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(54) **Title:** PROCESS FOR PRODUCING A NON-TRANSPARENT MICROVOIDED SELF-SUPPORTING FILM

(57) **Abstract:** A process for producing a non-transparent microvoided self- supporting film comprising the steps of: i) mixing at least one linear polyester having together monomer units consisting essentially of terephthalate, isophthalate and aliphatic dimethylene with the molar ratio of isophthalate monomer units to terephthalate monomer units being at least 0.02 to provide a linear polyester matrix; at least one amorphous high polymer with a higher glass transition temperature than the glass transition temperature of said linear polyester matrix and/or at least one crystalline high polymer having a higher melting point than the glass transition temperature of said linear polyester matrix; and optionally at least one ingredient from the group of ingredients consisting of inorganic opacifying pigments, whitening agents, UV-absorbers, light stabilizers, antioxidants, flame retardants and colorants in a kneader or an extruder; ii) forming the mixture produced in step i) in a thick film followed by quenching; iii) longitudinally stretching the thick film at a stretching force of >4 N/mm^2 to at least twice the initial length; and iv) transversly stretching the longitudinally stretched film from step (iii) to at least twice the initial width; the use of the non-transparent microvoided axially stretched film produced according to the above-described process as a synthetic paper; and the use of the non-transparent microvoided axially stretched film produced according to the above-described process image recording elements.

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PROCESS FOR PRODUCING A NON-TRANSPARENT MICROVOIDED SELF-SUPPORTING FILM

FIELD OF THE INVENTION

The present invention concerns a process for producing non-transparent microvoided self-supporting films.

BACKGROUND OF THE INVENTION

US 3,755,499 discloses a synthetic sheet for writing purposes which consists essentially of a linear polyester selected from the group consisting of polyethylene terephthalate, polyethylene isophthalate, and copolymers of ethylene terephthalate and ethylene isophthalate, and a high polymer having a higher glass transition point than that of said linear polyester at a mixing ration of from 7 to 35% by weight of the latter with respect to the polymer mixture, which high polymer is selected from the group consisting of a polymethylmethacrylate, a copolymer of acrylonitrile an styrene, a copolymer of acrylonitrile, butadiene and styrene, said synthetic sheet having a very finely coarsened surface due to said high polymer which is uniformly dispersed in said linear polyester to constitute the nuclei for the irregular surface thereof. Both simultaneous and sequential stretching of these mixed polymer materials are disclosed usually at 85 to 95°C with stretching ratios from 2 to 3.5 times the original length, the sheet being adjusted for writability and opacity in conformity with its eventual use. The object of the invention of US 3,755,499 is stated to be the provision of a synthetic sheet for writing and similar other purposes having improved surface condition, opacity, and other requisite properties. US 3,755,499 further discloses that the thermoplastic resin to be mixed may or may not have compatibility with the linear polyester, provided that it can be substantially uniformly mixed with and dispersed in the linear polyester at the time of forming, that the formed film, regardless of whether it is transparent or not, may produce a uniform mat surface upon being stretched and the film thus obtained is heat-shrinkable, acceptable in its writing properties, and possesses adequate opacity and that in order to further improve stability in the film size at a high temperature, it may be heat-treated at a temperature above the stretching temperature of the linear polyester and below the melting point of both mixing thermoplastic resin and the linear polyester. EXAMPLE 2 exemplifies the mixing of a copolymer of acrylonitrile and styrene having a glass transition temperature of 100 to 105°C with polyethylene terephthalate in concentrations of 7 and 35 % by weight and the forming of 150μm thick film samples by melt-extrusion through a T-die. These film sheets were then stretched simultaneously by a biaxial stretching machine at a stretch ratio twice as large as the original length of the film in the longitudinal as well as transverse directions thereof at 85°C and also stretched simultaneously biaxially three times longitudinally and three times transversely at 85°C. The resulting films were reported to have the following properties:

acrylonitrile-styrene copolymer (% by wt.)	7	7	35	35
Polyethylene terephthalate (% by wt.)	93	93	65	65
stretch ratio (L x W) times	2 x 2	3 x 3	2 x 2	3 X 3
thickness after stretching (μm)	48	26	45	25
rupture strength (kg/cm)	880	1210	650	730
elongation at Breaking Point(%)	110	45	55	23
light Transmission Factor (%)	80.8	84.2	72.3	77.6
haze value(%)	92.5	90.6	94.3	96.6
writability [pencil hardness]	≤ 4H	≤ 3H	≤ 4H	≤ 3H

US 3,755,499 fails to disclose the influence of addition of an inorganic opacifying pigment or of the image-wise heating on the opaque microvoided films disclosed therein.

EP-A 0 606 663 discloses a method of manufacturing an opaque polyester copolymer support for reflective photographic materials comprising an inorganic inert pigment, said polyester comprising units of ethylene terephthalate as the main repeating units, said method comprising the following steps in the order given: either supplying terephthalic acid and ethylene glycol to bis(β-hydroxy-ethyl)terephthalate or its oligomer so as to carry out the esterification step, or supplying dimethylterephthalate and ethylene glycol so as to carry out transesterification, polycondensing under conditions of increasingly reduced vacuum, either granulating the obtained polymer, followed by drying the granules and feeding them to an extruder, or directly feeding the obtained copolymer in melt-form to an extruder, extruding the polymer in the form of a sheet,

quenching and solidifying the resulting sheet on a quenching member, biaxially stretching the sheet, annealing the biaxially stretched film, characterised in that terephthalic acid or dimethyl-terephthalate respectively is replaced by another aromatic dicarboxylic acid or by the dimethylester of another aromatic dicarboxylic acid respectively, and/or ethylene glycol is replaced by another diol , said replacement(s) amounting to maximum 20 mol percent with respect to ethylene glycol and terephthalic acid or dimethylterephthalate respectively. EP-A 0 606 663 discloses as a preferred embodiment that the polyester copolymer is the polycondensation reaction product of ethylene glycol and either terephthalic acid, replaced for an amount up to a maximum of 20 mol% by isophthalic acid or dimethylterephthalate, replaced for an amount up to a maximum of 20 mol% by dimethyl isophthalate.

EP-A 0 654 503 discloses a shaped article prepared from a polymer blend of 50 to 97 wt.% of a linear polyester and 3 to 50 wt.% of a polymer containing styrene, wherein the percentages relate to the sum of the polyester and the polymer containing styrene. EP-A 0 654 503 also discloses that the polyester contains at least 80 wt.% polyethylene terephthalate and may contain up to 20 wt.% polyethylene isophthalate and exemplifies in EXAMPLE 7 a mixture of 85% by weight of polyester and 15% by weight of ABS 2, the polyester consisting of a mixture of 94% by weight of polyethylene terephthalate and 6% by weight of polyethylene isophthalate.

EP-A 1 291 155 discloses an embossable, coated polyethylene-terephthalate (PET) film comprising: a uniaxially oriented PET base film; and a coating applied to the PET base film, wherein the coating and the PET base film have as a composite been transversely stretched, said coating resin impregnating a surface portion of the PET base film upon said transverse stretching, thereby rendering the surface portion of the film susceptible to embossing. EP-A 1 291 155 also discloses that the PET base film is coextruded and forms at least two layers and a co-extrded co-polyester layer is described for EXAMPLES 4 and 5 consiting of an isophthalic acid co-terephthalic acid random co-polyester co-polymer with a mole ratio of about 18% isophthalic acid and 82% terephthalic acid.

The prior art non-transparent microvoided axially stretched film has suffered from insufficient opacity together with a lack of dimensional stability or sufficient dimensional stability and insufficient opacity. Moreover, for particular applications the whiteness of the non-transparent microvoided axially stretched film was insufficient.

