

Description

AMORPHOUS COLORED SHEET OF A CRYSTALLIZABLE THERMOPLASTIC

The invention relates to an amorphous, colored sheet of a crystallizable thermoplastic, the thickness of which is in the range from 1 to 20 mm. The sheet comprises at least one organic and/or an inorganic pigment as colorant. It is distinguished by homogeneous optical and very good mechanical properties. The invention furthermore relates to a process for the production of this sheet and to its use.

Amorphous, colored 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, 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 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 the extrusion step. External lubricants are necessary to prevent the material from sticking to walls and rolls.

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

10 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
15 with a loss of or extreme deterioration in the mechanical properties.

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
20 sheets are readily combustible, so that these sheets may not be employed, for example, for interior applications and in exhibition construction.

PMMA and PC sheets furthermore cannot be shaped in the cold. During cold shaping, PMMA sheets break up into
25 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 intrinsic viscosity of the PET employed is in the range
30 from 0.5 to 1.2. The PET sheet is heat-treated on 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% and 50%. The PET sheets disclosed in EP-A-0 471 528 have a thickness of 1 to 10 mm. Since the thermoformed shaped article produced from the 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 unimportant. As a rule, the optical properties of these sheets are poor and in need of optimization. The sheets comprise neither a dyestuff nor an organic or inorganic pigment.

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%. 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. The sheets comprise no dyestuff and no organic or inorganic pigments at all as colorants.

Since said sheets comprise no light stabilizer, they are only to a limited extent suitable for application outdoors.

Moreover, to date it has been possible to obtain amorphous sheets of crystallizable thermoplastics as the main constituent having a thickness of 1 mm or more only with unsatisfactory optical and mechanical properties, if at all.

The object of the present invention was to provide an amorphous, colored 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, a low light transmission and a high surface gloss.

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

- 5 Furthermore, the sheet according to the invention should be recyclable, in particular without loss of mechanical properties, and poorly combustible, so that, for example, it can also be used for interior applications and in exhibition construction.
- 10 The object is achieved by an amorphous, colored sheet having a thickness in the range from 1 to 20 mm, which comprises, as the main constituent, a crystallizable thermoplastic and at least one organic and/or inorganic pigment as colorant.
- 15 The present invention furthermore relates to a process for the production of this sheet having the features of claim 23. Preferred embodiments of this process are explained in the subclaims 24 to 29.

- 20 The concentration of the colorant is preferably in the range from 0.5 to 30% by weight, based on the weight of the crystallizable thermoplastic.

- 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 defining pigment particles a distinction is made between primary particles, aggregates and agglomerates.
- 25
- 30

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, 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 areas differs only little from the sum of the individual areas. If one refers to 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. These simultaneously occurring processes are termed dispersions. 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.

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.

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.

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.

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.

10 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
15 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
20 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
25 improve the light fastness. TiO_2 is known to be photo-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 yellow-
30 ing. Particularly suitable oxides include the oxides of aluminum, silicon, zinc or magnesium, or mixtures of two or more of these compounds. TiO_2 particles 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
35 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 groups are -OH, -OR, -COOX, (X = R, H or Na, R = alkyl
5 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-alkano-
10 ls having 12 to 24 carbon atoms, and also polydiorganosiloxanes and/or polyorganohydridosiloxanes, for example 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
15 from 0.7 to 1.5 g, of organic compound, based on 100 g of titanium dioxide particles. The coating is applied to the particles in aqueous suspension. The inorganic oxides are precipitated in the aqueous suspension from water-soluble
20 compounds, for example alkali metal aluminate, especially sodium aluminate, aluminum hydroxide, aluminum sulfate, aluminum nitrate, sodium silicate (waterglass) or silicic acid.

The term inorganic oxides, such as Al_2O_3 and SiO_2 , should also be understood as including the hydroxides or their
25 various dehydration stages, for example oxide hydrates, without their precise compositional 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
30 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
35 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 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 .

Examples of sulfide pigments are cadmium sulfide

selenides, cadmium-zinc sulfides, sodium aluminum silicate containing sulfur bonded polysulfide-style in the lattice.

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

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

10 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 ($-N=N-$). Azo pigments include monoazo pigments, disazo pigments, disazo condensation pigments, salts of
15 azo dye acids and mixtures of the azo pigments.

The amorphous colored sheet comprises at least one inorganic and/or organic pigment. In specific embodiments the amorphous sheet can also comprise mixtures of inorganic and/or organic pigments, and also soluble dyes as
20 well. In this context the concentration of the soluble dye is preferably in the range from 0.001 to 20% by weight, preferably 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 crystallizable
25 thermoplastic.

Among the soluble dyes, particular preference is given to those dyes which are soluble in fats and aromatic substances. These are azo dyes or anthraquinone dyes.

Suitable soluble dyes are, for example: Solvent Yellow
30 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, azo dyes such as

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.

The amorphous, colored sheet comprises, as the main constituent, a crystallizable thermoplastic. Suitable crystallizable or partly crystalline thermoplastics are, for example, polyethylene terephthalate, polybutylene terephthalate, cycloolefin polymers and cycloolefin copolymers, polyethylene terephthalate being preferred.

According to the invention, crystallizable thermoplastic is understood as meaning

- crystallizable homopolymers,
- crystallizable copolymers,
- crystallizable compound materials,
- crystallizable recycled material and
- other variations of crystallizable thermoplastics.

Amorphous sheet in the context of the present invention is understood as meaning those sheets which are non-crystalline, although the crystallizable thermoplastic employed has a crystallinity of between 5% and 65%, preferably between 25% 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%. The amorphous sheet according to the invention is essentially non-orientated.

The standard viscosity of the thermoplastic according to the invention SV (DCA), measured in dichloroacetic acid in accordance with DIN 53728, is between 800 and 6000, preferably between 950 and 5000 and particularly preferably between 1000 and 4000.

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

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

5 In a particularly preferred embodiment, the colored amorphous sheet according to the invention comprises, as the main constituent, crystallizable polyethylene terephthalate.

Processes for the preparation of the crystallizable thermoplastics are known to the expert.

10 Polyethylene terephthalates are usually prepared by polycondensation in the melt or by a two-stage polycondensation, the first step being carried out in the melt up to a moderate molecular weight - corresponding to a moderate intrinsic viscosity IV of about 0.5 to 0.7 - and
15 the further condensation being carried out by solid condensation. The polycondensation is in general carried out in the presence of known polycondensation catalysts or catalyst systems. In the solid condensation, PET chips are heated at temperatures in the range from 180 to 320°C
20 under reduced pressure or under an inert gas until the desired molecular weight is reached.

The preparation of polyethylene terephthalate is described in detail in a large number of patents, such as, for example, in JP-A-60-139 717, DE-C-2 429 087,
25 DE-A-27 07 491, DE-A-23 19 089, DE-A-16 94 461, JP-63-41 528, JP-62-39 621, DE-A-41 17 825, DE-A-42 26 737, JP-60-141 715, DE-A-27 21 501 and US-A-5,296,586.

