

Description

Amorphous sheet of a crystallizable polyalkylene naphthalate

The invention relates to an amorphous sheet of at least one crystallizable polyalkylene naphthalate, the thickness of which is in the range from 1 to 20 mm. The sheet is distinguished by very good optical and mechanical properties. The invention furthermore relates to a process for the production of this sheet.

Amorphous sheets having a thickness of between 1 and 20 mm are adequately known. These sheet-like structures are made of amorphous, non-crystallizable thermoplastics. Typical examples of such thermoplastics which are processed to sheets are, for example, polyvinyl chloride (PVC), polycarbonate (PC) and polymethyl methacrylate (PMMA). These semi-finished products are produced on so-called extrusion lines (cf. Polymer Werkstoffe [Polymeric materials], Volume II, Technology 1, p. 136, Georg Thieme Verlag, Stuttgart, 1984). The pulverulent or granular raw material is melted in an extruder. After extrusion, the amorphous thermoplastics can easily be reshaped via polishing stacks or other shaping dies as a result of the constantly increasing viscosity with decreasing temperature. After shaping, amorphous thermoplastics then have an adequate stability, i.e. a high viscosity in order to "stand by themselves" in the sizing die. However, they are still soft enough to be able to be shaped by the die. The melt viscosity and internal rigidity of amorphous thermoplastics in the sizing die is so high that the semi-finished product does not collapse before cooling in the sizing die. In the case of materials which decompose easily, such as, for example, PVC, particular processing aids, such as, for example, processing stabilizers against decomposition and lubricants against too high an internal friction and therefore uncontrollable heating, are needed during extrusion. External lubricants are necessary to prevent the material from sticking to walls and rolls.

In the processing of PMMA, for example, a devolatilizing extruder is employed for the purpose of removal of moisture.

5 In the production of sheets of amorphous thermoplastics, sometimes cost-intensive additives are necessary, which in some cases migrate and can lead to production problems as a result of evaporation and to surface deposits on the semi-finished product. PVC sheets are difficult to recycle or can be recycled only with special neutralization or electrolysis processes. PC and PMMA sheets are likewise difficult to recycle and can be recycled only with a loss of or extreme deterioration in the mechanical properties.

10 In addition to these disadvantages, PMMA sheets also have an extremely poor impact strength and splinter when fractured or under mechanical stress. In addition, PMMA sheets are as combustible as wood, so that they may not be employed, for example, for interior applications and in exhibition construction.

15 PMMA and PC sheets furthermore cannot be shaped in the cold. During cold shaping, PMMA sheets break up into hazardous splinters. During cold shaping of PC sheets, hair cracks and white fracture occur.

EP-A-0 471 528 describes a process for shaping an object from a polyethylene terephthalate (PET) sheet. The PET sheet is heat-treated on
20 both sides in a thermoforming mold in a temperature range between the glass transition temperature and the melting temperature. The shaped PET sheet is removed from the mold when the extent of crystallization of the shaped PET sheet is in the range from 25 to 50%. The PET sheets disclosed in EP-A-0 471 528 have a thickness of 1 to 10 mm. Since the
25 thermoformed shaped article produced from this PET sheet is partly crystalline and therefore no longer transparent and the surface properties of the shaped article are determined by the thermoforming process and the temperatures and shapes given by this, the optical properties (for example gloss, clouding and light transmission) of the PET sheets employed are
30 unimportant. As a rule, the optical properties of these sheets are poor and

in need of optimization.

US-A-3,496,143 describes vacuum thermoforming of a 3 mm thick PET sheet, the crystallization of which should be in the range from 5 to 25%. The crystallinity of the thermoformed shaped article is greater than 25%.

- 5 On these PET sheets also, no requirements are imposed in respect of optical properties. Since the crystallinity of the sheets employed is already between 5 and 25%, these sheets are cloudy and nontransparent.

- 10 The object of the present invention is to provide an amorphous sheet having a thickness of 1 to 20 mm which has both good mechanical and good optical properties.

The good optical properties include, for example, high light transmission, high surface gloss, extremely low haze and high clarity, depending on the embodiment.

- 15 The good mechanical properties include, inter alia, a high impact strength and a high fracture strength.

Furthermore, the sheet according to the invention should be recyclable, in particular without loss of mechanical properties, and low combustibility, so that, for example, it can also be used for interior applications and in exhibition construction.

- 20 This object is achieved by an amorphous sheet having a thickness in the range from 1 to 20 mm, which contains, as the main constituent, at least one crystallizable polyalkylene naphthalate.

- 25 The amorphous sheet contains, as principal constituent, at least one crystallizable polyalkylene naphthalate. Preference is given to polyethylene naphthalate, polypropylene naphthalate and polybutylene naphthalate, particular preference being given to polyethylene naphthalate (PEN).

The amorphous sheet can be transparent, transparently colored or opaquely colored.

5 In the transparent embodiment, the amorphous sheet has a surface gloss, measured in accordance with DIN 67530 (measurement angle 20°), which is greater than 110, preferably greater than 120. The light transmission, measured in accordance with ASTM D 1003, is greater than 80%, preferably greater than 82%, and the haze of the sheet, likewise measured in accordance with ASTM D 1003, is less than 15%, preferably less than 11%.