PRIOR ART:

Heretofore, the following prior art documents are known to the applicant:

US 3,755,499 published on August 28, 1973
EP-A 0 606 663 published on July 20, 1994
EP-A 0 654 503 published on May 24, 1995
EP-A 1 291 155 published on March 12, 2003
WO 94/04961A published on March 3, 1994
US 5,156,709 published on October 20, 1992

ASPECTS OF THE INVENTION:

It is therefore an aspect of the present invention to provide an improved non-transparent microvoided axially stretched film.

It is therefore a further aspect of the present invention to provide a process for producing an improved non-transparent microvoided axially stretched film.

It is therefore also an aspect of the present invention to provide a process for obtaining a transparent pattern in a non-transparent microvoided axially stretched film.

Further aspects and advantages of the invention will become apparent from the description hereinafter.

SUMMARY OF THE INVENTION

It has been found that a white, microvoided, non-transparent, self-supporting and biaxially stretched film with a continuous phase linear polyester matrix consisting essentially of monomer units of terephthalate, isophthalate and aliphatic dimethylene and having uniformly dispersed therein at least one amorphous high polymer with a higher glass transition temperature than the glass transition temperature of said linear polyester matrix and/or at least one crystalline high polymer having a higher melting point than the glass transition temperature of said linear polyester matrix can be surprisingly produced with higher optical densities, i.e. higher degrees of opacity, by using a linear polymer matrix in which the molar ratio of isophthalate monomer units to terephthalate monomer units in the linear polyester matrix is at least 0.02 and longitudinally stretching the extrudate at a stretching force > 4 N/mm^2.

Aspects of the present invention are realized by a process for producing a non-transparent microvoided self-supporting film comprising the steps of: i) mixing at least one linear polyester having together monomer units consisting essentially of terephthalate, isophthalate and aliphatic dimethylene with the molar ratio of isophthalate monomer units to terephthalate monomer units being at least 0.02 to provide a linear polyester matrix; at least one amorphous high polymer with a higher glass transition temperature than the glass transition temperature of said linear polyester matrix and/or at least one crystalline high polymer having a higher melting point than the glass transition temperature of said linear polyester matrix; and optionally at least one ingredient from the group of ingredients consisting of inorganic opacifying pigments, whitening agents, UV-absorbers, light stabilizers, antioxidants, flame retardants and colorants in a kneader or an extruder; ii) forming the mixture produced in step i) in a thick film followed by quenching; iii) longitudinally stretching the thick film at a stretching force of > 4 N/mm^2 to at least twice the initial length; and iv) transversly stretching the longitudinally stretched film from step (iii) to at least twice the initial width.

Aspects of the present invention have also been realized by a process for obtaining a transparent pattern comprising the step of: image-wise application of heat optionally supplemented by the application of pressure to a non-transparent microvoided biaxially stretched self-supporting film produced by a process comprising the steps of: i) mixing at least one linear polyester having together monomer units consisting essentially of terephthalate, isophthalate and aliphatic dimethylene with the molar ratio of isophthalate monomer units to terephthalate monomer units being at least 0.02 to provide a linear polyester matrix; at least one amorphous high polymer with a higher glass transition temperature than the glass transition temperature of said linear polyester matrix and/or at least one crystalline high polymer having a higher melting point than the glass transition temperature of said linear polyester matrix; and optionally at least one ingredient from the group of ingredients consisting of inorganic opacifying pigments, whitening agents, UV-absorbers, light stabilizers, antioxidants, flame retardants and colorants in a kneader or an extruder; ii) forming the mixture produced in step i) in a thick film followed by quenching; iii) longitudinally stretching the thick film at a stretching force of > 4 N/mm^2 to at least twice the initial length;

and iv) transversly stretching the longitudinally stretched film from step (iii) to at least twice the initial width.

Aspects of the present invention are also realized by the use of the non-transparent microvoided self-supporting film produced by the above-described process as a synthetic paper.

Aspects of the present invention are also realized by the use of the non-transparent microvoided self-supporting film produced by the above-described process in image recording elements.

Preferred embodiments of the present invention are disclosed in the detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

The term voids or microvoids, as used in disclosing the present invention, means microcells, minute closed cells, cavities, bubbles or pores or cellulation, which, for example, can be formed in an oriented polymeric film during stretching as the result of a void-initiating particle initiated by particles that are immiscible with the polyester matrix. The voids or microvoids can be unfilled or filled with air or a vapour of some sort. Even if initially unfilled the voids or microvoids may over time become filled with air or a vapour of some sort.

The term "opaque", means a percentage opacity to visible light of greater than 90% as determined according to ASTM D589-97 or according to opacity test T425m-60 as published by TAPPI, 360 Lexington Avenue, New York, USA.

The term film, as used in disclosing the present invention, is an extruded sheet of a particular composition or a sheet consisting of a multiplicity of films with the same or different compositions produced by co-extrusion of liquids with the same or different compositions in contact with one another. The terms film and foil are used interchangeably in the present disclosure.

The term linear polyester, as used in disclosing the present invention, means a polyester comprising hydrocarbon dimethylene and dicarboxylate monomer units.

The term foam, as used in disclosing the present invention, means a substance that is formed by trapping many gas bubbles in a liquid or solid.

The term dimethylene aliphatic monomer unit in a linear polyester, as used in disclosing the present invention, means a monomer unit derived from a dimethylene aliphatic diol or an ether thereof, wherein the term aliphatic includes alicylic.

The term density, as used in disclosing the present invention, means the weight of a 100 mm x 100 mm piece of film with a thickness measured in contact with an inductive probe with ball tip 3 mm in diameter divided by its volume. This value assumes that the surfaces of the piece of film are flat and parallel to one another. This value corresponds to the apparent density values reported in EP-A 0 496 323 and WO 2005/105903A.

The term inorganic opacifying pigment, as used in disclosing the present application, means a pigment capable of opacifying (i.e. rendering more opaque) which includes substantially white inorganic pigments having a refractive index of at least 1.4 and pigments, which as a dispersion in a polymer are capable upon stetching of causing opacity due to microvoiding.

The term whitening agent, as used in disclosing the present invention, means a white/colourless organic compound which exhibits a blue luminescence under the influence of ambient UV-light.

The term “support”, as used in disclosing the present invention, means a “self-supporting material” so as to distinguish it from a “layer” which may be coated as a solution or dispersion, evaporated or sputtered on a support, but which itself is not self-supporting. It also includes an optional conductive surface layer and any treatment necessary for, or layer applied to aid, adhesion.

The term “chain-polymerized block”, as used in disclosing the present invention, excludes condensation polymers and means a chain-polymerized polymer chain which may a block in a block copolymer or graft copolymer or may just be a chain-polymerized polymer chain.

The term overprintable, as used in disclosing the present invention, means capable of being overprinted by conventional impact and/or non-impact printing processes.

The term conventional printing processes, as used in disclosing the present invention, includes but is not restricted to ink-jet printing, intaglio printing, screen printing, flexographic printing, offset printing, stamp printing, gravure printing, dye transfer printing, thermal sublimation printing and thermal and laser-induced processes.

The term pattern, as used in disclosing the present invention, means a non-continuous layer which can be in any form of lines, squares, circles or any random configuration.

The term layer, as used in disclosing the present invention, means a (continuous) coating covering the whole area of the entity referred to e.g. a support.

The term "non-transparent film", as used in disclosing the present invention, means a film capable of providing sufficient contrast to a transparent image to make the image clearly perceptible. A non-transparent film can be an "opaque film", but need not necessarily be completely opaque in that there is no residual translucence i.e. no light penetration through the film. Optical density in transmission as measured with a MacBeth TR924 densitometer through a visible filter can provide a measure of the non-transparency of a film. ISO 2471 concerns the opacity of paper backing and is applicable when that property of a paper is involved that governs the extent to which one sheet visually obscures printed matter on underlying sheets of similar paper and defines opacity as "the ratio, expressed as a percentage, of the luminous reflectance factor of a single sheet of the paper with a black backing to the intrinsic luminous reflectance factor of the same sample with a white reflecting backing. 80g/m^2 copy paper, for example, is white, non-transparent and has an optical density of 0.5 as measured with a MacBeth TR924 densitometer through a yellow filter according to ISO 5-2 and metallized films typically have an optical density ranging from 2.0 to 3.0.