30 Polyethylene terephthalates having particularly high molecular weights can be prepared by polycondensation of dicarboxylic acid-diol precondensates (oligomers) at elevated temperature in a liquid heat transfer medium in the presence of customary polycondensation catalysts and,

if appropriate, cocondensable modifying agents, if the liquid heat transfer medium is inert and free from aromatic structural groups and has a boiling point in the range from 200 to 320°C, the weight ratio of dicarboxylic acid-diol precondensate (oligomer) employed to liquid heat transfer medium is in the range from 20:80 to 80:20, and the polycondensation is carried out in a boiling reaction mixture in the presence of a dispersion stabilizer.

10 The surface gloss of the sheet according to the invention, measured in accordance with DIN 67530 (measurement angle 20°) is preferably greater than 90, particularly preferably greater than 100 and the light transmission, measured in accordance with ASTM D 1003, is preferably less than 5%, particularly preferably less than 3%.

The sheet according to the invention furthermore has opaque, homogeneous optical properties.

In the case of polyethylene terephthalate, 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 8.0 kJ/m², particularly preferably in the range from 4.0 to 6.0 kJ/m².

Polyethylene terephthalate polymers having a crystallite melting point T_m , measured by DSC (Differential Scanning Calorimetry) with a heating-up rate of 10°C/minute, of from 220°C to 280°C, preferably from 230°C to 270°C, a crystallization temperature range T_c of between 75°C and 280°C, preferably 75°C and 260°C, a glass transition temperature T_g of between 65°C and 90°C and a density, measured in accordance with DIN 53479, of 1.30 to 1.45 g/cm³ and a crystallinity of between 5% and 65%, preferably 25% to 65%, are preferred polymers as starting

materials for production of the sheet.

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 M_w/M_n of the polyethylene terephthalate measured by means of GPC is preferably between 1.5 and 6.0, preferably between 2.5 and 6.0, and particularly preferably between 3.0 and 5.0.

10 In a particularly preferred embodiment, the sheet according to the invention is provided with a UV stabilizer as light stabilizer.

The concentration of the light stabilizer is preferably in the range from 0.01 to 5% by weight, based on the weight of the crystallizable thermoplastic.

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.

Polyethylene terephthalates, 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.

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
5 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.

The photooxidation of polyethylene terephthalates can also lead, via splitting of hydrogen in the α -position of
10 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).

UV stabilizers or UV absorbers as light stabilizers are
15 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 sheets, since they lead to a change in
20 color. Only organic and organometallic compounds which impart no or only an extremely slight change in color to the thermoplastic to be stabilized are suitable for amorphous sheets.

Suitable light stabilizers or UV stabilizers are, for
25 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
30 triazines being preferred.

In a particularly preferred embodiment, the colored, amorphous sheet according to the invention comprises, as the main constituent, a crystallizable polyethylene terephthalate and 0.01% by weight to 5.0% by weight of
35 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyl)oxy-phenol

(structure in Figure 1a) 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 (structure in Figure 1b). In a preferred embodiment, mixtures of these two UV stabilizers or mixtures of at least one of these two UV stabilizers with 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 terephthalate.

Weathering tests have shown that after 5 to 7 years of external use, the UV-stabilized sheets should show no yellowing, no embrittlement, no loss of gloss on the surface, no cracking on the surface and no deterioration in the mechanical properties.

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.

Furthermore, measurements have shown that the sheet according to the invention is poorly combustible and poorly flammable, so that it is suitable, for example, for interior applications and in exhibition construction.

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 particularly suitable for use as short-lived advertising signs or other advertising articles.

In the UV-stabilized embodiment, the sheet possesses enhanced weathering stability and increased UV stability. This means that the sheets are damaged only to an extremely low extent or not at all by weathering and

sunlight or by other UV radiation, making the sheets suitable for exterior applications and/or critical interior applications. In particular, after a number of years of external use, the sheets should not show any
5 yellowing, any embrittlement or cracking of the surface, nor any deterioration in the mechanical properties.

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

- 10 Such an extrusion line is shown in diagram form in Figure 2. It essentially comprises
- an extruder (1) as a plasticizing unit,
 - a slot die (2) as a die for shaping,
 - a polishing stack/calender (3) as a sizing die,
 - 15 - 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,
 - 20 - a stacking device (8).

The process comprises drying the crystallizable thermoplastic, if appropriate, and then melting it in the extruder, together with the colorant and, if appropriate, with the UV stabilizer, shaping the melt through a die
25 and then sizing it, polishing it and cooling it in the polishing stack, before the sheet is cut to dimension.

The process for the production of the sheet according to the invention is described in detail below using the example of polyethylene terephthalate.

- 30 The polyethylene terephthalate is preferably dried, before the extrusion, at 160 to 180°C for 4 to 6 hours.

The polyethylene terephthalate is melted in the extruder. The temperature of the PET melt is preferably in the

range from 250 to 320°C, it then 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.

5 The colorants (inorganic and/or organic pigments and, if desired, soluble dyes) and, if appropriate, the light stabilizer can be metered in in the desired concentration by the actual manufacturer of the raw material or can be metered into the extruder in the course of production of
10 the sheets.

Particular preference, however, is given to the addition of the coloring additive or additives by way of masterbatch technology or by way of the solid pigment preparation. In this case the organic and/or inorganic
15 pigment and, if desired, the soluble dye and/or the light stabilizer are dispersed completely in a solid carrier material. Suitable carriers are certain resins, the polymer to be colored itself, or else other polymers which are sufficiently compatible with the crystallizable
20 thermoplastic.

It is important that the particle size and bulk density of the solid pigment preparation or masterbatch are similar to the particle size and bulk density of the crystallizable thermoplastic, in order that homogeneous
25 distribution and thus coloration can take place.

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

The PET 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,
30 for example, in an I-, F-, L- or S-shape (Figure 3).

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

finally stacked.

The thickness of the PET sheet is essentially determined by the take-off, which is positioned at the end of the cooling zone, the cooling (polishing) rolls coupled to
5 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.

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 restrictor bar can be bent by tension and pressure screws. The thickness is set by adjusting the lips. It is important to ensure that the
15 PET and the lip have a uniform temperature, since otherwise the PET melt flows out in different thicknesses as a result of the different flow paths.

The sizing die, i.e. the polishing calender, gives the PET melt the shape and the dimensions. This is effected
20 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 tem-
25 perature of the calender rolls must be lower than the crystallite melting temperature in order to avoid sticking of the PET melt. The PET melt leaves the slot die with a temperature of 240 to 300°C. The first polishing/cooling roll has a temperature of between 50°C
30 and 80°C, depending on the output and sheet thickness. The second, somewhat cooler roll cools the second or other surface.