10 The clarity of the transparent sheet, determined at an angle of less than 2.5° (ASTM D 1003), is preferably greater than 90%, particularly preferably greater than 92%.

15 In the transparently colored embodiment, the amorphous sheet contains at least one soluble dye. The concentration of soluble dye is preferably in the range from 0.001 to 20% by weight, based on the weight of the polyalkylene naphthalate.

Soluble dyes are taken to mean substances which are molecularly dissolved in the polymer (DIN 55949).

20 The color change as a consequence of dyeing the amorphous sheet is based on wavelength-dependent absorption and/or scattering of light. Dyes can only absorb, not scatter, light, since the physical prerequisite for scattering is a certain minimum particle size.

25 Coloring by means of dyes is a solution process. As the result of this solution process, the dye is molecularly dissolved, for example in the PEN polymer. Such dyeings are referred to as transparent or translucent or opalescent.

From the various classes of soluble dyes, particular preference is given to

fat- and aromatic-soluble dyes. These are, for example, azo and anthraquinone dyes. They are particularly suitable for dyeing PEN, since, owing to the high glass transition temperature of PEN, migration of the dye is limited (literature J. Koerner: Soluble dyes in the plastics industry in "VDI-

- 5 Gesellschaft Kunststofftechnik: Einfärben von Kunststoffen, VDI-Verlag, Düsseldorf 1975).

Examples of suitable soluble dyes are: Solvent Yellow 93, a pyrazolone derivative, Solvent Yellow 16, A fat-soluble azo dye, Fluorol Green-Gold, a fluorescent polycyclic dye, Solvent Red 1, an azo dye, azodyes such as
10 Thermoplastic Red BS, Sudan Red BB, Solvent Red 138, an anthraquinone derivative, fluorescent benzopyran dyes, such as Fluorol Red GK and Fluorol Orange GK, Solvent Blue 35, an anthraquinone dye, Solvent Blue, a phthalocyanine dye, and many others. Mixtures of two or more of these soluble dyes are also suitable.

- 15 In accordance with the invention, the soluble dye can already have been added in the desired concentration by the raw-material producer or can be added in the extruder during sheet production.

- However, the dye additive is particularly preferably added via masterbatch technology. The soluble dye is fully dispersed and/or dissolved in a solid
20 carrier material. Suitable carrier materials are certain resins, the polyalkylene naphthalate itself or alternatively other polymers which are sufficiently compatible with the polyalkylene naphthalate.

- It is important that the particle size and bulk density of the masterbatch are similar to the particle size and bulk density of the polyalkylene naphthalate,
25 so that homogeneous distribution and consequently homogeneous, transparent coloring can take place.

The surface gloss of the transparently colored sheet, measured in accordance with DIN 67530 (measurement angle 20°), is greater than 100, preferably greater than 110, the light transmission, measured in

accordance with ASTM D 1003, is in the range from 5 to 80%, preferably in the range from 10 to 70%, and the haze of the sheet, measured in accordance with ASTM D 1003, is in the range from 2 to 40%, preferably in the range from 3 to 35%.

- 5 In the colored embodiment, the amorphous sheet contains at least one organic and/or inorganic pigment as colorant. The concentration of the colorant is preferably in the range from 0.5 to 30% by weight, based on the weight of polyalkylene naphthalate.

- 10 When considering colorants, a distinction is made in accordance with DIN 55944 between dyes and pigments. Pigments are virtually insoluble in the polymer under the respective processing conditions, whereas dyes are soluble (DIN 55949). The coloring action of the pigments is brought about by the particles themselves. The term pigment is in general linked to a particle size from 0.01 μm to 1.0 μm . According to DIN 53206, when
15 defining pigment particles a distinction is made between primary particles, aggregates and agglomerates.

- Primary particles as are generally produced in the synthesis possess a pronounced tendency to aggregate as a result of their extremely small particle size. This produces, by areal aggregation of the primary particles,
20 the aggregates, which thus have a smaller surface area than that corresponding to the sum of the surface area of their primary particles. As a result of the agglomeration of primary particles and/or aggregates at corners and edges, agglomerates are formed, whose total surface area differs only little from the sum of the individual areas. If one refers to
25 pigment particle size without more detailed indications, this refers to the aggregates as are essentially present following coloration.

- In pigments which are in powder form the aggregates have always come together to form agglomerates, which during the process of coloration must be disrupted, wetted by the polymer and homogeneously distributed.
30 These simultaneously occurring processes are termed dispersion. In the

case of coloring with dyes, on the other hand, the process involved is one of solution, as a result of which the dye is present in molecularly dissolved form.

5 In contrast to the inorganic pigments, in the case of certain organic pigments complete insolubility is not the case, especially not in the instance of pigments of simple composition having low molecular weights.

10 Dyes are adequately described by their chemical structure. Pigments which are in each case of identical chemical composition, however, can be prepared in and exist in different crystal modifications. A typical example of this is the white pigment titanium dioxide, which can exist in the rutile form and in the anatase form.

15 In the case of pigments it is possible by coating, i.e. by aftertreating the pigment particle surface, using organic or inorganic agents, to improve the utility properties. This improvement consists in particular in facilitating dispersion and in raising the light stability and resistance to weathering and chemicals. Typical coating agents for pigments are fatty acids, fatty acid amides, siloxanes and aluminum oxides, for example.