The term transparent, as used in disclosing the present invention, means having the property of transmitting at least 50% of the incident visible light without diffusing it and preferably at least 70% of the incident visible light without diffusing it.

The term flexible, as used in disclosing the present invention, means capable of following the curvature of a curved object such as a drum e.g. without being damaged.

The term "colorant", as used in disclosing the present invention, means dyes and pigments.

The term "dye", as used in disclosing the present invention, means a colorant having a solubility of 10 mg/L or more in the medium in which it is applied and under the ambient conditions pertaining.

The term "pigment" is defined in DIN 55943, herein incorporated by reference, as an inorganic or organic, chromatic or achromatic colouring agent that is practically insoluble in the dispersion medium under the pertaining ambient conditions, hence having a solubility of less than 10 mg/L therein.

Process for producing a non-transparent microvoided film

Aspects of the present invention are realized by a process for producing a non-transparent microvoided self-supporting film comprising the steps of: i) mixing at least one linear polyester having together monomer units consisting essentially of terephthalate, isophthalate and aliphatic dimethylene with the molar ratio of isophthalate monomer units to terephthalate monomer units being at least 0.02 to provide a linear polyester matrix; at least one amorphous high polymer with a higher glass transition temperature than the glass transition temperature of said linear polyester matrix and/or at least one crystalline high polymer having a higher melting point than the glass transition temperature of said linear polyester matrix; and optionally at least one ingredient from the group of ingredients consisting of inorganic opacifying pigments, whitening agents, UV-absorbers, light stabilizers, antioxidants, flame retardants and colorants in a kneader or an extruder; ii) forming the mixture produced in step i) in a thick film followed by quenching; iii) longitudinally stretching the thick film at a stretching force of > 4 N/mm^2 to at least twice the initial length; and iv) transversly stretching the longitudinally stretched film from step (iii) to at least twice the initial width.

According to a first embodiment of the process, according to the present invention, the concentration of the uniformly dispersed at least one amorphous high polymer and/or the at least one crystalline high polymer in the polymer film is 5 to 35% by weight, preferably 9 to 25% by weight.

According to a second embodiment of the process, according to the present invention, the weight ratio of the linear polyester to the at least one amorphous polymer and/or the at least one crystalline high polymer dispersed therein is in the range of 1.85:1 to 19.0:1, with a range of 2.7:1 to 13:1 being preferred, 3.0:1 to 10:1 being particularly preferred.

According to a third embodiment of the process, according to the present invention, the amorphous high polymer particles or crystalline high polymer particles dispersed in the continuous phase have a diameter of less than 10 μm, with particles having a number average particle size of 0.5 to 5 μm being preferred and particles with an average particle size of 1 to 2 μm being particularly preferred. The smaller the particle size, the higher the opacity.

According to a fourth embodiment of the process, according to the present invention, the film is exclusive of a polyether such as polyethylene oxide. Such polyethers decrease the density and may decompose producing additional non-uniformly distributed voids.

According to a fifth embodiment of the process, according to the present invention, the film is provided with at least one of alphanumeric characters, an embossed pattern, an optionally embossed hologram and a continuous, half-tone or digital image.

According to a sixth embodiment of the process, according to the present invention, the film is provided on at least one side with a transparent overprintable layer i.e. suitable for impact or non-impact printing. This transparent overprintable layer can be provided over at least one of alphanumeric characters, an embossed pattern, an optionally embossed hologram and a continuous, half-tone or digital image on a surface of the non-transparent microvoided axially stretched self-supporting film.

According to a seventh embodiment of the process, according to the present invention, the film is provided on at least one side with a transparentizable porous overprintable layer i.e. suitable for impact or non-impact printing e.g. ink-jet printing. Transparentizable porous layers transparentized by the application of a liquid with an appropriate refractive index, which can also be applied image-wise, are as disclosed in EP-A 1 362 710 and EP-A 1 398 175. This transparentizable overprintable layer can be provided over at least one of alphanumeric characters, an embossed pattern, an optionally embossed hologram and a continuous, half-tone or digital image on a surface of the non-transparent microvoided axially stretched self-supporting film with a transparent pattern.

Transparentization of part of the transparentizable porous receiving layer can itself produce an image or the non-transparentized area of the opaque porous receiving layer can itself represent an image. The transparent pattern can, for example, be part of a banknote, a share certificate, a ticket, a credit card, an identity document or a label for luggage and packages.

According to an eighth embodiment of the process, according to the present invention, the polymeric film has a thickness in the range from about 10 µm to about 500 µm, with from about 50 µm to about 300 µm being preferred.

According to a ninth embodiment of the process, according to the present invention, the polymeric film is provided with a subbing layer. This subbing layer makes it possible to improve wettability and adhesive property of the polymeric film and preferably comprises a polyester resin, a polyurethane resin, a poly(ester urethane) resin or an acrylic resin.

The quenched extruded thick film has a thickness of approximately 10 to approximately 6000 μm, with a thickness of approximately 100 μm to 5000 μm being preferred.

The biaxially stretched polymeric film, according to the present invention, is realized by first stretching in one direction (e.g. in the machine direction = MD) and then stretching in a second direction [e.g. perpendicularly to the machine direction = TD (transversal direction)]. This orients the polymer chains thereby increasing the density and crystallinity. Longitudinal orientation in the direction of extrusion can be carried out with the aid of two rolls running at different speeds corresponding to the desired stretching ratio by setting the surface speed V2 of the rotating rollers relative to the linear extrusion speed V1 so that the stretch ratio is V2/V1. The longitudinal stretching ratio should be sufficient to create voids.

The longitudinal stretching operations known in the art to produce axially and biaxially oriented polyester film may be used. For instance, the combined film layers are passed between a pair of infra red heaters which heats the layers to a temperature above the glass transition temperature of the polyester (about 80°C for polyethylene terephthalate and about 60°C for polyethylene isphthalate) in the region where the stretching occurs. The temperature above should be close to the glass transition temperature of the continuous phase polymer in order to improve opacity. In the case of polyethylene terephthalate, the longitudinal stretching is generally carried out at from about 80 to about 140°C. During longitudinal stretching opacity is realized as a result of the voids produced in the film extending longitudinally from each particle of dispersed polymer.

Transverse stretching is carried out at an angle substantially 90° to the direction of longitudinal stretching, with the angle being typically between about 70° and 90°. For transverse orientation use is generally made of an appropriate tenter frame, clamping both edges of the film and then drawing toward the two sides by heating the combined layers with the primer layer(s) thereon by, for example, passing through hot air heaters which heat the film above the glass transition temperature. In the case of polyethylene terephthalate and its copolymers, the transverse stretching is carried out at from about 80 to about 170°C, with from about 85 to about 150° being preferred. The transverse stretching of the film causes the voids to extend transversely.

The production of the biaxially stretched polymeric film, according to the present invention, is produced by longitudinally stretching the thick film to at least twice the initial length at a stretching tension > 4.0 N/mm^2 and after intermediate quenching the longitudinal stretching is followed by transverse stretching at an angle substantially 90° to the first stretching process to at least thrice the initial width at a stretching tension of preferably > 4.0 N/mm^2 preferably at a temperature at or below 30°C above the glass transition temperature of the continuous phase and particularly preferably at or below 20°C above the glass transition temperature of the continuous phase.

According to a tenth embodiment of the process, according to the present invention, the longitudinal stretching force is > 5 N/mm^2, with a longitudinal stretching force > 6.0 N/mm^2 being preferred and a longitudinal stretching force > 7.0 N/mm^2 being particularly preferred.

According to an eleventh embodiment of the process, according to the present invention, the transverse stretching is performed with a force > 4.0 N/mm^2, with a transversal stretching force > 5 N/mm^2 being preferred and a transversal stretching force > 6.0 N/mm^2 being particularly preferred and a transversal stretching force > 7.0 N/mm^2 being especially preferred.