If the temperature of the first polishing/cooling roll is outside the stated range of 50°C to 80°C, it is difficult

to obtain an amorphous sheet having a thickness of 1 mm or more in the desired quality.

While the sizing device freezes the PET surfaces as smoothly as possible and cools the profile to the extent
5 that it is dimensionally stable, the after-cooling device lowers the temperature of the PET sheet to virtually room temperature. After-cooling can take place on a roller board. The speed of the take-off should be coordinated
10 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 sheets can comprise a separating saw as a device for cutting to length, the edge trimmer, the stacking unit
15 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 properties of the sheet are measured at the control station.

As a result of the surprising large number of excellent
20 properties, the colored and amorphous 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, for signs, in shop fitting and shelf construction, as
25 advertising articles, as menu stands and as basketball target boards.

In the UV-stabilized embodiment, the sheet according to the invention is also suitable for external applications, such as, for example, roofing, exterior paneling, cover-
30 ings, for applications in the building sector and balcony paneling.

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

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

5 Measurement methods

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 10 the standards ASTM-D 523-78 and ISO 2813, the angle of incidence was set at 20°. Under the angle of incidence set, a 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 15 proportional electrical value. The measurement value is dimensionless and must be stated together with the angle of incidence.

Whiteness

The whiteness is determined with the aid of the electric 20 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 25 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).

Surface defects:

The surface defects are determined visually.

30 Charpy impact strength a_n :

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

Izod 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 53728.

- 10 The intrinsic viscosity is calculated as follows from the standard viscosity

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

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:

- 20 The molecular weights M_w and M_n and the resulting polydispersity M_w/M_n are measured by means of gel permeation chromatography.

Weathering (both sides), UV stability:

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

Test apparatus	: Atlas Ci 65 Weather Ometer
Test conditions	: ISO 4892, i.e. simulated weathering
Irradiation time	: 1000 hours (per side)
30 Irradiation	: 0.5 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.
- 10 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.
- 15 All the UV-stabilized sheets were weathered on both sides
for 1000 hours each per side with the Atlas Ci 65 [lacu-
na] Ometer from Atlas in accordance with the test speci-
fication ISO 4892, and were then tested in respect of
mechanical properties, discoloration, surface defects,
clouding and gloss.
- 20 Example 1:
- A 3 mm thick, white colored, amorphous sheet which
comprises, as the main constituent, a polyethylene tere-
phthalate polymer and 6% by weight of titanium dioxide
is produced.
- 25 The titanium dioxide is of the rutile type and is 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 μm .
- 30 The polyethylene terephthalate from which the colored
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%, the crystallite melting point according to DSC measurements being 258°C. The crystallization temperature range T_c is between 83°C and 258°C, the after-crystallization temperature (also cold-crystallization temperature) T_{cn} being 144°C. The polydispersity M_w/M_n of the polyethylene terephthalate polymer is 2.14. The glass transition temperature is 83°C.

The titanium dioxide is added in the form of a masterbatch. The masterbatch is composed of 30% by weight of the titanium dioxide described as the active compound component and 70% by weight of the polyethylene terephthalate polymer described as the carrier material.

Before the extrusion, 80% by weight of the polyethylene terephthalate polymer and 20% by weight of the titanium dioxide masterbatch are dried in a drier at 170°C for 5 hours, and then extruded in a single-screw extruder at an extrusion temperature of 286°C through a slot die onto a polishing calender, the rolls of which are arranged S-shaped, and polished to a sheet 3 mm thick. The first calender roll has a temperature of 73°C and the subsequent rolls each have a temperature of 67°C. The speed of the take-off and of the calender rolls is 6.5 m/minute.

After the after-cooling, the white, 3 mm thick PET sheet is trimmed at the edges with separating saws, cut to length and stacked.

The sheet produced, which is colored white, shows the following properties:

-	Thickness	:	3 mm
-	Surface gloss 1st side	:	128
30	(Measurement angle 20°)		
	2nd side	:	127
-	Light transmission	:	0%
-	Whiteness	:	110
-	Coloration	:	white, homogeneous

- Surface defects : none
(specks, bubbles,
orange peel)
- Charpy impact strength
- 5 a_n : no fracture
- Izod notched impact
strength a_k : 4.8 kJ/m²
- Cold shaping : good
- Crystallinity : 0%

10 Example 2

A colored sheet is produced analogously to Example 1, a polyethylene terephthalate which has the following properties being employed:

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

- 25 The titanium dioxide masterbatch is composed of 30% by weight of the titanium dioxide described under Example 1 and of 70% by weight of the polyethylene terephthalate of this Example.

- 30 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 speed of the take-off and of the calender rolls is 2.9 m/minute.

The PET sheet produced, which is colored an opaque white, has the following properties:

	-	Thickness	:	6 mm
	-	Surface gloss 1st side	:	121
5		(Measurement angle 20°)		
		2nd side	:	118
	-	Light transmission	:	0%
	-	Whiteness	:	123
	-	Coloration	:	white, homogeneous
10	-	Surface defects	:	none
		(specks, bubbles, orange peel)		
	-	Charpy impact strength		
		a_n	:	no fracture
15	-	Izod notched impact		
		strength a_k	:	5.1 kJ/m ²
	-	Cold shaping	:	good
	-	Crystallinity	:	0%

Example 3:

20 A colored 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 50°C. The speed of the take-off and of the calender rolls is 1.7 m/minute.

25 The PET sheet produced has the following profile of properties:

	-	Thickness	:	10 mm
	-	Surface gloss 1st side	:	116
		(Measurement angle 20°)		
30		2nd side	:	114
	-	Light transmission	:	0%
	-	Whiteness	:	132
	-	Coloration	:	white, homogeneous

- Surface defects : none
(specks, bubbles,
orange peel)
- Charpy impact strength
- 5 a_n : no fracture
- Izod notched impact
strength a_k : 5.3 kJ/m²
- Cold shaping : good
- Crystallinity : 0%

10 Example 4

A colored sheet is produced analogously to Example 3, a polyethylene terephthalate which has the following properties being employed:

- SV (DCA) : 1200
- 15 IV (DCA) : 0.91 dl/g
- Density : 1.37 g/cm³
- Crystallinity : 36%
- Crystallite melting point T_m : 242°C
- Crystallization temperature
- 20 range T_c : 82°C to 242°C
- After-(cold-)crystall-
ization temperature T_{cn} : 157°C
- Polydispersity M_w/M_n : 2.2
- Glass transition temperature: 82°C

- 25 The titanium dioxide masterbatch is composed of 30% by weight of the titanium dioxide described under Example 1 and of 70% by weight of the polyethylene terephthalate polymer of this example.

- 30 The extrusion temperature is 274°C. The first calender roll has a temperature of 50°C and the subsequent rolls have a temperature of 45°C. The speed of the take-off and of the calender rolls is 1.2 m/minute.