20 Examples of suitable inorganic pigments are the white pigments titanium dioxide, zinc sulfide and tin sulfide, which may be coated with organic and/or inorganic substances.

25 The titanium dioxide particles can comprise anatase or rutile, but preferably predominantly rutile which in comparison to anatase exhibits greater opacity. In a preferred embodiment, at least 95% by weight of the titanium dioxide particles consist of rutile. They can be prepared by a customary process, for example by the chloride or the sulfate process. The mean particle size is relatively low and is preferably in the range from 0.10 to 0.30 μm .

By using titanium dioxide of the type described, no vacuoles form within the

polymer matrix during production of sheets.

The titanium dioxide particles can have a coating of inorganic oxides as is usually employed as a coating for TiO_2 white pigment in papers or coating compositions, to improve the light fastness. TiO_2 is known to be photo-
5 active. Under the action of UV rays, free radicals form on the surface of the particles. These free radicals may migrate to the film-forming constituents of the coating composition, leading to degradation reactions and yellowing. Particularly suitable oxides include the oxides of aluminum, silicon, zinc or magnesium, or mixtures of two or more of these compounds. TiO_2 particles
10 having a coating of two or more of these compounds are described, for example, in EP-A-0 044 515 and in EP-A 0 078 633. The coating can also comprise organic compounds having polar and apolar groups. During the preparation of the sheet by extrusion of the polymer melt, the organic compounds must be of sufficient thermal stability. Examples of polar
15 groups are -OH, -OR, -COOX (X = R, H or Na, R = alkyl having 1 to 34 carbon atoms). Preferred organic compounds are alkanols and fatty acids having 8 to 30 carbon atoms in the alkyl group, especially fatty acids and primary n-alkanols having 12 to 24 carbon atoms, and also polydi-organosiloxanes and/or polyorganohydridosiloxanes, for example
20 polydimethylsiloxane and polymethylhydridosiloxane.

The coating on the titanium dioxide particles usually consists of from 1 to 12 g, in particular from 2 to 6 g, of inorganic oxides and from 0.5 to 3 g, in particular from 0.7 to 1.5 g, of organic compound, based on 100 g of titanium dioxide particles. The coating is preferably applied to the particles
25 in aqueous suspension. The inorganic oxides are precipitated in the aqueous suspension from water-soluble compounds, for example alkali metal aluminate, especially sodium aluminate, aluminum hydroxide, aluminum sulfate, aluminum nitrate, sodium silicate (waterglass) or silicic acid.

30 The term inorganic oxides, such as Al_2O_3 and SiO_2 , should also be understood as including the hydroxides or their various dehydration stages,

for example oxide hydrates, without their precise composition and structure being known. The oxide hydrates of, for example, aluminum and/or silicon are precipitated onto the TiO_2 pigment after calcining and grinding in aqueous suspension, and the pigments are then washed and dried. This precipitation can therefore take place directly in a suspension as is produced in the synthesis process following calcining and the subsequent wet grinding. The precipitation of the oxides and/or oxide hydrates of the respective metals takes place from the water-soluble metal salts within the known pH range; for aluminum, for example, aluminum sulfate in aqueous solution (pH less than 4) is employed, and the oxide hydrate is precipitated by adding aqueous ammonia solution or sodium hydroxide solution in the pH range between 5 and 9, preferably between 7 and 8.5. Starting from a waterglass or alkali metal aluminate solution, the pH of the initially charged TiO_2 suspension should be in the strongly alkaline range (pH greater than 8). In this case precipitation is effected by adding mineral acid, such as sulfuric acid, in the pH range from 5 to 8. Following precipitation of the metal oxides, the suspension is subsequently stirred for from 15 minutes to about 2 hours, during which the precipitated coats undergo aging. The coated product is separated off from the aqueous dispersion and, after washing, is dried at elevated temperature, especially at from 70 to 110°C.

Typical inorganic black pigments are carbon black modifications which may likewise be coated, carbon pigments which differ from the carbon black pigments by a higher ash content, and black oxide pigments, such as iron oxide black and copper, chromium and iron oxide mixtures (mixed phase pigments).

Suitable inorganic color pigments are colored oxide pigments, hydroxyl-containing pigments, sulfide pigments and chromates.

Examples of colored oxide pigments are iron oxide red, titanium dioxide-nickel oxide-antimony oxide mixed phase pigments, titanium dioxide-chromium oxide-antimony oxide mixed phase pigments, mixtures of the oxides of iron, zinc and titanium, chromium oxide iron oxide brown, spinels

of the system cobalt-aluminum-titanium-nickel-zinc oxide, and mixed phase pigments based on other metal oxides.

Examples of typical hydroxyl-containing pigments are oxide hydroxides of trivalent iron, such as FeOOH .

- 5 Examples of sulfide pigments are cadmium sulfide selenides, cadmium-zinc sulfides, sodium aluminum silicate containing sulfur bonded polysulfide-style in the lattice.

Examples of chromates are the lead chromates, which can exist in the crystal forms monoclinic, rhombic and tetragonal.

- 10 All color pigments can, like the white and black pigments, be either uncoated, or coated with inorganic and/or organic substances.

The organic color pigments are generally divided into azo pigments and so-called nonazo pigments.

- The characteristic feature of the azo pigments is the azo group ($-\text{N}=\text{N}-$).
15 Azo pigments include monoazo pigments, diazo pigments, diazo condensation pigments, salts of azo dye acids and mixtures of the azo pigments.

