strength a_n	: no fracture
	- Izod notched impact strength a_k	: 4.0 kJ/m ²
20	- cold formability	: good
	- crystallinity	: 0%
	- density	: 1.33 g/cm ³

After weathering for 1000 hours per side using the Atlas Ci 65 Weather-O-Meter, the PET sheet exhibits the following properties:

	- thickness	: 3 mm
	- surface gloss, 1st side	: 192
	(measurement angle 20°) 2nd side	: 190
	- light transmission	: 91.1%

- clarity : 100%
- haze : 1.5%
- overall discoloration ΔE : 0.24
- dark discoloration ΔL : -0.19
- 5 - red-green discoloration ΔA : -0.08
- blue-yellow discoloration ΔB : 0.12
- surface defects
(cracks, embrittlement) : none
- yellow value G : 5
- 10 - Charpy impact strength a_n : no fracture
- Izod notched impact strength a_k : 4.0 kJ/m²
- cold formability : good

Example 3

15 A transparent amorphous sheet is produced analogously to Example 1 using a polyethylene terephthalate with the following properties:

- SV (DCA) : 1100
- IV (DCA) : 0.85 dl/g
- Density : 1.38 g/cm³
- 20 - Crystallinity : 44%
- Crystalline melting point T_m : 245°C
- Crystallization temperature
range T_c : 82°C to 245°C
- After- or cold-crystallization
25 temperature T_{CN} : 152°C
- Polydispersity M_w/M_n : 2.02
- Glass transition temperature : 82°C

A transparent, amorphous sheet with a thickness of 6 mm

is produced which contains, as principal constituents, the polyethylene terephthalate described and 0.6% by weight of the UV stabilizer 2,2'-methylene-bis-(6-(2H-benzotriazole-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol
5 (®Tinuvin 360 from Ciba-Geigy), based on the weight of the polymer.

Tinuvin 360 has a melting point of 195°C and is thermally stable up to about 250°C.

As in Example 1, 0.6% by weight of UV stabilizer are
10 incorporated into the polyethylene terephthalate directly by the producer of the raw material.

The extrusion temperature is 280°C. The first calender roll has a temperature of 66°C and the subsequent rolls have a temperature of 60°C. The take-off rate and the
15 speed of the calender rolls are 2.9 m/min.

The transparent, amorphous PET sheet produced has the following property profile:

	- thickness	: 6 mm
	- surface gloss, 1st side	: 175
20	(measurement angle 20°) 2nd side	: 173
	- light transmission	: 88.6%
	- clarity	: 99.6%
	- haze	: 2.5%
	- surface defects per m ²	: none
25	(fisheyes, orange peel, bubbles, etc)	
	- Charpy impact strength a _n	: no fracture
	- Izod notched impact strength a _k	: 4.8 kJ/m ²
	- cold formability	: good, no defects
30	- crystallinity	: 0%

- density : 1.33 g/cm³

After weathering for 1000 hours per side using the Atlas Ci 65 Weather-O-Meter, the PET sheet exhibits the following properties:

5	- thickness	: 6 mm
	- surface gloss, 1st side	: 171
	(measurement angle 20°) 2nd side	: 169
	- light transmission	: 88.3%
	- clarity	: 99.5%
10	- haze	: 2.7%
	- overall discoloration ΔE	: 0.56
	- dark discoloration ΔL	: -0.21
	- red-green discoloration ΔA	: -0.11
	- blue-yellow discoloration ΔB	: +0.51
15	- surface defects (cracks, embrittlement)	: none
	- yellow value G	: 6
	- Charpy impact strength a_n	: no fracture
	- Izod notched impact strength a_k	: 4.6 kJ/m ²
20	- cold formability	: good, no defects

Example 4:

A transparent amorphous sheet is produced analogously to Example 3. The extrusion temperature is 275°C. The first calender roll has a temperature of 57°C and the subsequent rolls have a temperature of 50°C. The take-off rate and the calender roll speed are 1.7 m/min. The sheet is stabilized as described in Example 3.