The white colored PET sheet produced shows the following

profile of properties:

	-	Thickness	:	15 mm
	-	Surface gloss 1st side	:	112
		(Measurement angle 20°)		
5		2nd side	:	111
	-	Light transmission	:	0%
	-	Whiteness	:	138
	-	Coloration	:	white, homogeneous
	-	Surface defects	:	none
10		(specks, bubbles, orange peel)		
	-	Charpy impact strength		
		a_n	:	no fracture
	-	Izod notched impact		
15		strength a_k	:	5.4 kJ/m ²
	-	Cold shaping	:	good
	-	Crystallinity	:	0.4%

Example 5

20 A colored sheet is produced analogously to Example 2. 50% by weight of the polyethylene terephthalate polymer from Example 2 are mixed with 30% by weight of recycled material of this polyethylene terephthalate polymer and 20% by weight of the titanium dioxide masterbatch.

25 The colored PET sheet produced has the following profile of properties:

	-	Thickness	:	6 mm
	-	Surface gloss 1st side	:	119
		(Measurement angle 20°)		
		2nd side	:	118
30	-	Light transmission	:	0%
	-	Whiteness	:	125
	-	Coloration	:	white, homogeneous
	-	Surface defects	:	none
35		(specks, bubbles, orange peel)		

- Charpy impact strength
 - a_n : no fracture
- Izod notched impact strength a_k : 5.0 kJ/m²
- 5 - Cold shaping : good
- Crystallinity : 0%

Example 6

10 A colored sheet is produced analogously to Example 1. The plate is not white but is colored green. The 3 mm thick, green colored sheet comprises as the main constituent the polyethylene terephthalate polymer from Example 1 and 7% by weight of Pigment Green 17.

Pigment Green 17 is a chromium oxide (Cr₂O₃) from BASF (®Sicopalgrün 9996).

15 Like the titanium dioxide, the chromium oxide is added in the form of a masterbatch. The masterbatch is composed of 35% by weight of chromium oxide (®Sicopalgrün 9996) and 65% by weight of the polyethylene terephthalate polymer from Example 1.

20 Prior to extrusion, 80% by weight of the polyethylene terephthalate polymer from Example 1 are mixed with 20% by weight of the chromium oxide masterbatch, and the mixture is dried at 170°C for 5 hours.

25 Then a 3 mm thick, green colored sheet is prepared, as described in Example 1, which has the following properties:

- Thickness : 3 mm
- Surface gloss 1st side : 130
(Measurement angle 20°)
- 30 2nd side : 129
- Light transmission : 0.5%
- Coloration : green, homogeneous

- Surface defects : none
(specks, bubbles,
orange peel)
- Charpy impact strength
- 5 a_n : no fracture
- Izod notched impact
strength a_k : 4.6 kJ/m²
- Cold shaping : good
- Crystallinity : 0%

10 Example 7

A colored sheet is produced analogously to Example 2. The sheet comprises 3% by weight of titanium dioxide and 3.5% by weight of chromium oxide.

15 The titanium dioxide masterbatch is composed of 30% by weight of the titanium dioxide described under Example 1 and of 70% by weight of the polyethylene terephthalate polymer from Example 2.

20 The chromium oxide masterbatch is composed of 35% by weight of the chromium oxide described under Example 6 (Sicopalgrün 9996) and of 65% by weight of the polyethylene terephthalate polymer from Example 2.

25 Prior to extrusion, 80% by weight of the polyethylene terephthalate polymer from Example 2 are mixed with 10% by weight of the titanium dioxide masterbatch, and 10% by weight of the chromium oxide masterbatch and the mixture is dried at 170°C for 5 hours.

Then a 6 mm thick sheet is prepared, as described in Example 2, which has the following properties:

- Thickness : 6 mm
- 30 - Surface gloss 1st side : 125
(Measurement angle 20°)
2nd side : 125
- Light transmission : 0%

- Coloration : opaque light green,
homogeneous
- Surface defects : none
(specks, bubbles,
5 orange peel)
- Charpy impact strength
 a_n : no fracture
- Izod notched impact
strength a_k : 5.3 kJ/m²
- 10 - Cold shaping : good
- Crystallinity : 0%

Comparison Example 1

A colored sheet is produced analogously to Example 1. The
polyethylene terephthalate employed has a standard
15 viscosity SV (DCA) of 760, which corresponds to an
intrinsic viscosity IV (DCA) of 0.62 dl/g. The other
properties are identical to the properties of the
polyethylene terephthalate from Example 1 in the context
of measurement accuracy. The titanium dioxide master-
20 batch, the process parameters and the temperature are
chosen as in Example 1. As a result of the low viscosity,
no sheet production is possible. The stability of the
melt is inadequate, so that the melt collapses before
cooling on the calender rolls.

25 Comparison Example 2:

A colored sheet is produced analogously to Example 2, the
polyethylene terephthalate from Example 2 and the
titanium dioxide masterbatch from Example 2 also being
employed. The first calender roll has a temperature of
30 83°C and the subsequent rolls each have a temperature of
77°C.

The gloss is significantly reduced. The sheet shows
surface defects and structures. Optical properties are
unacceptable for a colored application.

The sheet produced has the following profile of properties:

	-	Thickness	:	6 mm
	-	Surface gloss 1st side	:	85
5				(cloudy and clear spots)
		(Measurement angle 20°)		
		2nd side	:	82
				(cloudy and clear spots)
	-	Light transmission	:	0%
10	-	Coloration	:	appears inhomogeneous, as the surface shows significant structures, bubbles and cracks
	-	Surface defects	:	appears inhomogeneous, as the surface shows significant structures bubbles and cracks
15				(specks, bubbles, orange peel)
20	-	Charpy impact strength		
		a_2	:	no fracture
	-	Izod notched impact strength a_k	:	5.1 kJ/m ²
	-	Cold shaping	:	good
25	-	Crystallinity	:	about 9%

Example 8:

A 3 mm thick, UV-stabilized, white colored, amorphous sheet which comprises, as the main constituent, the polyethylene terephthalate according to Example 1 and 6% by weight of titanium dioxide and 1.0% by weight of the UV stabilizer 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyl)oxyphenol (®Tinuvin 1577 from Ciba-Geigy) is produced analogously to Example 1.

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

1% by weight of the UV stabilizer Tinuvin is incorporated into the polyethylene terephthalate directly by the producer of the raw material.

5 Before the extrusion, 80% by weight of the polyethylene terephthalate treated with 1.0% by weight of Tinuvin 1577 and 20% by weight of the titanium dioxide masterbatch are dried in a dryer at 170°C for 5 hours.

The white colored sheet produced shows the same properties as the sheet according to Example 1.