According to a twelfth embodiment of the process, according to the present invention, the longitudinal stretching temperature is not more than 40°C above the glass transition temperature of the linear polyester matrix, with a longitudinal stretching temperature of not more that 30°C above the glass transition temperature of the linear polyester matrix being preferred and a longitudinal stretching temperature of not more that 20°C above the glass transition temperature of the linear polyester matrix being especially preferred.

According to a thirteenth embodiment of the process, according to the present invention, the transverse stretching temperature is not more than 40°C above the glass transition temperature of the linear polyester matrix, with a transverse stretching temperature of not more that 30°C above the glass transition temperature of the linear polyester matrix being preferred and a transverse stretching temperature of not more that 20°C above the glass transition temperature of the linear polyester matrix being especially preferred.

Longitudinal and transverse stretching may be performed simultaneously e.g. with an apparatus produced by Brückner.

The stretching ratio for longitudinal stretching is preferably between about 2 and about 6, with between about 2.5 and about 5 being preferred and between 3 and 4 being particularly preferred. The higher the stretching ratio, the higher the opacity.

According to a fourteenth embodiment of the process, according to the present invention, the longitudinal stretching ratio is at least 2.5, with at least 3.0 being preferred.

Transverse stretching ratio is preferably in the range of from about 2 to about 6, with a range of 2.5 to about 5 being preferred and a range of from about 3 to about 4 being particularly preferred. The opacity increases at higher stretching rates in %/min and also at lower transverse stretching temperatures.

According to a fifteenth embodiment of the process, according to the present invention, the transversal stretching ratio is at least 2.5, with at least 3.0 being preferred.

The production process may further comprise, as a further step, a thermal fixation step to counter shrinkage. For example the biaxially stretched film is passed through a second set of hot air heaters which blow hot air at a temperature of between 140 and 240°C onto the film layers to heat-set or thermofix the film layers. The heat-set temperature must be sufficient to obtain crystallization of the polyester but care must be taken not to overheat the layers since the voids can collapse. On the other hand increasing the heat-set temperature improves the dimensional stability of the film. An appropriate mix of properties can be obtained by varying the heat-set temperature. The preferred heat-set or thermofixation temperature in the case of polyethylene terephthalate or polyethylene naphthalate is at or above 140°C.

Before or after longitudinal stretching a first subbing layer, called a primer layer, may be applied to the non-voided polyester layer by a coating means such as an air knife coating system. The first subbing layer is for example formed from a (meth)acrylate copolymer, a poly(meth)acrylate, a polyurethane, a sulphonated polyester, a styrene-(meth)acrylate copolymer or a chloride containing copolymer such as vinylidene chloride copolymer in latex form having some hydrophilic functionality through the presence of a copolymerized unsaturated carboxylic acid which is applied as an aqueous dispersion.

According to a sixteenth embodiment of the process, according to the present invention, the film is exclusive of foam.

According to a seventeenth embodiment of the process, according to the present invention, the film is exclusive of foaming agent and/or decomposition products of a foaming agent.

Optical density of the film due to microvoids

The optical density of the film measured in transmission with a visible filter due to microvoids is obtained by measuring the optical density of the film without void-producing ingredients as a function of film thickness to provide comparative values. The optical density of a film measured in transmission with a visible filter due to voids is then obtained by biaxially stretching a composition to which has been added the void-inducing ingredient and subtracting the measured optical density measured in transmission with a visible filter from the optical density measured in transmission with a visible filter for the film composition without void-inducing ingredient for the film thickness expected on the basis of the longitudinal and transverse drawing ratios.

Linear polyester

According to an eighteenth embodiment of the process, according to the present invention, the molar ratio of isophthalate monomer units to terephthalate monomer units is at least 0.04, with a molar ratio of at least 0.05 being preferred, a molar ratio of at least 0.065 being particularly preferred and a molar ratio of at least 0.075 being especially preferred.

According to a nineteenth embodiment of the process, according to the present invention, the molar ratio of isophthalate monomer units to terephthalate monomer units is at least 0.11, with a molar ratio of at least 0.13 being preferred and a molar ratio of at least 0.15 being particularly preferred.

According to a twentieth embodiment of the process, according to the present invention, the molar ratio of isophthalate monomer units to terephthalate monomer units is at least 0.17, with a molar ratio of at least 0.20 being preferred and a molar ratio of at least 0.25 being particularly preferred.

According to a twenty-first embodiment of the process, according to the present invention, the molar ratio of isophthalate monomer units to terephthalate monomer units is 0.50 or less, with a molar ratio of 0.45 or less being preferred and a molar ratio of 0.30 or less being particularly preferred.

According to a twenty-second embodiment of the process, according to the present invention, the number average molecular weight of the linear polyester is 10,000 to 30,000.

Examples of suitable aliphatic dimethylenes include ethylene, propylene, methylpropylene, tetramethylene, pentamethylene, hexamethylene, neopentylene [$-CH_2C(CH_3)_2-CH_2$], 1,4-cyclohexane-dimethylene, 1,3-cyclohexane-dimethylene, 1,3-cyclopentane-dimethylene, norbornane-dimethylene, $-CH_2CH_2(OCH_2CH_2)_n-$, where n is an integer with 1 to 5 being preferred, and mixtures thereof.

According to a twenty-third embodiment of the process, according to the present invention, the aliphatic dimethylene monomer units are selected from the group consisting of ethylene, tetramethylene, neopentylene, norbornane-dimethylene and 1,4-cyclohexane-dimethylene.

According to a twenty-fourth embodiment of the process, according to the present invention, the aliphatic monomer units consist of ethylene units and neopentylene and/or 1,4-cyclohexanedimethylene units and the molar ratio of neopentylene and/or 1,4-cyclohexanedimethylene monomer units to ethylene monomer units is at least 0.02, with a molar ratio of at least 0.04 being preferred and a molar ratio of 0.065 being particularly preferred.

According to a twenty-fifth embodiment of the process, according to the present invention, the linear polyester comprises at least two linear polyester resins. Upon heating, e.g. during mixing in an extruder, the different linear aromatic polyester resins present will undergo metathesis, condensing and decondensing so as to evolve upon sufficiently long heating into a single resin.

Such polyesters are well known in the art and may be produced by well-known techniques, for example, those described in US 2,465,319 and US 2,901,466.

According to a twenty-sixth embodiment of the polymeric film, according to the present invention, the polymeric film further contains an electroconductivity enhancing additive e.g. a metallic salt which ionizes in the melt giving enhanced electroconductivity such as magnesium acetate, manganese salts and cobalt sulphate. Suitable salt concentrations are about 3.5×10^{-4} moles/mole polyester. Enhanced polyester melt viscosity enables improved pinning of the melt on the chilling roller maintained at a temperature of 5 to 25°C (preferably 15 to 30°C) to cool the extrudate thereby enabling higher stretching forces to be realized and hence enhanced void-forming and a higher degree of opacification.

The linear polyester utilized in the present invention should have a glass transition temperature from 40°C to 150°C, preferably from 50 to 120°C and should be orientable.

According to a twenty-seventh embodiment of the process, according to the present invention, the linear polyester has an inherent viscosity determined in a 0.5g/dL solution of 60 wt% phenol and 40 wt% ortho-dichlorobenzene at 25°C of at least 0.45 dl/g with an inherent viscosity of 0.48 to 0.9 dl/g being preferred and an inherent viscosity of 0.5 to 0.8 dl/g being particularly preferred.

Amorphous high polymer

The amorphous high polymer used in the polymeric film, used in the present invention, has a glass transition temperature higher than the glass transition temperature of the continuous phase in which it is dispersed e.g. a linear polyester. Poly(ethylene terephthalate), for example, has a glass transition temperature of ca. 80°C.