The PET sheet produced has the following property profile:

- thickness : 10 mm
- surface gloss, 1st side : 163
- (measurement angle 20°) 2nd side : 161
- light transmission : 86.5%
- 5 - clarity : 99.2%
- haze : 4.95%
- surface defects per m² : none
- (fisheyes, orange peel, bubbles, etc)
- 10 - Charpy impact strength a_n : no fracture
- Izod notched impact strength a_k : 5.1 kJ/m²
- cold formability : good, no defects
- crystallinity : 0.1%
- density : 1.33 g/cm³
- 15 After weathering for 1000 hours per side using the Atlas Ci 65 Weather-O-Meter, the PET sheet exhibits the following properties:
 - thickness : 10 mm
 - surface gloss, 1st side : 160
 - (measurement angle 20°) 2nd side : 159
 - 20 - light transmission : 86.2%
 - clarity : 99.1%
 - haze : 5.0%
 - overall discoloration ΔE : 0.47
 - 25 - dark discoloration ΔL : -0.18
 - red-green discoloration ΔA : -0.09
 - blue-yellow discoloration ΔB : +0.42

- surface defects
(cracks, embrittlement) : none
- yellow value G : 5
- Charpy impact strength a_n : no fracture
- 5 - Izod notched impact strength a_k : 4.5 kJ/m²
- cold formability : good, no defects

Comparative Example 1:

A transparent, amorphous sheet is produced analogously to Example 1. In contrast to Example 1, the sheet contains
10 no UV stabilizer. The polyethylene terephthalate employed, the extrusion parameters, the process parameters and the temperatures are selected as in Example 1.

The transparent PET sheet produced has the following property profile:

- 15 - thickness : 3 mm
- surface gloss, 1st side : 200
- (measurement angle 20°) 2nd side : 198
- light transmission : 91.4%
- clarity : 100%
- 20 - haze : 1.3%
- surface defects per m² : none
- (fisheyes, orange peel, bubbles, etc)
- Charpy impact strength a_n : no fracture
- 25 - Izod notched impact strength a_k : 4.3 kJ/m²
- cold formability : good, no defects
- crystallinity : 0%
- density : 1.33 g/cm³

After weathering for 1000 hours per side using the Atlas

Ci 65 Weather-O-Meter, the PET sheet exhibits the following properties:

	- thickness	: 3 mm
	- surface gloss, 1st side	: 98
5	(measurement angle 20°) 2nd side	: 95
	- light transmission	: 79.5%
	- clarity	: 81.2%
	- haze	: 7.8%
	- overall discoloration ΔE	: 3.41
10	- dark discoloration ΔL	: -0.29
	- red-green discoloration ΔA	: -0.87
	- blue-yellow discoloration ΔB	: +3.29
	- surface defects (cracks, embrittlement)	: embrittlement
15	- yellow value G	: 17
	- Charpy impact strength a_n	: complete fracture at 34.8 kJ/m ²
	- Izod notched impact strength a_k	: 1.3 kJ/m ²
	- cold formability	: cracking

20 The sheet exhibits a clearly visible "yellow" discoloration. The surfaces are matt and embrittled.

Comparative Example 2

25 A transparent, amorphous sheet is produced analogously to Example 3. In contrast to Example 3, the sheet contains no UV stabilizer. The polyethylene terephthalate employed, the extrusion parameters, the process parameters and the temperatures are selected as in Example 3.

The transparent PET sheet produced has the following property profile:

	- thickness	: 6 mm
	- surface gloss, 1st side	: 180
	(measurement angle 20°) 2nd side	: 178
	- light transmission	: 88.9%
5	- clarity	: 99.6%
	- haze	: 2.3%
	- surface defects per m ²	: none
	(fisheyes, orange peel, bubbles, etc)	
10	- Charpy impact strength a _n	: no fracture
	- Izod notched impact strength a _k	: 4.8 kJ/m ²
	- cold formability	: good, no defects
	- crystallinity	: 0%
	- density	: 1.33 g/cm ³
15	After weathering for 1000 hours per side using the Atlas Ci 65 Weather-O-Meter, the PET sheet exhibits the following properties:	
	- thickness	: 6 mm
	- surface gloss, 1st side	: 91
20	(measurement angle 20°) 2nd side	: 87
	- light transmission	: 72.5%
	- clarity	: 78.3%
	- haze	: 12.9%
	- overall discoloration ΔE	: 3.61
25	- dark discoloration ΔL	: -0.26
	- red-green discoloration ΔA	: -0.91
	- blue-yellow discoloration ΔB	: +3.48