10 After weathering for in each case 1000 hours per side with [lacuna] Atlas Ci 65 Weather Ometer, the PET sheet shows the following properties:

- Thickness : 3 mm
- Surface gloss 1st side : 125
- 15 (Measurement angle 20°)
- 2nd side : 123
- Light transmission : 0%
- Whiteness : 108%
- Coloration : white, homogeneous
- 20 - Surface defects : none
- (cracks, embrittlement)
- Charpy impact strength
- a_n : no fracture
- Izod notched impact
- 25 strength a_k : 4.6 kJ/m²
- Cold shaping : good
- Crystallinity : 0%

Example 9

30 A colored sheet UV-stabilized using 1% Tinuvin 1577 is produced analogously to Example 8, the polyethylene terephthalate according to Example 2 being employed.

The titanium dioxide masterbatch is composed of 30% by weight of the titanium dioxide described under Example 1

and of 70% by weight of the polyethylene terephthalate of this Example.

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

The process used here corresponds to that according to Example 2. The sheet produced, which is colored an opaque white, has the same properties as the sheet according to
10 Example 2.

After weathering for in each case 1000 hours per side with [lacuna] Atlas Ci 65 Weather Ometer, the PET sheet has the following properties:

- Thickness : 6 mm
- 15 - Surface gloss 1st side : 118
(Measurement angle 20°)
2nd side : 117
- Light transmission : 0%
- Whiteness : 121%
- 20 - Coloration : white, homogeneous
- Surface defects : none
(cracks, embrittlement)
- Charpy impact strength
a_n : no fracture
- 25 - Izod notched impact
strength a_k : 5.0 kJ/m²
- Cold shaping : good
- Crystallinity : 0%

Example 10

30 A colored sheet UV-stabilized using 1.0% by weight of Tinuvin 1577 is produced analogously to Example 9. 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 speed of the take-off and of

the calender rolls is 1.7 m/minute.

The process employed here corresponds to the process according to Example 3. The PET sheet produced has the same profile of properties as the sheet according to
5 Example 3.

After weathering for in each case 1000 hours per side with [lacuna] Atlas Ci 65 Weather Ometer, the PET sheet has the following properties:

	-	Thickness	:	10 mm
10	-	Surface gloss 1st side	:	115
		(Measurement angle 20°)		
		2nd side	:	112
	-	Light transmission	:	0%
	-	Whiteness	:	128%
15	-	Coloration	:	white, homogeneous
	-	Surface defects	:	none
		(cracks, embrittlement)		
	-	Charpy impact strength		
		a_n	:	no fracture
20	-	Izod notched impact		
		strength a_k	:	5.2 kJ/m ²
	-	Cold shaping	:	good
	-	Crystallinity	:	0%

Example 11

25 A colored sheet UV-stabilized using 1% by weight of Tinuvin 1577 is produced analogously to Example 10, the polyethylene terephthalate described in Example 4 being employed.

30 The titanium dioxide masterbatch is composed of 30% by weight of the titanium dioxide described under Example 1 and of 70% by weight of the polyethylene terephthalate of this example.

The extrusion temperature is 274°C. The first calender

roll has a temperature of 50°C and the subsequent rolls have a temperature of 45°C. The speed of the take-off and of the calender rolls is 1.2 m/minute.

5 The process used here corresponds to the process according to Example 4. The white colored PET sheet produced shows the same profile of properties as the sheet according to Example 4.

10 After weathering for in each case 1000 hours per side with [lacuna] Atlas Ci 65 Weather Ometer, the PET sheet has the following properties:

- Thickness : 15 mm
- Surface gloss 1st side : 110
(Measurement angle 20°)
- 15 - 2nd side : 109
- Light transmission : 0%
- Whiteness : 134%
- Coloration : white, homogeneous
- Surface defects : none
(cracks, embrittlement)
- 20 - Charpy impact strength
- a_n : no fracture
- Izod notched impact
- strength a_k : 5.2 kJ/m²
- Cold shaping : good
- 25 - Crystallinity : 0.4%

Example 12

30 A colored sheet UV-stabilized using 1.0% by weight of ®Tinuvin 1577 is produced analogously to Example 9. 50% by weight of the polyethylene terephthalate from Example 2 are mixed with 30% by weight of recycled material of this polyethylene terephthalate and 20% by weight of the titanium dioxide masterbatch.

The process employed here corresponds to the process according to Example 5. The colored PET sheet produced

has the same profile of properties as the sheet according to Example 5.

- After weathering for in each case 1000 hours per side with [lacuna] Atlas Ci 65 Weather Ometer, the PET sheet
- 5 has the following properties:
- Thickness : 6 mm
 - Surface gloss 1st side : 116
(Measurement angle 20°)
 - 2nd side : 116
 - 10 - Light transmission : 0%
 - Whiteness : 122%
 - Coloration : white, homogeneous
 - Surface defects : none
(cracks, embrittlement)
 - 15 - Charpy impact strength
 - a_n : no fracture
 - Izod notched impact
 - strength a_k : 4.7 kJ/m²
 - Cold shaping : good
 - 20 - Crystallinity : 0%

Example 13

- A white colored sheet is produced analogously to Example 9. 0.8% by weight of the UV stabilizer 2,2'-methylene-bis-(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-
- 25 tetramethylbutyl)-phenol (®Tinuvin 360 from Ciba-Geigy), based on the weight of the polymer, is employed as the UV stabilizer.

Tinuvin 360 has a melting point of 195°C and is heat-stable up to about 350°C.

- 30 As in Example 8, 0.8% by weight of the UV stabilizer Tinuvin 360 is incorporated into the polyethylene terephthalate directly by the producer of the raw materials.

The UV-stabilized sheet produced has the following properties:

	-	Thickness	:	6 mm
	-	Surface gloss 1st side	:	123
5		(Measurement angle 20°)		
		2nd side	:	122
	-	Light transmission	:	0%
	-	Whiteness	:	128
	-	Coloration	:	white, homogeneous
10	-	Surface defects	:	none
		(specks, bubbles, orange peel)		
	-	Charpy impact strength		
		a_n	:	no fracture
15	-	Izod notched impact		
		strength a_k	:	5.2 kJ/m ²
	-	Cold shaping	:	good
	-	Crystallinity	:	0%

After weathering for in each case 1000 hours per side with the Atlas Ci 65 Weather Ometer, the PET sheet has the following properties:

	-	Thickness	:	6 mm
	-	Surface gloss 1st side	:	118
		(Measurement angle 20°)		
25		2nd side	:	117
	-	Light transmission	:	0%
	-	Whiteness	:	123%
	-	Coloration	:	white, homogeneous
	-	Surface defects	:	none
30		(cracks, embrittlement)		
	-	Charpy impact strength		
		a_n	:	no fracture
	-	Izod notched impact		
		strength a_k	:	5.0 kJ/m ²
35	-	Cold shaping	:	good
	-	Crystallinity	:	0%

Comparison Example 3

A white colored, UV-stabilized sheet is produced analogously to Example 8. The polyethylene terephthalate employed has a standard viscosity SV (DCA) of 760, which
5 corresponds to an intrinsic viscosity IV (DCA) of 0.62 dl/g. The other properties are identical to the properties of the polyethylene terephthalate from Example 1 in the context of measurement accuracy. The
10 titanium dioxide masterbatch, the process parameters and the temperature are chosen as in Example 1. As a result of the low viscosity, no sheet production is possible. The stability of the melt is inadequate, so that the melt collapses before cooling on the calender rolls.