The glass transition temperatures and refractive indices for various amorphous high polymers are given in the table below:

	T_g [°C]	Refractive index for sodium line at 589.3 nm [ASTM D642]
polystyrene	100	1.57 - 1.60
poly-α-methyl-styrene	168	1.610
poly-4-methyl-styrene	93	-
poly-α-vinyl-naphthalene	159	1.6818
polyacrylonitrile	85	1.514, 1.5187
polymethacrylonitrile	120	1.520
polymethyl methacrylate	105	1.49, 1.4893
polyacrylamide	165	-
copolymer of acrylonitrile and styrene	112	1.56 - 1.57, 1.57
copolymer of 28.5wt% acrylonitrile and 71.5 wt% styrene	108	1.56 - 1.57, 1.57
ABS	110	1.53 - 1.54

According to a twenty-eighth embodiment of the process, according to the present invention, the uniformly dispersed amorphous high polymer is crosslinked or non-crosslinked.

According to a twenty-ninth embodiment of the process, according to the present invention, the amorphous high polymer comprises at least one chain-polymerized block.

According to a thirtieth embodiment of the process, according to the present invention, the amorphous high polymer comprises at least one chain-polymerized block and the at least one chain-polymerized block is selected from the group consisting of polystyrene, styrene copolymers, SAN-polymers, polyacrylates, acrylate-copolymers, polymethacrylates and methacrylate-copolymers.

According to a thirty-first embodiment of the process, according to the present invention, the amorphous high polymer comprises at least one chain-polymerized styrene copolymer block selected from the group consisting of SAN-polymers, ABS-polymers and SBS-polymers.

According to a thirty-second embodiment of the process, according to the present invention, the amorphous high polymer comprises at least one chain-polymerized SAN-polymer block, wherein the concentration of AN-monomer units in the SAN-polymer is 15 to 35% by weight.

According to a thirty-third embodiment of the process, according to the present invention, the amorphous high polymer is exclusive of a cellulose ester.

According to a thirty-fourth embodiment of the process, according to the present invention, the amorphous high polymer is at least partially crosslinked e.g. at least partially crosslinked poly(methyl methacrylate) or at least partially crosslinked copolymers of acrylonitrile and styrene.

According to a thirty-fifth embodiment of the process, according to the present invention, the film has a linear polyester as continuous phase and dispersed therein is a high polymer having a degree of crosslinking of at least 10%.

According to a thirty-sixth embodiment of the process, according to the present invention, the amorphous high polymer is a SAN polymer, the SAN polymer concentration being preferably at least 5% by weight of the film, with at least 10% by weight of the film being particularly preferred.

The SAN polymer additive of the present composition is a known class of polymer consisting essentially of a random copolymer of a styrenic monomer component, including styrene as well as an alpha-lower alkyl-substituted styrene or mixtures thereof and an acrylonitrilic monomer component including acrylonitrile as well as an alpha-lower alkyl substituted acrylonitrile or mixtures thereof.

By lower-alkyl is meant a straight or branched chain alkyl group of 1 to 4 carbon atoms exemplified by the methyl, ethyl, isopropyl and t-butyl groups. In readily available SAN polymers, the styrene component is generally styrene, alpha-straight chain alkyl substituted styrene, typically alpha-methyl-styrene, or mixtures thereof with styrene being preferred. Similarly in the readily available SAN polymers, the acrylonitrile component is generally acrylonitrile, alpha-methyl-acrylonitrile or mixtures thereof with acrylonitrile being preferred.

In the SAN polymer the styrene component is present in a major weight proportion, i.e. in a weight proportion of greater than 50%, typically about 65% to about 90%, especially about 70% to about 80%, based on the combined weight of the styrene component and the acrylonitrile component. The acrylonitrile component is present in a minor proportion, i.e. in a weight proportion of less than 50%, typically about 10% to about 35% especially about 20% to 30% based on the combined weight of the styrene monomer component and the acrylonitrile monomer component. Styrene-acrylonitrile copolymers are currently commercially available with an acrylonitrile content of 15 to 35% by weight, with 18 to 32% by weight being preferred and 21 to 30% by weight being particularly preferred.

The SAN polymer class is more particularly identified and described in R. E. Gallagher, U.S. Pat. No. 3,988,393, issued Oct. 26, 1976 (especially at Column 9, lines 14-16 and in Claim 8), in "Whittington's Dictionary of Plastics", Technomic Publishing Co., First Edition, 1968, page 231, under the section headed "Styrene-Acrylonitrile Copolymers (SAN)", and R. B. Seymour, "Introduction to Polymer Chemistry", McGraw-Hill, Inc., 1971, page 200, (last two lines) to page 201 (first line). The preparation of a SAN polymer by copolymerization of styrene and acrylonitrile is more particularly described in the "Encyclopedia of Polymer Science and Technology", John Wiley and Sons, Inc., Vol. 1, 1964, pages 425-435.

According to a thirty-seventh embodiment of the process, according to the present invention, the amorphous high polymer is a non-crosslinked SAN polymer having a number average molecular weight in the range of 30,000 to 100,000, preferably in the range of 40,000 to 80,000. Typical SAN-polymers have number averaged molecular weights of 45,000 to 60,000 and polymer dispersities (M_w/M_n) of 1.2 to 2.5.

According to a thirty-eighth embodiment of the process, according to the present invention, the amorphous high polymer is a non-crosslinked SAN polymer having a weight average molecular weight in the range of 50,000 to 200,000, preferably in the range of 75,000 to 150,000. The higher the molecular weight of the SAN polymer, the larger the size of the dispersed SAN polymer particles.

Crystalline high polymer

The crystalline high polymer used in the polymeric film, according to the present invention, has a melting point higher than the glass transition temperature of the continuous phase polymer in which it is dispersed e.g. a linear polyester. Crystalline high polymers with sufficiently high melting points include polyethylene, polypropylene and poly(4-methyl-1-pentene).

According to a thirty-ninth embodiment of the process, according to the present invention, the film has a linear polyester as continuous phase and dispersed therein are crystalline high polymer particles having a number averaged particle size of 0.5 to 5 µm, with 1 to 2 µm being preferred.

The melting points and refractive indices for various polyethylenes and polypropylenes are given in the table below:

	T_m [°C]	Refractive index for sodium line at 589.3 nm [ASTM D642]
polyethylene	95	1.51-1.54
high density polyethylene	141	1.51-1.54
isotactic polypropylene	165	1.49
syndiotactic polypropylene	189	1.49
polypropylene (atactic)		1.4735
Poly(4-methyl-pentene)	235	1.4630

Inorganic opacifying pigment

According to a fortieth embodiment of the process, according to the present invention, the film further further comprises at least one inorganic opacifying pigment selected from the group consisting of silica, zinc oxide, zinc sulphide, lithopone, barium sulphate, calcium carbonate, titanium dioxide, aluminium phosphate and clays. The titanium dioxide may have an anatase or rutile morphology and may be stabilized by alumina oxide and/or silicon dioxide. The aluminium phosphate can be an amorphous hollow pigment e.g. the Biphor™ pigments from BUNGE.

The refractive indices of these pigments is given in the table below:

inorganic opacifying pigment	refractive index for sodium line at 589.3 nm
kaolinite	1.53-1.57
bentonite	1.557
china clay	1.56
silica - silica gel	1.55
silica - cristobalite	1.487, 1.484
silica - quartz	1.544, 1.553
calcium carbonate	1.59, 1.6, 1.58
calcium carbonate - calcite	1.486, 1.64 - 1.66
barium sulphate - baryte	1.637, 1.638, 1.649, 1.64
Lithopone 30% (zinc sulphide/barium sulphate)	1.84
zinc oxide (ultrafine)	1.9
zinc oxide (zincite)	2.008, 2.029
zinc sulphide	2.37
titanium dioxide - anatase	2.554, 2.493, 2.55
titanium dioxide - rutile	2.616, 2.903, 2.76

According to a forty-first embodiment of the process, the film comprises ≤ 5% by weight of inorganic opacifying pigment i.e. the total quantity of inorganic opacifying pigment present regardless of type is ≤ 5% by weight, with ≤ 3% by weight of inorganic opacifying pigment being preferred.