- surface defects
(cracks, embrittlement) : embrittlement,
cracks
- yellow value G : 18
- Charpy impact strength a_n : complete frac-
ture at 46.2
kJ/m²
- 5 - Izod notched impact strength a_k : 1.6 kJ/m²
- cold formability : cracking

The sheet exhibits a clearly visible "yellow" discoloration. The surfaces have been strongly attacked (matt, embrittled, cracking).

10 Comparative Example 3:

A UV-stabilized, transparent, translucent sheet is produced analogously to Example 3, likewise using the polyethylene terephthalate, the UV stabilizer and the masterbatch from Example 3. The first calender roll has
15 a temperature of 83°C and the subsequent rolls each have a temperature of 77°C.

The sheet produced is extremely hazy and virtually opaque. The light transmission, the clarity and the gloss are significantly reduced. The sheet exhibits surface
20 defects and structures. The optical properties are unacceptable for a transparent application.

The sheet produced has the following property profile:

- thickness : 6 mm
- surface gloss, 1st side : 86
- 25 (measurement angle 20°) 2nd side 88
- light transmission : 8%
- clarity : not measurable

- haze : not measurable
 - surface defects per m² : bubbles, orange
(fisheyes, orange peel, bubbles, peel
etc)
 - 5 - Charpy impact strength a_n : no fracture
 - Izod notched impact strength a_k : 5.0 kJ/m²
 - cold formability : good
 - crystallinity : approx. 8%
 - density : 1.34 g/cm³
- 10 Owing to the unacceptable optical properties, the 6 mm sheet was not subjected to a weathering test.



Claims

1. A transparent, amorphous sheet having a thickness in the range from 1 to 20 mm which contains, as principal constituent, a crystallizable thermoplastic, and contains at least one UV light stabilizer.
5
2. A sheet as claimed in claim 1, wherein the concentration of the UV stabilizer is in the range from 0.01 to 5% by weight, based on the weight of the crystallizable thermoplastic.
10
3. A sheet as claimed in claim 1 or 2, wherein the UV stabilizer is selected from 2-hydroxybenzotriazoles and triazines.
4. A sheet as claimed in claim 3, wherein the UV stabilizer used is at least one compound selected from 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyl)oxyphenol and 2,2'-methylene-bis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol).
15
5. A sheet as claimed in any one of the preceding claims, wherein the surface gloss, measured in accordance with DIN 67530 (measurement angle 20°), is greater than 120.
20
6. A sheet as claimed in any one of the preceding claims, wherein the light transmission, measured in accordance with ASTM D 1003, is greater than 84%.
25
7. A sheet as claimed in any one of the preceding claims, wherein the haze, measured in accordance with ASTM D 1003, is less than 15%.
8. A sheet as claimed in any one of the preceding claims, wherein the crystallizable thermoplastic has a crystallinity in the range from 5 to 65%.
30



9. A sheet as claimed in one of the preceding claims, wherein the crystallizable thermoplastic used is selected from polyethylene terephthalate, polybutylene terephthalate, a cycloolefin polymer and a cycloolefin copolymer.
5
10. A sheet as claimed in claim 9, wherein the crystallizable thermoplastic used is polyethylene terephthalate.
11. A sheet as claimed in claim 10, wherein the polyethylene terephthalate contains recycled polyethylene terephthalate.
10
12. A sheet as claimed in claim 10 or 11, wherein the measurement of the Charpy impact strength a_n , measured in accordance with ISO 179/1D, is not accompanied by a fracture.
15
13. A sheet as claimed in any one of claims 10 to 12, wherein the Izod notched impact strength a_k , measured in accordance with ISO 180/1A, is in the range from 2.0 to 8.0 kJ/m².
14. A sheet as claimed in any one of claims 10 to 13, wherein the clarity, measured in accordance with ASTM D 1003 at an angle of less than 2.5°, is greater than 96%.
20
15. A sheet as claimed in any one of claims 10 to 14, wherein the polyethylene terephthalate has a crystalline melting point, measured by DSC at a heating rate of 10°C/min, in the range from 220° to 280°C.
25
16. A sheet as claimed in any one of claims 10 to 15, wherein the polyethylene terephthalate has a crystallization temperature, measured by DSC at a heating rate of 10°C/min, in the range from 75° to 280°C.
30