- The amorphous colored sheet contains at least one inorganic and/or organic pigment. In specific embodiments the amorphous sheet can also
20 contain mixtures of inorganic and/or organic pigments, and also soluble dyes as well. In this context the concentration of the soluble dye is preferably in the range from 0.01 to 20% by weight, and with particular preference in the range from 0.5 to 10% by weight, based on the weight of the polyalkylene naphthalate.

- 25 In accordance with the invention, the colorants (inorganic and/or organic pigments and, if desired, dyes) can already have been added in the

desired concentration by the raw-material producer or can be added in the extruder during sheet production.

5 However, the color additive(s) is particularly preferably added via masterbatch technology or via solid-pigment preparation. The organic and/or inorganic pigment and, if desired, the soluble dye are fully dispersed in a solid carrier material. Suitable carriers are certain resins, the polymer to be colored itself or alternatively other polymers which are sufficiently compatible with the polyalkylene naphthalate.

10 It is important that the particle size and density of the solid-pigment preparation and of the master batch are similar to the particle size and bulk density of the polyalkylene naphthalate, so that homogeneous distribution and thus coloring can take place.

15 The surface gloss of the colored sheet, measured in accordance with DIN 67530 (measurement angle 20°), is preferably greater than 90 and the light transmission, measured in accordance with ASTM D 1003, is preferably less than 5%.

The colored sheet furthermore has opaque, homogeneous optical properties.

20 In a further, preferred embodiment, the amorphous sheet furthermore contains at least one UV stabilizer as light stabilizer, the concentration of the UV stabilizer preferably being between 0.01 and 5% by weight, based on the weight of the polyalkylene naphthalate.

25 Light, in particular the ultraviolet portion of solar radiation, i.e. the wavelength range from 280 to 400 nm, initiates degradation processes in thermoplastics, as a consequence of which not only does the visual appearance change, owing to a change in color or yellowing, but the mechanical-physical properties are also adversely affected.

Inhibition of these photooxidative degradation processes is of considerable industrial and economic importance, since otherwise the possible uses of numerous thermoplastics are limited drastically.

5 Polyalkylene naphthalates, for example, start to absorb UV light even at below 360 nm, and their absorption increases considerably below 320 nm and is very pronounced below 300 nm. The maximum absorption is between 280 and 300 nm.

10 In the presence of oxygen, chiefly chain splitting but no crosslinking is observed. Carbon monoxide, carbon dioxide and carboxylic acids are the predominant photooxidation products in terms of amount. In addition to direct photolysis of the ester groups, oxidation reactions which likewise result in the formation of carbon dioxide via peroxide radicals must also be taken into consideration.

15 The photooxidation of polyalkylene naphthalates can also lead, via splitting of hydrogen in the α -position of the ester groups, to hydroperoxides and decomposition products thereof and to associated chain splitting (H. Day, D.M. Wiles: J. Appl. Polym. Sci 16, 1972, page 203).

20 UV stabilizers or UV absorbers as light stabilizers are chemical compounds which can intervene in the physical and chemical processes of light-induced degradation. Carbon black and other pigments can partly have the effect of light protection. However, these substances are unsuitable for transparent sheets, since they lead to discoloration or a change in color. Only organic and organometallic compounds which impart no or only an extremely slight color or change in color to the thermoplastic to be
25 stabilized are suitable for transparent amorphous sheets.

Suitable UV stabilizers as light stabilizers are, for example, 2-hydroxybenzophenones, 2-hydroxybenzotriazoles, organonickel compounds, salicylic esters, cinnamic acid ester derivatives, resorcinol monobenzoates, oxalic acid anilides, hydroxybenzoic esters, sterically

hindered amines and triazines, 2-hydroxybenzotriazoles and triazines being preferred.

In a particularly preferred embodiment, the amorphous sheet according to the invention contains, as the main constituent, a crystallizable
5 polyethylene naphthalate and 0.01% by weight to 5.0% by weight of 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyl)oxy-phenol or 0.01% by weight to 5.0% by weight of 2,2'-methylene-bis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)-phenol. In a preferred embodiment, mixtures of these two UV stabilizers or mixtures of at least one of these two UV stabilizers with
10 other UV stabilizers can also be employed, the total concentration of light stabilizers preferably being between 0.01% by weight and 5.0% by weight, based on the weight of crystallizable polyethylene naphthalate.

According to the invention, crystallizable polyalkylene naphthalate is understood as meaning

- 15 - crystallizable polyalkylene naphthalate homopolymers,
 - crystallizable polyalkylene naphthalate copolymers,
 - crystallizable polyalkylene naphthalate compound materials,
 - crystallizable polyalkylene naphthalate recycled material and
 - other variations of crystallizable polyalkylene naphthalate.
- 20 Preferred copolymers and compound materials in this context are mixtures of polyalkylene naphthalates and polyalkylene terephthalates, in particular mixtures of polyethylene naphthalate (PEN) and polyethylene terephthalate (PET).

Amorphous sheet in the context of the present invention is understood as
25 meaning those sheets which are noncrystalline, although the crystallizable thermoplastic employed preferably has a crystallinity of between 10% and 65%. Noncrystalline, i.e. essentially amorphous, means that the degree of crystallinity is in general below 5%, preferably below 2%, and particularly preferably is 0%.