Comparison Example 4

15 The sheet which was obtained according to Example 1 and corresponds to the sheet according to Example 8, but comprises no UV stabilizer, is exposed to weathering.

After weathering for in each case 1000 hours per side with [lacuna] Atlas Ci 65 Weather Ometer, the PET sheet
20 has the following properties:

- Thickness : 3 mm
- Surface gloss 1st side : 88
(Measurement angle 20°)
- 2nd side : 86
- 25 - Light transmission : 0%
- Whiteness : 81%
- Coloration : whitish-yellow
- Surface defects : surface is dull and
(cracks, embrittlement) shows significant
30 yellowing
- Charpy impact strength
a_n : complete fracture
at 44.2 kJ/m²
- Izod notched impact
35 strength a_k : 1.6 kJ/m²

- Cold shaping : crack formation
- Crystallinity : 0%

Considered visually, the sheet shows a significant yellowing.

5 Example 14

A 3 mm thick, white colored, amorphous sheet which comprises, as the main constituent, polyethylene terephthalate and 6% by weight of titanium dioxide is produced.

- 10 The titanium dioxide is of the rutile type and is 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 μm .
- 15 The polyethylene terephthalate from which the colored sheet is produced has a standard viscosity SV (DCA) of 3490, which corresponds to an intrinsic viscosity IV (DCA) of 2.45 dl/g. The moisture content is < 0.2% and the density (DIN 53479) is 1.35 g/cm³. The crystallinity
- 20 is 19%, the crystallite melting point according to DSC measurements being 243°C. The crystallization temperature range T_c is between 82°C and 243°C. The polydispersity M_w/M_n of the polyethylene terephthalate is 4.3, M_w being 225,070 g/mol and M_n being 52,400 g/mol. The glass
- 25 transition temperature is 83°C.

- The titanium dioxide is added in the form of a masterbatch. The masterbatch is composed of 30% by weight of the titanium dioxide described as the active compound component and 70% by weight of the polyethylene terephthalate described as the carrier material.
- 30

Before the extrusion, 80% by weight of the polyethylene terephthalate and 20% by weight of the titanium dioxide masterbatch are dried in a dryer at 170°C for 5 hours,

and are then extruded in a single-screw extruder at an extrusion temperature of 286°C through a slot die onto a polishing calender, the rolls of which are arranged S-shaped, and polished to a sheet 3 mm thick. The first
5 calender roll has a temperature of 73°C and the subsequent rolls each have a temperature of 67°C. The speed of the take-off and of the calender rolls is 6.5 m/minute.

10 After the after-cooling, the white, 3 mm thick PET sheet is trimmed at the edges with separating saws, cut to length and stacked.

The white sheet produced, which is colored shows the following properties:

	-	Thickness	:	3 mm
15	-	Surface gloss 1st side	:	131
		(Measurement angle 20°)		
		2nd side	:	129
	-	Light transmission	:	0%
	-	Whiteness	:	112
20	-	Coloration	:	white, homogeneous
	-	Surface defects	:	none
		(specks, bubbles, orange peel and the like)		
	-	Charpy impact strength		
25		a _n	:	no fracture
	-	Izod notched impact strength a _k	:	4.8 kJ/m ²
	-	Cold shaping	:	good
	-	Crystallinity	:	0%

30 Example 15

A colored sheet is produced analogously to Example 14, a polyethylene terephthalate which has the following properties being employed:

	SV (DCA)	:	2717
35	IV (DCA)	:	1.9 dl/g

Density	:	1.38 g/cm ³
Crystallinity	:	44%
Crystallite melting point T_m	:	245°C
Crystallization temperature		
5 range T_c	:	82°C to 245°C
M_w	:	175,640 g/mol
M_n	:	49,580 g/mol
Polydispersity M_w/M_n	:	2.02
Glass transition temperature:	:	82°C

- 10 The titanium dioxide masterbatch is composed of 30% by weight of the titanium dioxide described under Example 15 and of 70% by weight of the polyethylene terephthalate of this Example.

- 15 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 speed of the take-off and of the calender rolls is 2.9 m/minute.

The PET sheet produced, which is colored an opaque white, has the following properties:

- | | | | |
|----|---|---|-----------------------|
| 20 | - Thickness | : | 6 mm |
| | - Surface gloss 1st side | : | 124 |
| | (Measurement angle 20°) | | |
| | 2nd side | : | 121 |
| | - Light transmission | : | 0% |
| 25 | - Whiteness | : | 125 |
| | - Coloration | : | white, homogeneous |
| | - Surface defects | : | none |
| | (specks, bubbles, orange peel and the like) | | |
| 30 | - Charpy impact strength | | |
| | a_n | : | no fracture |
| | - Izod notched impact strength a_k | : | 5.1 kJ/m ² |
| | - Cold shaping | : | good |
| 35 | - Crystallinity | : | 0% |

Example 16

A colored sheet is produced analogously to Example 15. 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 speed of the take-off and of the calender rolls is 1.7 m/minute.

The PET sheet produced has the following profile of properties:

	-	Thickness	:	10 mm
10	-	Surface gloss 1st side	:	118
		(Measurement angle 20°)		
		2nd side	:	115
	-	Light transmission	:	0%
	-	Whiteness	:	134
15	-	Coloration	:	white, homogeneous
	-	Surface defects	:	none
		(specks, bubbles, orange peel and the like)		
	-	Charpy impact strength		
20		a_n	:	no fracture
	-	Izod notched impact strength a_k	:	5.3 kJ/m ²
	-	Cold shaping	:	good
	-	Crystallinity	:	0%

25 Example 17

A colored sheet is produced analogously to Example 16, a polyethylene terephthalate which has the following properties being employed:

	SV (DCA)	:	3173
30	IV (DCA)	:	2.23 dl/g
	Density	:	1.34 g/cm ³
	Crystallinity	:	12%
	Crystallite melting point T_m	:	240°C

Crystallization temperature			
	range T_c	:	82°C to 240°C
	M_w	:	204,660 g/mol
	M_n	:	55,952 g/mol
5	Polydispersity M_w/M_n	:	3.66
	Glass transition temperature:		82°C

10 The titanium dioxide masterbatch is composed of 30% by weight of the titanium dioxide described under Example 14 and of 70% by weight of the polyethylene terephthalate of this example.

The extrusion temperature is 274°C. The first calender roll has a temperature of 50°C and the subsequent rolls have a temperature of 45°C. The speed of the take-off and of the calender rolls is 1.2 m/minute.