- 5 17. A sheet as claimed in any one of claims 10 to 16, wherein the polyethylene terephthalate employed has a standard viscosity SV (DCA), measured in dichloroacetic acid in accordance with DIN 53728, in the range from 800 to 1800.
- 10 18. A process for the production of a transparent, amorphous sheet as claimed in any one of claims 1 to 17, which comprises melting the crystallizable thermoplastic in the extruder together with the UV stabilizer, extruding the melt through a die, calibrating, smoothing and cooling the extrudate in a polishing stack with at least two rolls, and cutting of the sheet to size, where the first roll of the polishing stack has a temperature in the range from 15 50 to 80°C.
19. The process as claimed in claim 18, wherein the crystallizable thermoplastic is dried before melting in the extruder.
- 20 20. The process as claimed in claim 18 or 19, wherein the crystallizable thermoplastic is polyethylene terephthalate.
21. The process as claimed in claim 20, wherein the polyethylene terephthalate is dried at from 160 to 180°C for from 4 to 6 hours before extrusion.
- 25 22. The process as claimed in claim 20 or 21, where the temperature of the PET melt is in the range from 250 to 320°C.
- 30 23. The process as claimed in any one of claims 20 to 22, wherein the UV stabilizer is added by masterbatch technology.
23. The use of a transparent, amorphous sheet as claimed



- 32 -

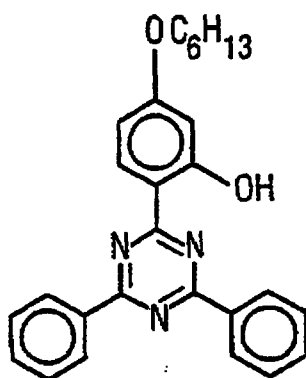
in any one of claims 1 to 17 for external applications.

Abstract of the disclosure

Amorphous, transparent, UV-stabilized sheet of a crystallizable thermoplastic

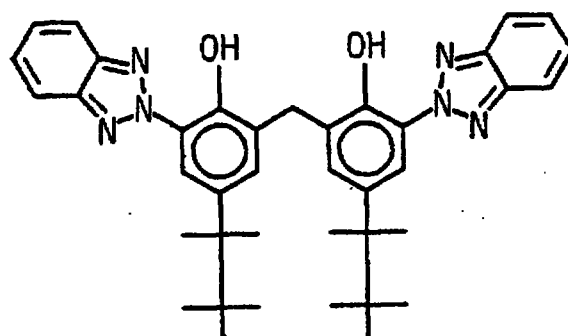
The invention relates to a transparent, amorphous sheet having a thickness in the range from 1 to 20 mm which contains, as principal constituent, a crystallizable thermoplastic, and contains at least one UV light stabilizer, to a process for the production of the sheet, and to the use of the sheet.