In addition, a good ability to be shaped in the cold without fracture, without hair cracks and/or without white fracture was found completely unexpectedly, so that the sheet according to the invention can be shaped and bent without the action of temperature.

- 5 Furthermore, measurements have shown that the polyalkylene naphthalate sheet according to the invention has low combustibility and low flammability, so that it is suitable, for example, for interior applications and in exhibition construction.

- 10 The sheet according to the invention furthermore can be recycled without problems, without pollution of the environment and without loss in the mechanical properties, which means that it is suitable, for example, for use as short-lived advertising signs or other advertising articles.

- 15 In a particularly preferred embodiment, the amorphous sheet according to the invention contains, as the main constituent, crystallizable polyethylene naphthalate.

- 20 In the case of polyethylene naphthalate, preferably no fracture occurs on the sheet during measurement of the Charpy impact strength a_n (measured in accordance with ISO 179/1D). Furthermore, the Izod notched impact strength a_k (measured in accordance with ISO 180/1A) of the sheet is preferably in the range from 2.0 to 12.0 kJ/m², particularly preferably in the range from 3.0 to 8.0 kJ/m².

- 25 Polyethylene naphthalates having a crystallite melting point T_m , measured by DSC (Differential Scanning Calorimetry) with a heating-up rate of 10°C/minute, of from 240°C to 300°C, preferably 250°C to 290°C, a crystallization temperature range T_c of between 100°C and 290°C, a glass transition temperature T_g of between 100°C and 140°C and a density, measured in accordance with DIN 53479, of 1.30 to 1.45 g/cm³ and a crystallinity of between 10% and 65% are preferred polymers as starting materials for production of the sheet.

The standard viscosity SV (DCA) of the polyethylene naphthalate, measured in dichloroacetic acid in accordance with DIN 53728, is between 600 and 1400, preferably between 750 and 1250 and particularly preferably between 800 and 1100.

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

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

- 10 The bulk density, measured in accordance with DIN 53466, is preferably between 0.75 kg/dm³ and 1.0 kg/dm³, and particularly preferably between 0.80 kg/dm³ and 0.90 kg/dm³.

The polydispersity of the polyethylene naphthalate M_w/M_n , measured by means of GPC, is preferably between 1.5 and 4.0 and particularly preferably between 2.0 and 3.5.

- 15 The production of the amorphous sheet according to the invention can be carried out, for example, by an extrusion process in an extrusion line.

Such an extrusion line is shown in diagrammatic form in Fig. 1. It essentially comprises

- an extruder (1) as a plasticizing unit,
- a slot die (2) as a die for shaping,
- 20 - a polishing stack/calender (3) as a sizing die,
- a cooling bed (4) and/or a roller conveyor (5) for after-cooling,
- take-off rolls (6),
- a separating saw (7),
- an edge trimming device (9) and, if appropriate,
- 25 - a stacking device (8).

The process comprises drying the polyalkylene naphthalate, if appropriate, then melting it in the extruder, if appropriate together with the soluble dye, the colorant and/or the UV stabilizer, extruding the melt through a die and

then sizing it, polishing it and cooling it in the polishing stack, before the sheet is cut to size.

The soluble dye, the colorant and/or the UV stabilizer is preferably added via masterbatch technology. In this case, the soluble dye, the colorant
5 and/or the UV stabilizer is fully dispersed in a solid carrier material.

Suitable carrier materials are certain resins, the polyalkylene naphthalate itself, or alternatively other polymers which are sufficiently compatible with the polyalkylene naphthalate.

The process for the production of the sheet according to the invention is
10 described in detail below for polyethylene naphthalate (PEN).

The PEN is preferably dried, before the extrusion, at 160 to 180°C for 4 to 6 hours.

The PEN and, if appropriate, the additive masterbatches are then melted in the extruder. The temperature of the PEN melt is preferably in the range
15 from 250 to 320°C, it being possible for the temperature of the melt to be established essentially both by the temperature of the extruder and by the residence time of the melt in the extruder.

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

20 The PEN melted by the extruder and shaped by a slot die is sized by polishing calender rolls, i.e. cooled intensively and polished. The calender rolls can be arranged, for example, in an I-, F-, L- or S-shape.

The PEN material can then be after-cooled on a roller conveyor, trimmed to size at the edges, cut to length and finally stacked.

25 The thickness of the PEN sheet is essentially determined by the take-off, which is positioned at the end of the cooling zone, the cooling (polishing)

rolls coupled to this in terms of speed, and the conveying speed of the extruder on the one hand and the distance between the rolls on the other hand.

5 Both single-screw and twin-screw extruders can be employed as the extruder.

10 The slot die preferably comprises the dismountable die body, the lips and the restrictor bar for flow regulation via the width. For this, the control bar can be bent by tension and pressure screws. The thickness is set by adjusting the lips. It is important to ensure that the PEN and the lip have a uniform temperature, since otherwise the PEN melt flows out in different thicknesses as a result of the different flow paths.

15 The sizing die, i.e. the polishing calender, gives the PEN melt the shape and the dimensions. This is effected by freezing to below the glass transition temperature by means of cooling and polishing. Shaping should no longer take place 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 crystallite melting temperature in order to avoid sticking of the PEN melt. The PEN melt leaves the slot die with a temperature of 240 to 300°C. The 20 first polishing/cooling roll has a temperature of between 50°C and 80°C, depending on the output and sheet thickness. The second, somewhat cooler roll cools the second or other surface.