15 The white colored PET sheet produced shows the following profile of properties:

	- Thickness	:	15 mm
	- Surface gloss 1st side	:	115
	(Measurement angle 20°)		
20	2nd side	:	112
	- Light transmission	:	0%
	- Whiteness	:	141
	- Coloration	:	white, homogeneous
	- Surface defects	:	none
25	(specks, bubbles, orange peel and the like)		
	- Charpy impact strength		
	a_n	:	no fracture
	- Izod notched impact		
30	strength a_k	:	5.4 kJ/m ²
	- Cold shaping	:	good
	- Crystallinity	:	0%

Example 18

A colored sheet is produced analogously to Example 15. 50% by weight of the polyethylene terephthalate from Example 15 are mixed with 30% by weight of recycled material from this polyethylene terephthalate and 20% by weight of the titanium dioxide masterbatch.

The colored PET sheet produced has the following profile of properties:

	-	Thickness	:	6 mm
10	-	Surface gloss 1st side	:	121
		(Measurement angle 20°)		
		2nd side	:	120
	-	Light transmission	:	0%
	-	Whiteness	:	127
15	-	Coloration	:	white, homogeneous
	-	Surface defects	:	none
		(specks, bubbles, orange peel and the like)		
	-	Charpy impact strength		
20		a _n	:	no fracture
	-	Izod notched impact strength a _k	:	5.0 kJ/m ²
	-	Cold shaping	:	good
	-	Crystallinity	:	0%

25 Example 19

A colored sheet is produced analogously to Example 14. The sheet is not white, but is colored green. The 3 mm thick, green colored sheet comprises as the main constituent the polyethylene terephthalate from Example 14 and 7% by weight of Pigment Green 17.

Pigment Green 17 is a chromium oxide (Cr₂O₃) from BASF (®Sicopalgrün 9996).

Like the titanium dioxide, the chromium oxide is added in

the form of a masterbatch. The masterbatch is composed of 35% by weight of chromium oxide ([®]Sicopalgrün 9996) and 65% by weight of the polyethylene terephthalate from Example 14.

5 Prior to extrusion, 80% by weight of the polyethylene terephthalate from Example 14 are mixed with 20% by weight of chromium oxide masterbatch and the mixture is dried at 170°C for 5 hours.

10 Then a 3 mm thick, green colored sheet is prepared as described in Example 14, which has the following properties:

	-	Thickness	:	3 mm
	-	Surface gloss 1st side	:	128
		(Measurement angle 20°)		
15		2nd side	:	126
	-	Light transmission	:	0.2%
	-	Coloration	:	green, homogeneous
	-	Surface defects	:	none
		(specks, bubbles,		
20		orange peel and the like)		
	-	Charpy impact strength		
		a _n	:	no fracture
	-	Izod notched impact		
		strength a _k	:	4.6 kJ/m ²
25	-	Cold shaping	:	good
	-	Crystallinity	:	0%

Example 20

A colored sheet is produced analogously to Example 15. The sheet contains 3% by weight of titanium dioxide and 30 3.5% by weight of chromium oxide.

The titanium dioxide masterbatch is composed of 30% by weight of the titanium dioxide described under Example 14 and of 70% by weight of the polyethylene terephthalate from Example 15.

The chromium oxide masterbatch is composed of 35% by weight of the chromium oxide described under Example 19 (Sicopalgrün 9996) and of 65% by weight of the polyethylene terephthalate from Example 15.

- 5 Prior to extrusion, 80% by weight of the polyethylene terephthalate from Example 15 are mixed with 10% by weight of titanium dioxide masterbatch and 10% of chromium oxide masterbatch and the mixture is dried at 170°C for 5 hours.
- 10 Then a 6 mm thick sheet is prepared as described in Example 15, which has the following profile of properties:

	-	Thickness	:	6 mm
	-	Surface gloss 1st side	:	126
15		(Measurement angle 20°)		
		2nd side	:	124
	-	Light transmission	:	0%
	-	Coloration	:	opaque light green, homogeneous
20	-	Surface defects	:	none
		(specks, bubbles, orange peel and the like)		
	-	Charpy impact strength		
		a_n	:	no fracture
25	-	Izod notched impact		
		strength a_k	:	5.3 kJ/m ²
	-	Cold shaping	:	good
	-	Crystallinity	:	0%

Example 21

- 30 A 3 mm thick, colored, amorphous sheet which comprises, as the main constituent, the polyethylene terephthalate and the titanium dioxide from Example 14 and 1.0% by weight of the UV stabilizer 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyl)oxyphenol (®Tinuvin 1577 from
- 35 Ciba-Geigy) is produced analogously to Example 14.

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

1.0% by weight of the UV stabilizer is incorporated into the polyethylene terephthalate directly by the producer
5 of the raw materials.

The drying, extrusion and process parameters are chosen as in Example 14.

The sheet produced, which is colored white, shows the following properties:

10	-	Thickness	:	3 mm
	-	Surface gloss 1st side	:	130
		(Measurement angle 20°)		
		2nd side	:	129
	-	Light transmission	:	0%
15	-	Whiteness	:	114
	-	Coloration	:	white, homogeneous
	-	Surface defects	:	none
		(specks, bubbles, orange peel and the like)		
20	-	Charpy impact strength		
		a _n	:	no fracture
	-	Izod notched impact strength a _x	:	4.8 kJ/m ²
	-	Cold shaping	:	good
25	-	Crystallinity	:	0%

After weathering for in each case 1000 hours per side with the Atlas Ci 65 Weather Ometer, the PET sheet has the following properties:

	-	Thickness	:	3 mm
30	-	Surface gloss 1st side	:	126
		(Measurement angle 20°)		
		2nd side	:	125
	-	Light transmission	:	0%
	-	Whiteness	:	110
35	-	Coloration	:	white, homogeneous

- Surface defects : none
(cracks, embrittlement)
- Charpy impact strength
a_n : no fracture
- 5 - Izod notched impact
strength a_k : 4.6 kJ/m²
- Cold shaping : good
- Crystallinity : 0%

Example 22

- 10 A 3 mm thick, colored, amorphous sheet is produced analogously to Example 21. The UV stabilizer 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-(hexyl)-oxyphenol (®Tinuvin 1577) is metered in in the form of a masterbatch. The masterbatch is composed of 5% by weight
- 15 of ®Tinuvin 1577 as the active compound component and 95% by weight of the polyethylene terephthalate from Example 14.

- Before the extrusion, 60% by weight of the polyethylene terephthalate and 20% by weight of the titanium dioxide
- 20 masterbatch from Example 14 are dried with 20% by weight of the masterbatch at 170°C for 5 hours. The extrusion and sheet production are carried out analogously to Example 14.