According to a forty-second embodiment of the process, according to the present invention, the film further comprises an inorganic opacifying pigment having a number averaged particle size between 0.1 and 10 µm, with 0.2 to 2 µm being preferred.

Addition of an inorganic opacifying pigment has the advantage of stabilizing the orientation of the polyester, so that the non-transparent microvoided axially stretched self-supporting film can be stabilized at temperatures of 175°C without substantially affecting the opacity of the non-transparent microvoided axially stretched self-supporting film. Without the presence of an inorganic opacifying pigment, such as $BaSO_4$ or TiO_2, thermofixing of the polyester is possible, but only at the expense of some of the opacity of the non-transparent microvoided axially stretched self-supporting film. Moreover, pigments with a refractive index below 2.0 do not of themselves provide substantial opacity due to the small refractive index differences between the pigment and the polymer matrix.

Titanium dioxide particles dispersed in polymer films have been found not to induce microvoiding upon stretching the films.

Whitening agent

According to a forty-third embodiment of the process, according to the present invention, the concentration of whitening agent is ≤ 0.5% by weight, with ≤ 0.1% by weight being preferred, ≤ 0.05% by weight being particularly preferred, ≤ 0.035% by weight being especially preferred.

According to a forty-fourth embodiment of the process, according to the present invention, the film further comprises a whitening agent selected from the group consisting of bis-benzoxazoles e.g. bis-benzoxazolyl-stilbenes and bis-benzoxazolyl-thiophenes; benzotriazole-phenylcoumarins; naphthotriazole-phenylcoumarins; triazine-phenylcoumarins and bis(styryl)biphenyls.

Suitable whitening agents are:

UVITEX ® OB		CIBA
UVITEX ® OB-ONE		CIBA
Eastobrite OB	2,5-thiophenediylbis(5-tert-butyl-1,3-benzoxazole)	Eastman Chemical
	bis-benzoxazolyl-stilbene	
	bis-benzoxazolyl-thiophene	

Flame retardant

According to a forty-fifth embodiment of the process, according to the present invention, the film further comprises a flame retardant selected from the group consisting of: brominated compounds; organophosphorus compounds; melamine; melamine-derivatives, e.g. melamine salts with organic or inorganic acids such as boric acid, cyanuric acid, phosphoric acid or pyro/poly-phosphoric acid, and melamine homologues such as melam, melem and melon; metal hydroxides e,g. aluminium hydroxide and magnesium hydroxide; ammonium polyphosphates and zinc borate e.g. with a composition of $xZnO.yB_2O_3.zH_2O$ such as $2ZnO.3B_2O_3.3.5H_2O$.

Suitable flame retardants include:

SAYTEX® HP-7010 P/G	brominated polystyrene	Albemarle Corporation
SAYTEX® HP-3010	brominated polystyrene	Albemarle Corporation
SAYTEX® 8010	ethane-1,2-bis(pentabromo-phenyl)	Albemarle Corporation
SAYTEX® BT-93	ethylene bis-tetrabromo-	Albemarle Corporation

	phthalimide	
SAYTEX® BT-93W	Ethylene bis-tetrabromo-phthalimide	Albemarle Corporation
SAYTEX® CP-2000	brominated compound	Albemarle Corporation
SAYTEX® 120	tetradecabromo-diphenoxy benzene	Albemarle Corporation
SAYTEX® 102E	Decabromodiphenyl oxide	Albemarle Corporation
SAYTEX® 9006L	brominated compound	Albemarle Corporation
SAYTEX® HP-900	brominated compound	Albemarle Corporation
SAYTEX® HP-800A	brominated compound	Albemarle Corporation
SAYTEX® HP-800AG	brominated compound	Albemarle Corporation
SAYTEX® BC70HS	brominated compound	Albemarle Corporation
NcendX P-30	organophosphorus compound	Albemarle Corporation
MARTINAL® OL-104	aluminium hydroxide	Albemarle Corporation
MARTINAL® OL-104/LE	aluminium hydroxide	Albemarle Corporation
MARTINAL® OL-104/WE	aluminium hydroxide	Albemarle Corporation
MARTINAL® OL-104/LFF	aluminium hydroxide	Albemarle Corporation
MARTINAL® OL-104/LCD	aluminium hydroxide	Albemarle Corporation
MARTINAL® OL-107	aluminium hydroxide	Albemarle Corporation
MARTINAL® OL-107/LE	aluminium hydroxide	Albemarle Corporation
MARTINAL® OL-107/LFF	aluminium hydroxide	Albemarle Corporation
MARTINAL® OL-107/LCD	aluminium hydroxide	Albemarle Corporation
MARTINAL® OL/Q-107	aluminium hydroxide	Albemarle Corporation
MARTINAL® OL-111/LE	aluminium hydroxide	Albemarle Corporation
MAGNIFIN® H3	magnesium hydroxide	Albemarle Corporation
MAGNIFIN® H5	magnesium hydroxide	Albemarle Corporation
MAGNIFIN® H7	magnesium hydroxide	Albemarle Corporation
MAGNIFIN® H10	magnesium hydroxide	Albemarle Corporation
MAGNIFIN® T2C	magnesium hydroxide	Albemarle Corporation
MAGNIFIN® T3C	magnesium hydroxide	Albemarle Corporation
MELAPUR® MCXL	melamine cyanurate	CIBA
MELAPUR® MC50	melamine cyanurate	CIBA
MELAPUR® MC25	melamine cyanurate	CIBA
MELAPUR® 200 70	melamine polyphosphate	CIBA
MELAPUR® MP	melamine phosphate	CIBA
FIREBRAKE® ZB	a zinc borate compound	LUZENAC
FIREMASTER® PBS-64	brominated styrene-based technology	GREAT LAKES CHEMICAL CORP.
FIREMASTER® PBS-64HW	brominated styrene-based technology	GREAT LAKES CHEMICAL CORP.
FIREMASTER® CP-44B	copolymer of brominated styrene & glycidyl methacrylate	GREAT LAKES CHEMICAL CORP.

Antioxidant

According to a forty-sixth embodiment of the process, according to the present invention, the film further comprises an antioxidant selected for the group consisting of organotin derivatives, sterically hindered phenols, sterically hindered phenol derivatives and phosphites.

Suitable flame retardants include:

ETHANOX® 310	Organotin catalyzed penta-erythritol tetrakis (3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate)	Albemarle Corporation
ETHANOX® 310TF	"Tin-free" pentaerythritol tetrakis (3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate)	Albemarle Corporation
ETHANOX® 314	1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-tria-zine-2,4,6(1h,3h,5h)-trione	Albemarle Corporation
ETHANOX® 330	1,3,5-trimethyl-2,4,6-tris (3,5-di-tert-butyl-4-hydroxy-benzyl) benzene	Albemarle Corporation
ETHANOX® 376	octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate	Albemarle Corporation
ETHAPHOS™ 368	tris-(2,4-di-t-butylphenyl) phosphite	Albemarle Corporation
ETHAPHOS™ 326	Bis (2,4-di-t-butylphenyl) pentaerythritol diphosphite	Albemarle Corporation
IRGANOX® 259		CIBA
IRGANOX® 1010		CIBA
IRGANOX® 1425		CIBA
IRGANOX® B 900		CIBA
HOSTANOX® O 3	Bis[3,3'-bis-(4'-hydroxy-3'-tert-butyl-phenyl)butanoic acid]glycol ester	CLARIANT
HOSTANOX® O 10	tetrakis[methylene(3,5-di-t-butyl-4-hydroxy-benzyl)isocyanurate	CLARIANT
HOSTANOX® O 310	1/1 mixture of HOSTANOX® O 10 & HOSTANOX® O 3	CLARIANT
HOSTANOX® 245	ethylene bis(oxyethylene)bis-[3-(5-t-butyl-4-hydroxy-m-tolyl)-propionate]	CLARIANT

Light stabilizers

According to a forty-seventh embodiment of the process, according to the present invention, the film further comprises a hindered amine light stabilizer.