25 While the sizing device freezes the PEN surfaces as smoothly as possible and cools the profile to the extent that it is dimensionally stable, the after-cooling device lowers the temperature of the PEN sheet to virtually room temperature. After-cooling can take place on a roller board. The speed of the take-off should be coordinated precisely with the speed of the calender rolls in order to avoid defects and variations in thickness.

As additional devices, the extrusion line for production of PEN sheets can

comprise a separating saw as a device for cutting to length, the edge trimmer, the stacking unit and a control station. The edge or margin trimmer is advantageous, since under certain circumstances the thickness in the margin region may be nonuniform. The thickness and visual
5 properties of the sheet are measured at the control station.

As a result of the surprising large number of excellent properties, the amorphous polyalkylene naphthalate sheet according to the invention is outstandingly suitable for a large number of various uses, for example for interior paneling, for exhibition construction and exhibition articles, as
10 displays, for signs, for protective glazing of machines and vehicles, in the lighting sector, in shop fitting and shelf construction, as advertising articles, as menu stands, as basketball backboards, as room dividers and also for external applications, for example as a substitute for glass.

The invention is illustrated in more detail in the following with the aid of
15 embodiment examples, without being limited by these.

Measurement of the individual properties is carried out here in accordance with the following standards or techniques.

Measurement methods

20 Surface gloss:

The surface gloss is determined in accordance with DIN 67 530. The reflector value is measured as the optical parameter for the surface of a sheet. In accordance with the standards ASTM-D 523-78 and ISO 2813, the angle of incidence was set at 20°. Under the angle of incidence set, a
25 ray of light strikes the flat test surface and is reflected or scattered by this. The rays of light incident on the photoelectronic receiver are indicated as a proportional electrical value. The measurement value is dimensionless and must be stated together with the angle of incidence.

Light transmission:

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

- 5 The light transmission is measured in a "Hazeguard plus" measuring instrument in accordance with ASTM 1003.

Haze and clarity:

Haze is the percentage of transmitted light that deviates from the incident light bundle by on average greater than 2.5° . The clarity is determined at an angle of less than 2.5° .

- 10 The haze and clarity are measured using a "Hazeguard plus" measuring instrument in accordance with ASTM 1003.

Whiteness

- 15 The whiteness is determined with the aid of the electric remission photometer "ELREPHO" from Zeiss, Oberkochen (DE), standard light source C, 2° normal observer. The whiteness is defined as

$$WG = RY + 3RZ - 3RX.$$

WG = whiteness, RY, RZ, RX = corresponding reflection factors when using the Y, Z and X color measurement filter. The white standard used is a compression molding formed from barium sulfate (DIN 5033, Part 9).

- 20 **Surface defects:**
The surface defects are determined visually.

Charpy impact strength a_n :

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

Izod notched impact strength a_k :

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

Density:

- 5 The density is determined in accordance with DIN 53479.

SV (DCA), IV (DCA):

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

- 10 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:

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

Molecular weight, polydispersity:

The molecular weights M_w and M_n and the resulting polydispersity M_w/M_n are measured by means of gel permeation chromatography (GPC).

- 20 Weathering (both sides), UV stability:

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

25	Test apparatus	:	Atlas Ci 65 Weather Ometer
	Test conditions	:	ISO 4892, i.e. simulated weathering
	Irradiation time	:	1000 hours (per side)
	Irradiation	:	05 W/m ² , 340 nm
	Temperature	:	63°C

Relative atmospheric

humidity : 50%

Xenon lamp : Inner and outer filter of borosilicate

5 Irradiation cycles : 102 minutes UV light, then 18 minutes UV light with spraying of the specimens with water, then 102 minutes UV light again and so on.

Color change:

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

The symbols have the following meanings:

ΔL : Brightness difference

+ ΔL : The sample is brighter than the standard

- ΔL : The sample is darker than the standard

15 ΔA : Difference in the red-green region

+ 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

20 - ΔB : The sample is bluer than the standard

ΔE : Overall color change

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

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

25 Numerical values of ≤ 0.3 are negligible and mean that there is no significant color change.

Yellow value:

The yellow value G is the deviation from colorlessness toward "yellow" and is measured in accordance with DIN 6167. Yellowness G values of ≤ 5 are visually imperceptible.

- 5 In the following examples and comparison examples, the sheets are in each case single-layered, opaquely colored sheets of different thickness produced on the extrusion line described.

Example 1:

- 10 The polyethylene naphthalate from which the transparent sheet is produced has a standard viscosity SV (DCA) of 810, which corresponds to an intrinsic viscosity IV (DCA) 0.65 dl/g. The moisture content is $< 0.2\%$ and the density (DIN 53479) is 1.33 g/cm^3 . The crystallinity is 15%, the crystalline melting point according to DSC measurements being 270°C . The polydispersity M_w/M_n of the polyethylene naphthalate is 2.14. The
15 glass transition temperature is 119°C .