Fig. 1a



2-(4,6-Diphenyl-1,3,5-triazin-2-yl)-5-(hexyl)oxyphenol

Fig. 1b



2,2'-Methylene-bis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-phenol

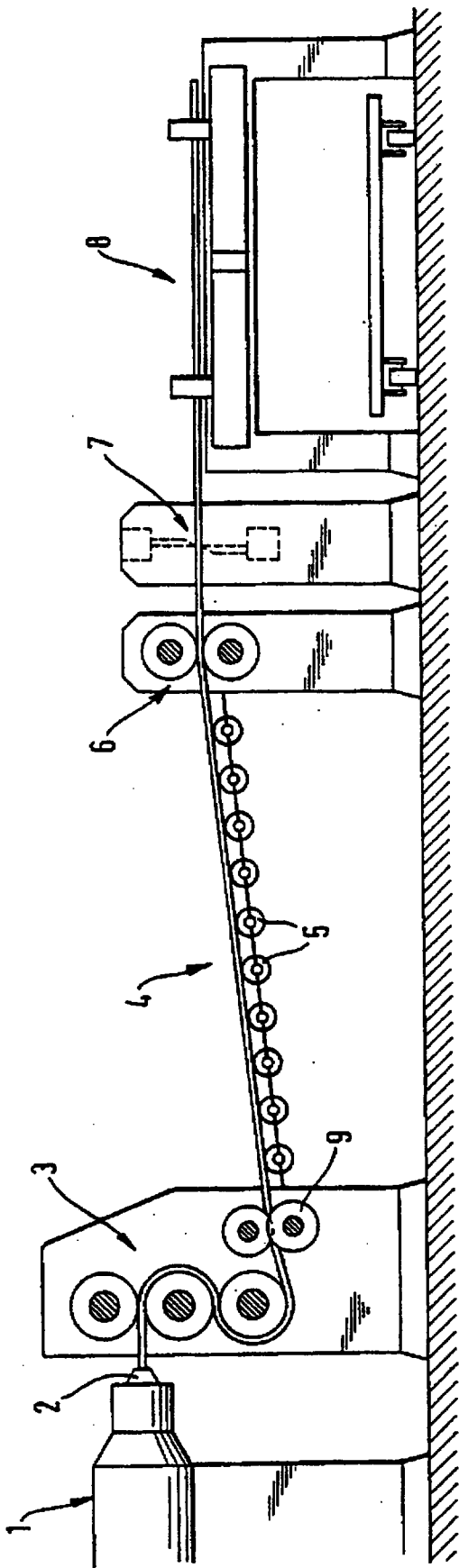
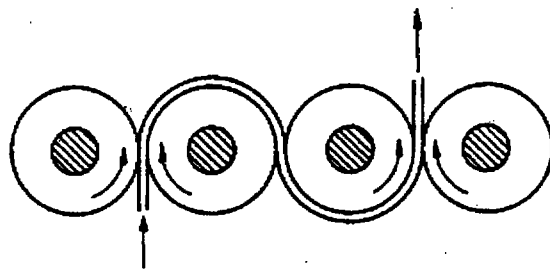


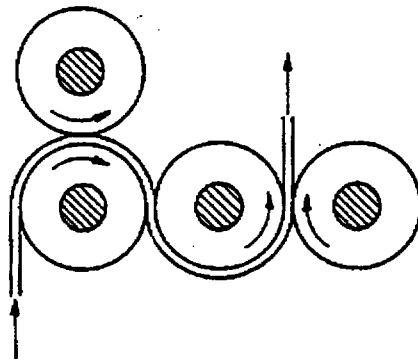
Fig. 2

Fig. 3a



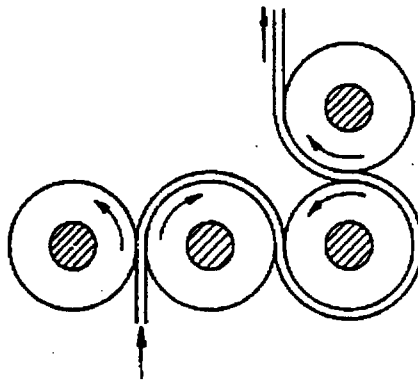
I-CALENDER

Fig. 3b



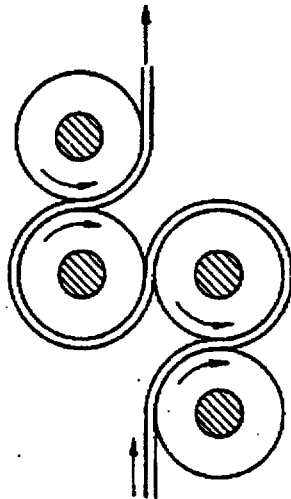
F-CALENDER

Fig. 3c



L-CALENDER

Fig. 3d



S-CALENDER

Fig. 3