Suitable light stabilizers include:

LS-01	CHIMASSORB 119	CIBA
LS-02	CHIMASSORB 944	CIBA
LS-03	TINUVIN® 123	CIBA
LS-04	TINUVIN® 144	CIBA
LS-05	TINUVIN® 622	CIBA

LS-06	TINUVIN® 765	CIBA
LS-07	TINUVIN® 770	CIBA
LS-08	TINUVIN® 783	CIBA
LS-09	TINUVIN® 791	CIBA
LS-10	TINUVIN ® B 75	CIBA
LS-11	TINUVIN ® B 241	CIBA

UV-absorbers

According to a forty-eighth embodiment of the process, according to the present invention, the film further comprises an UV-absorber selected from the group consisting of benzotriazole derivatives and triazine derivatives.

Suitable UV-absorbers include:

UV-01	CHIMASSORB		CIBA
UV-02	TINUVIN® 213		CIBA
UV-03	TINUVIN® 234		CIBA
UV-04	TINUVIN® 327		CIBA
UV-05	TINUVIN® 360		CIBA
UV-06	TINUVIN ® 1577		CIBA
UV-07	HOSTAVIN® PR-25	propanedioic acid,[(4-methoxy-phenyl)-methylene]-, dimethyl ester	CLARIANT
UV-08	SANDUVOR® VSU	2-ethyl-2’-ethoxy-oxalanilide	CLARIANT
UV-09	HOSTAVIN® B-CAP	tetra-ethyl-2,2’-(1,4-phenylene-dimethylidene)-bismalonate	CLARIANT
UV-10	HOSTAVIN® ARO 8	2-hydroxy-4-n-octyloxybenzophenone	CLARIANT

Image recording element

Aspects of the present invention are also realized by the use of the non-transparent self-supporting film produced according to the present invention in image recording elements.

According to a first embodiment of the use of the non-transparent self-supporting film produced according to the present invention in image recording elements, according to the present invention, the film is provided on at least one side with a transparent overprintable layer i.e. for impact and non-impact printing.

According to a second embodiment of the use of the non-transparent self-supporting film produced according to the present invention in image recording elements, according to the present invention, the film is provided on at least one side with a non-transparent overprintable layer i.e. suitable for at least one impact and non-impact print technique.

According to a third embodiment of the use of the non-transparent self-supporting film produced according to the present invention in image recording elements, according to the present invention, according to the present invention, the film is provided on at least one side with a non-transparent transparentizable overprintable layer i.e. i.e. suitable for at least one impact and non-impact print technique.

According to a fourth embodiment of the use of the non-transparent self-supporting film produced according to the present invention in image recording elements, according to the present invention, the film is provided on at least one side with an ink-jet receiving layer. Typical receiving layers are either porous in the case of aqueous or solvent inks or pastes to enable rapid drying to the touch or are non-porous in the case of phase-change inks or curable inks e.g. radiation curable inks. Porous receiving layers typically comprise at least one pigment such as silica or alumina; at least one binder, such as an ammonium salt of a styrene-acrylate-acrylic acid terpolymer; a surfactant e.g. an anionic surfactant such as an aliphatic sulphonate; optionally a levelling agent, such as polydimethylsiloxane, and optionally a mordant.

According to a fifth embodiment of the use of the non-transparent self-supporting film produced according to the present invention in image recording elements, according to the present invention, the film is provided on at least one side with an imaging layer e.g. a photographic layer e.g. a silver halide emulsion layer; a photothermographic element and a substantially light-insensitive thermographic element; and the dye receiver layer of a dye thermal transfer system.

According to a sixth embodiment of the use of the non-transparent self-supporting film produced according to the present invention in image recording elements, according to the present invention, the film is provided on at least one side with a writable layer e.g. with a pencil, ball-point pen and fountain pen.

Process for obtaining a transparent pattern

Aspects of the present invention have been realized by a process for obtaining a transparent pattern comprising the step of: image-wise application of heat optionally supplemented by the application of pressure to a non-transparent microvoided biaxially stretched self-supporting film produced by a process comprising the steps of: i) mixing at least one linear polyester having together monomer units consisting essentially of terephthalate, isophthalate and aliphatic dimethylene with the molar ratio of isophthalate monomer units to terephthalate monomer units being at least 0.02 to provide a linear polyester matrix; at least one amorphous high polymer with a higher glass transition temperature than the glass transition temperature of said linear polyester matrix and/or at least one crystalline high polymer having a higher melting point than the glass transition temperature of said linear polyester matrix; and optionally at least one ingredient from the group of ingredients consisting of inorganic opacifying pigments, whitening agents, UV-absorbers, light stabilizers, antioxidants, flame retardants and colorants in a kneader or an extruder; ii) forming the mixture produced in step i) in a thick film followed by quenching; iii) longitudinally stretching the thick film at a stretching force of > 4 N/mm^2 to at least twice the initial length; and iv) transversly stretching the longitudinally stretched film from step (iii) to at least twice the initial length.

According to a first embodiment of the process for obtaining a transparent pattern, according to the present invention, the heat is applied by a heated or hot stamp, a thermal head, a heated or hot bar or a laser. The heating can be carried out from one or both sides of the film. Optical density changes of at least 0.4 can be readily realized or up to 40% without significant changes in film thickness. Moreover, the transparentization effect realized by the process for obtaining a transparent pattern, according to the present invention, results from a combination of heat supplied by a heat source, the pressure between the heat source and the film and the time the heat source is applied. The heat has to be applied for at least 1 ms either continuously or non-continuously. Heating with a thermal head can be with a single heat pulse, but multiple short heating pulses are preferred to avoid overheating of the heating elements. When a thermal head is used a foil can be used between the thermal head and the non-transparent microvoided biaxially stretched self-supporting film during the heating process e.g. a 6 µm thick PET-film can be interposed between the non-transparent microvoided film and the thermal head to prevent possible contamination of the thermal head. Thermal head printers, such as the DRYSTAR-printers supplied by AGFA-GEVAERT N.V., can be used produce the transparent pattern of the present invention e.g. as personalized watermarks.

This transparentization effect is accompanied by a relief pattern, which can be detected by touch i.e. in a tactile manner, and by changes in glossiness. This relief pattern is more pronounced the higher the temperature of the heat source e.g. in the case of A SAN-polymer as dispersed phase this embossing effect increasing with temperature between 110°C and 190°C. The tactile relief obtained by applying a hot stamp to a non-transparent microvoided biaxially stretched self-supporting film is much more pronounced than that obtained using a thermal head.

The degree of transparency realized depends upon the stamp/thermal head printing conditions: time, temperature and pressure. The thermofixation history of the material is also important. The heated-induced transparentization of the non-transparent microvoided biaxially stretched self-supporting film can be carried out before or after the optional application of a layer, such as an ink-jet receiving layer and before or after transparentization. The relative positioning of the transparentized areas and transparency in the support can be of value as an additional security measure.

According to a second embodiment of the process for obtaining a transparent pattern, according to the present invention, the heat is applied non-continuously.

According to a third embodiment of the process for obtaining a transparent pattern, according to the present invention, a transparent overprintable layer is provided on the film prior to the image-wise application of heat.

According to a fourth embodiment of the process for obtaining a transparent pattern, according to the present invention, a transparent overprintable layer is provided on the film after the image-wise application of heat.

Industrial application

Non-transparent microvoided axially stretched films, according to the present invention, can be used as synthetic paper for printing and other applications, as a relector in LCD displays and photovoltaic devices, as a support for imaging materials e.g. impact and non-impact (e.g. electrophotography, electrography and ink jet) receiving materials, photothermographic recording materials, substantially light-insensitive thermographic recording materials, dye sublimation printing, thermal transfer printing, etc., in security and anti-counterfeiting applications e.g. in tickets, labels, tags, an ID-card, a bank card, a legal document, banknotes and packaging and can also be integrated into packaging.