- Before extrusion, the polyethylene naphthalate is dried for 5 hours at 170°C in a drier and then extruded in a single-screw extruder at an extrusion temperature of 286°C through a flat film die onto a smoothing
20 calender whose walls are arranged in an S-shape, and smoothed to give a sheet with a thickness of 2 mm. The first calender roll has a temperature of 65°C , and the subsequent rolls each of a temperature of 58°C . The take-off rate and the calender-roll speed are 4.0 m/min.

After cooling, the transparent PEN sheet with a thickness of 2 mm is trimmed at the edges using separating saws, cut to length and stacked.

- 25 The transparent PEN sheet produced has the following property profile:

- | | |
|--------------------------|--------|
| - thickness | : 2 mm |
| - surface gloss 1st side | : 170 |

	(measurement angle 20°)	2nd side	: 165
	- light transmission		: 86%
	- clarity		: 98%
	- haze		: 1.5%
5	- surface defects per m ² (specks, orange-peel skin, bubbles, etc.)		: none
	- Charpy impact strength a _n		: no fracture
	- cold shapeability		: good, no defects
	- crystallinity		: 0%
10	- density		: 1.31 g/m ³

Example 2:

A transparent sheet is produced analogously to Example 1, using a polyethylene naphthalate with the following properties:

	SV (DCA)	: 1100
15	IV (DCA)	: 0.85 dl/g
	density	: 1.32 g/cm ³
	crystallinity	: 24%
	crystalline melting point T _m	: 254°C
	polydispersity M _w /M _n	: 2.02
20	Glass transition temperature	: 117°C

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 speed of the calender rolls are 1.9 m/min.

The transparent PEN sheet produced has the following property profile:

25	- thickness	: 6 mm
	- surface gloss 1st side	: 172

	(measurement angle 20°)	2nd side	:	170
	- light transmission		:	88.1%
	- clarity		:	99.6%
	- haze		:	2.6%
5	- surface defects per m ² (specks, orange-peel skin, bubbles, etc.)		:	none
	- Charpy impact strength a _n		:	no fracture
	- cold shapeability		:	good, no defects
	- crystallinity		:	0%
10	- density		:	1.32 g/m ³

Example 3:

A transparent sheet is produced analogously to Example 2,

The extrusion temperature is 275°C. The first calender roll has a temperature of 57°C, and the subsequent rolls have a temperature of

15 50°C. The take-off rate and the speed of the calender rolls are 1.7 m/min.

The PEN sheet produced has the following property profile:

	- thickness		:	10 mm
	- surface gloss 1st side		:	151
	(measurement angle 20°)	2nd side	:	148
20	- light transmission		:	86.5%
	- clarity		:	99.2%
	- haze		:	4.95%
	- surface defects per m ² (specks, orange-peel skin, bubbles, etc.)		:	none
25	- Charpy impact strength a _n		:	no fracture
	- cold shapeability		:	good, no defects
	- crystallinity		:	0.1%

- density : 1.33 g/m³

Example 4:

A transparent sheet is produced analogously to Example 2. 70% of polyethylene naphthalate from Example 2 are blended with 30% of recycled material made from this polyethylene naphthalate.

The transparent PEN sheet produced has the following property profile:

- thickness : 6 mm
- surface gloss 1st side : 168
(measurement angle 20°) 2nd side : 166
- light transmission : 87.3%
- clarity : 99.4%
- haze : 3.2%
- surface defects per m² : none
(specks, orange-peel skin, bubbles, etc.)
- Charpy impact strength a_n : no fracture
- cold shapeability : good, no defects
- crystallinity : 0%
- density : 1.32 g/m³

Example 5

A transparently colored, amorphous sheet with a thickness of 6 mm which contains, as principal constituents, the polyethylene naphthalate from Example 2 and 2% by weight of a soluble dye Solvent Red 138, an anthraquinone derivative from BASF (@Thermoplast G), is produced.

The soluble dye Solvent Red 128 is added in the form of a masterbatch. The masterbatch consists of 20% by weight of the dye Solvent Red 138 and 80% by weight of the polyethylene naphthalate described above.

Before extrusion, 90% by weight of polyethylene naphthalate and 10% by weight of the masterbatch is dried for 5 hours at 170°C in a drier and then extruded in a single-screw extruder at an extrusion temperature of 280°C through a flat film die onto a smoothing calender whose walls are arranged in an S-shape, and smoothed to give a sheet with a thickness of 6 mm. The first calender roll has a temperature of 66°C, and the subsequent rolls each have a temperature of 60°C. The take-off rate and the calender-roll speed are 2.9 m/min.

After cooling, the transparently colored PEN sheet with a thickness of 6 mm is trimmed at the edges using separating saws, cut to length and stacked.

The PEN sheet produced, which is transparently colored red, has the following property profile:

	- thickness	:	6 mm
15	- surface gloss 1st side	:	118
	(measurement angle 20°) 2nd side	:	115
	- light transmission	:	28.1%
	- clarity	:	97.1%
	- haze	:	9.6%
20	- surface defects per m ²	:	none
	(specks, orange-peel skin, bubbles, etc.)		
	- Charpy impact strength a _n	:	no fracture
	- cold shapeability	:	good, no defects
	- crystallinity	:	0%
25	- density	:	1.34 g/m ³

Example 6:

A white-colored, amorphous sheet with a thickness of 3 mm which contains, as principal constituents, the polyethylene naphthalate from Example 2 and 6% by weight of titanium dioxide is produced.