- The white colored sheet produced shows the following
- 25 properties:

- Thickness : 3 mm
- Surface gloss 1st side : 129
(Measurement angle 20°)
- 2nd side : 128
- 30 - Light transmission : 0%
- Whiteness : 112
- Coloration : white, homogeneous
- Surface defects : none
(specks, bubbles,

orange peel and the like)

- Charpy impact strength
 - a_n : no fracture
- Izod notched impact
- 5 strength a_k : 4.6 kJ/m²
- Cold shaping : good
- Crystallinity : 0%

After weathering for in each case 1000 hours per side
with the Atlas Ci 65 Weather Ometer, the PET sheet has
10 the following properties:

- Thickness : 3 mm
- Surface gloss 1st side : 126
(Measurement angle 20°)
- 2nd side : 124
- 15 - Light transmission : 0%
- Whiteness : 109
- Coloration : white, homogeneous
- Surface defects : none
(cracks, embrittlement)
- 20 - Charpy impact strength
 - a_n : no fracture
- Izod notched impact
- strength a_k : 4.3 kJ/m²
- Cold shaping : good
- 25 - Crystallinity : 0%



Patent Claims

**THIS SHEET HAS BEEN
REPLACED**

1. A colored, amorphous sheet having a thickness in the range from 1 to 20 mm, which comprises, as the main constituent, a crystallizable thermoplastic and at least one colorant selected from an organic and inorganic pigment.
5
2. A sheet as claimed in claim 1, wherein the concentration of the pigment is in the range from 0.5 to 30% by weight, based on the weight of the crystallizable thermoplastic.
10
3. A sheet as claimed in claim 1 or 2, wherein the sheet additionally comprises a soluble dye.
4. A sheet as claimed in claim 3, wherein the concentration of the soluble dye is in the range from 0.001 to 20% by weight, based on the weight of the crystallizable thermoplastic.
15
5. A sheet as claimed in claim 3 or 4, wherein the soluble dye is a fat- and aromatics-soluble azo or anthraquinone dye.
- 20 6. A sheet as claimed in one of the preceding claims, wherein the surface gloss, measured in accordance with DIN 67530 (measurement angle 20°) is greater than 90.
- 25 7. A sheet as claimed in at least one of the preceding claims, wherein the light transmission, measured in accordance with ASTM D 1003, is less than 5%.
- 30 8. A sheet as claimed in one of the preceding claims, wherein the crystallizable thermoplastic employed has a standard viscosity SV (DCA), measured in dichloroacetic acid in accordance with DIN 53728, which is in the range from 800 to 6000.

This Sheet Has Been Replaced





* C L M S *

THIS SHEET HAS BEEN
REPLACED

- 5 9. A sheet as claimed in claim 8, wherein the crystallizable thermoplastic employed has a standard viscosity SV (DCA), measured in dichloroacetic acid in accordance with DIN 53728, which is in the range from 950 to 5000.
- 10 10. A sheet as claimed in one of the preceding claims, which has a degree of crystallinity of less than 5%.
- 10 11. A sheet as claimed in one of the preceding claims, wherein the crystallizable thermoplastic is chosen from polyethylene terephthalate (PET), polybutylene terephthalate (PBT), a cycloolefin polymer and a cycloolefin copolymer.
- 15 12. A sheet as claimed in claim 11, wherein polyethylene terephthalate is used as the crystallizable thermoplastic.
13. A sheet as claimed in claim 12, wherein the polyethylene terephthalate comprises polyethylene terephthalate recycled material.
- 20 14. A sheet as claimed in claim 12 or 13, wherein no fracture occurs during measurement of the Charpy impact strength a_k , measured in accordance with ISO 179/1D.
- 25 15. A sheet as claimed in one of claims 12 to 14, 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.
- 30 16. A sheet as claimed in one of claims 12 to 15, wherein the polyethylene terephthalate has a crystallite melting point, measured by DSC at a heating-up rate of 10°C/minute, in the range from 220° to 280°C.

This Sheet Has Been Replaced





* C L M S *

- 52 -

THIS SHEET HAS BEEN
REPLACED

17. A sheet as claimed in one of claims 12 to 16,
wherein the polyethylene terephthalate has a
crystallization temperature, measured by DSC with a
heating-up rate of 10°/minute, in the range from 75°
to 280°C.
18. A sheet as claimed in one of claims 12 to 17,
wherein the polyethylene terephthalate employed has
a crystallinity in the range from 5 to 65%.
19. A sheet as claimed in one of the preceding claims,
which additionally comprises a UV stabilizer.
20. A sheet as claimed in claim 19, wherein the concen-
tration of the UV stabilizer is in the range from
0.01 to 5% by weight, based on the weight of the
crystallizable thermoplastic.
21. A sheet as claimed in claim 19 or 20, wherein at
least one UV stabilizer chosen from 2-hydroxybenzo-
triazoles and triazines is used.
22. A sheet as claimed in claim 21, wherein at least one
UV stabilizer chosen from 2-(4,6-diphenyl-1,3,5-
triazin-2-yl)-5-(hexyl)oxy-phenol and 2,2'-
methylene-bis(6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-
tetramethylbutyl)-phenol is used.
23. A process for the production of an amorphous,
colored sheet as claimed in one of the preceding
claims, which comprises the following steps: melting
of the crystallizable thermoplastic together with
the colorant in an extruder, shaping of the melt
through a die and subsequent sizing, polishing and
cooling with at least two rolls in the polishing
stack, before the sheet is cut to size, the first
roll of the polishing stack having a temperature in
the range from 50°C to 80°C.

This Sheet Has Been Replaced





THIS SHEET HAS BEEN
REPLACED

- 53 -

24. The process as claimed in claim 23, wherein the crystallizable thermoplastic is dried before being melted.
- 5 25. The process as claimed in claim 23 or 24, wherein the UV stabilizer is melted in the extruder together with the colorant and the thermoplastic.
- 10 26. The process as claimed in one of claims 23 to 25, wherein the addition of the colorant and/or of the UV stabilizer is carried out via masterbatch technology.
27. The process as claimed in one of claims 23 to 26, wherein PET is used as the crystallizable thermoplastic.
- 15 28. The process as claimed in claim 27, wherein the PET is dried at 160 to 180°C for 4 to 6 hours before being melted.
29. The process as claimed in claim 27 or 28, wherein the temperature of the PET melt is in the range from 250 to 320°C.
- 20 30. The use of a colored, amorphous sheet as claimed in one of claims 1 to 22 for interior applications and in exhibition construction.
31. The use outdoors of the sheets treated with a UV stabilizer as claimed in one of claims 19 to 22.

This Sheet Has Been Replaced



**Abstract:**

Amorphous, colored sheet of a crystallizable thermoplastic

The invention relates to an amorphous, colored sheet having a thickness in the range from 1 to 20 mm, which comprises, as the main constituent, a crystallizable thermoplastic and at least one organic and/or inorganic colorant, to a process for its production and to its use. The sheet according to the invention can moreover comprise a UV stabilizer.