The titanium dioxide is of the rutile type and has been coated with an inorganic coating of Al_2O_3 and with an organic coating of polydimethylsiloxane. The titanium dioxide has a mean particle diameter of $0.2\text{ }\mu\text{m}$.

- 5 The titanium dioxide is added in the form of a masterbatch. The masterbatch consists of 30% by weight of the titanium dioxide described and 70% by weight of the polyethylene naphthalate described.

- Before extrusion, the 80% by weight of polyethylene naphthalate and 20% by weight of the titanium dioxide masterbatch is dried for 5 hours at 170°C
- 10 in a drier and then extruded in a single-screw extruder at an extrusion temperature of 286°C through a flat film die onto a smoothing calender whose walls 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
- 15 rate and the calender-roll speed are 6.5 m/min.

After cooling, the white colored PEN sheet with a thickness of 3 mm is trimmed at the edges using separating saws, cut to length and stacked.

The white-colored sheet produced has the following properties:

- | | | | |
|----|---|---|-------------|
| | - thickness | : | 3 mm |
| 20 | - surface gloss 1st side | : | 123 |
| | (measurement angle 20°) 2nd side | : | 122 |
| | - light transmission | : | 0% |
| | - whiteness | : | 110 |
| | - coloring | : | white, |
| | | | homogeneous |
| 25 | - surface defects | : | none |
| | (specks, orange-peel skin, bubbles, etc.) | | |
| | - Charpy impact strength a_n | : | no fracture |

- cold shapeability : good
- crystallinity : 0%

Example 7:

- 5 A transparent, amorphous sheet with a thickness of 3 mm which contains, as principal constituent, the polyethylene naphthalate from Example 2 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.

- 10 In order to achieve homogeneous distribution, 1.0% by weight of the UV stabilizer are incorporated directly into the polyethylene naphthalate by the raw-material producer.

- 15 Before extrusion, the polyethylene naphthalate is dried for 5 hours at 170°C in a drier and then extruded in a single-screw extruder at an extrusion temperature of 286°C through a flat film die onto a smoothing calender whose walls 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.

- 20 After cooling, the transparent colored PEN sheet with a thickness of 3 mm is trimmed at the edges using separating saws, cut to length and stacked.

The transparent sheet produced has the following properties:

- | | | | |
|----|----------------------------------|---|------|
| | - thickness | : | 3 mm |
| | - surface gloss 1st side | : | 168 |
| 25 | (measurement angle 20°) 2nd side | : | 161 |
| | - light transmission | : | 85% |

	- clarity	:	97%
	- haze	:	1.8%
	- surface defects per m ² (specks, orange-peel skin, bubbles, etc.)	:	none
5	- Charpy impact strength a_n	:	no fracture
	- cold shapeability	:	good, no defects
	- crystallinity	:	0%
	- density	:	1.33 g/cm ³
After weathering for 1000 hours on each side by means of an Atlas Ci 65			
10	Weather Ometer, the PEN sheet has the following properties:		
	- thickness	:	3 mm
	- surface gloss 1st side	:	162
	(measurement angle 20°) 2nd side	:	153
	- light transmission	:	84.1%
15	- clarity	:	96%
	- haze	:	2.0%
	- overall discoloration ΔE	:	0.22
	- dark discoloration ΔL	:	-0.18
	- red-green discoloration ΔA	:	-0.08
20	- blue-yellow discoloration ΔB	:	0.10
	- surface defects (cracks, embrittlement)	:	none
	- yellow value G	:	4
	- Charpy impact strength a_n	:	no fracture
25	- cold shapeability	:	good

Patent Claims:



1. An amorphous sheet having a thickness in the range from 1 to 20 mm, which contains, as the main constituent, at least one polyalkylene naphthalate.
- 5 2. A sheet as claimed in claim 1, which contains at least one dye which is soluble in the polyalkylene naphthalate.
3. A sheet as claimed in claim 1 or 2, which contains at least one organic and/or inorganic pigment as colorant.
4. A sheet as claimed in at least one of claims 1 or 3, which contains at
10 least one UV stabilizer as light stabilizer.
5. A sheet as claimed in at least one of claims 1 to 4, wherein the polyalkylene naphthalate used is polyethylene naphthalate, polypropylene naphthalate and/or polybutylene naphthalate.
6. A sheet as claimed in at least one of claims 1 to 5, wherein the
15 polyalkylene naphthalate used is polyethylene naphthalate.
7. A process for the production of an amorphous sheet as claimed in at least one of claims 1 to 6, which comprises melting the polyalkylene naphthalate in the extruder, extruding the melt through a die and then sizing it, polishing it and cooling it with at least two rolls in the polishing
20 stack, before the sheet is cut to size.
8. The process as claimed in claim 7, wherein the polyalkylene naphthalate is melted together with the soluble dye, the colorant and/or the UV stabilizer.
9. The process as claimed in claim 7 or 8, wherein the polyalkylene
25 naphthalate is dried before it is melted in the extruder.



10. The process as claimed in at least one of claims 7 to 9, wherein the polyalkylene naphthalate used is polyethylene naphthalate (PEN).
11. The process as claimed in claim 10, wherein the temperature of the PEN melt is in the range from 250 to 320°C.
- 5 12. The process as claimed in claim 10 or 11, wherein the first roll of the polishing stack has a temperature which is in the range from 50 to 80°C.