The invention is illustrated hereinafter by way of comparative examples and examples. The percentages and ratios given in these examples are by weight unless otherwise indicated.

Subbing layer Nr. 01 on the emulsion side of the support:

copolymer of 88% vinylidene chloride, 10% methyl acrylate and 2% itaconic acid	79.1 mg/m^2
Kieselsol® 100F, a colloidal silica from BAYER	18.6 mg/m^2
Mersolat® H, a surfactant from BAYER	0.4 mg/m^2
Ultravon® W, a surfactant from CIBA-GEIGY	1.9 mg/m^2

Ingedients used in the EXAMPLES:

POLYESTER:

PET-nr			MFI 270°C/ 1.20 kg [cm^3/10 min]	Inherent viscosity ** [η] [dl/g]	T$_g$ [°C]
01	T03*	polyethylene terephthalate	34.8	0.60	80.5
02	T04*	polyethylene terephthalate	34.8	0.60	80.5
03	WP75#	polyester of 98.5 mol% terephthalate, 1.5 mol% isophthalate and 100 mol% ethylene units		0.77	80
04	DP9990#	polyester of 90 mol% terephthalate, 10 mol% isophthalate and 100 mol% ethylene units		0.60	
05	DP9730#	polyester of 70 mol% terephthalate, 30 mol% isophthalate and 100 mol% ethylene units			

* AGFA-GEVAERT N.V.

La Seda

** inherent viscosity was determined in a 0.5g/dL solution of 60 wt% phenol and 40 wt% ortho-dichlorobenzene at 25°C in an Ubbelohde viscometer

STYRENE-ACRYLONITRILE COPOLYMERS:

SAN-nr		Wt% acrylonitrile	Wt% styrene	MFI at 270°C/1.20 kg [mL/10 min]	Mn	Mw	T$_g$ [°C]
01	TYRIL 905*	20	80	7.1			105.2

02	TYRIL 867E*	25	75	5.8			106.5
03	SAN 140*	27.5	72.5	53.2	47,640	99,820	108.8
04	LURAN 368R#	28	72	3.9			107.3
05	TYRIL 790*	29	71	12.1			106.3
06	SAN 124*	28.5	71.5	37.9	53,940	109,350	108.1
07	LURAN 388S#	33	67	3.6			108.7

* DOW CHEMICAL
# BASF
MFI = Melt Flow Index

MAGNUM 8391: an ABS resin with a Vicat softening temperature of 95°C from DOW CHEMICAL

TPX® DX820: a high rigidity poly(4-methylpentene) from MITSUI CHEMICAL

TITANIUM DIOXIDE: Renol-white/PTX 506, a masterbatch from CLARIANT GmbH containing 65% by weight TiO_2 and 35 wt% polyester

COMPARATIVE EXAMPLES 1 to 3

The PET-types and SAN-types used for producing the extrudates used in producing of the films of COMPARATIVE EXAMPLES 1 to 3 are given in Table 3. The PET, SAN, TiO_2 and UVITEX OB-one in the weight percentages given in Table 1 were mixed and then dried at 150°C for 4 hours under vacuum (< 100 mbar), the mixtures then melted in a PET-extruder and extruded through a sheet die and cooled to produce the extrudates of COMPARATIVE EXAMPLES 1 to 3.

Table 1:

Comparative Example nr	PET01 [wt%]	PET02 [wt%]	PET03 [wt%]	SAN type	TiO_2 [wt%]	OB-one [ppm]
1	98	-	-	-	2	150
2	47	-	47	-	6	-
3	44	-	44	-	12	-

The extrudates of COMPARATIVE EXAMPLES 1 to 3 were then longitudinally stretched with an INSTRON apparatus in which the extrudates are heated in an oven mounted on the apparatus under the conditions given in Table 2 to yield the axially stretched films of COMPARATIVE EXAMPLES 1/LS1, 2/LS1 and 3/LS1 respectively.

Table 2:

Comparative Example nr.	Stretch ratio	Stretch force [N/mm^2]	Thickness [µm]	OD TR924
1/LS1	3.3	6.0	319	0.81

2/LS1	3.3	5.0	340	1.26
3/LS1	3.3	5.0	335	1.59

Transversal stretching was then performed on the longitudinally stretched films with a stretch time of 30 s and stretching speed of 1000 %/min under the conditions given in Table 3. Finally the films were thermally fixated at 175°C for 1 minute giving the substantially opaque films of COMPARATIVE EXAMPLES 1/LS1, 2/LS2 and 3/LS3.

The optical densities of the films of COMPARATIVE EXAMPLES 1/LS1/BS1, 2/LS1/BS1 and 3/LS1/BS1 were measured in transmission mode with a MACBETH TR924 densitometer with a visible filter and the results given in Table 3.

Table 3:

Comparative Example nr.	Stretch ratio	Stretch temperature [°C]	Thickness [µm]	OD (TR924) after thermal fixation
1/LS1/BS1	3.3	135	120	0.45
2/LS1/BS1	3.3	135	140	0.90
3/LS1/BS1	3.3	135	135	1.12

* the higher the stretching tension the lower the stretch temperature

The films of COMPARATIVE EXAMPLES 1/LS/BS, 2/LS/BS and 3/LS/BS were each mounted in an Instron 4411 apparatus and were heated at various temperatures between 120 and 190°C for 5 seconds with a soldering iron in the upper clamp making contact with the film at a pressure of 0.5 N/mm^2. The optical densities of the film after the tests were measured in transmission with a MacBeth TR924 densitometer with a visible filter and the film thicknesses were also measured. The results are summarized below in Tables 4 and 5 respectively.

Table 4:

Film of Comparative Example nr	OD before heating	OD after heating for 5s at a pressure of 0.5 N/mm^2 at					ΔOD at 150°C	% reduction in OD
		120°C	130°C	150°C	170°C	190°C		
1/LS/BS	0.45	0.47	0.46	0.46	0.47	0.45	-0.01	-0.01
2/LS/BS	0.90	0.90	0.91	0.89	0.88	0.85	0.01	0.01
3/LS/BS	1.12	1.14	1.14	1.11	1.11	1.08	0.01	0.01

Table 5:

Film of	Layer thick-	Layer thickness after heating for 5s at a

Comparative Example nr	ness before heating	pressure of 0.5 N/mm^2 at				
		120°C	130°C	150°C	170°C	190°C
1/LS/BS	93	92	91	93	92	85
2/LS/BS	138	139	142	137	132	115
3/LS/BS	137	136	135	139	131	119

Within experimental error no transparentization was observed upon heating the films of COMPARATIVE EXAMPLES 1/LS/BS, 2/LS/BS and 3/LS/BS. This shows that in the absence of dispersed SAN-polymer particles there is no transparentization of films containing titanium dioxide i.e. there is no micro-void formation.

COMPARATIVE EXAMPLE 4

The 1083 µm thick extrudate of COMPARATIVE EXAMPLE 4 with a composition of 2% by weight of titanium dioxide, 100 ppm UVITEX OB-one and 98% by weight of PET02 was produced as described for COMPARATIVE EXAMPLES 1 to 3 and had an optical density measured with a MacBeth TR924 densitometer in transmission mode with a visible filter of 1.35. The extrudate was stretched in the length direction as described in COMPARATIVE EXAMPLES 1 to 3 under the conditions given in Table 6. The thickness values were measured by averaging measurements obtained by contacting the upper surface at 16 different positions at a measuring force of 0.8N using a SONY U30A thickness gauge with a resolution of 1 µm, an accuracy of 2 µm and a contact ball 3 mm in diameter.

Table 6:

Comparative Example nr.	Stretch ratio	Stretch force [N/mm^2]	Thickness [µm]	OD (TR924)	OD [X-rite]
4/LS1	3.3	6	323	0.805	0.55
4/LS2	3.3	4	328	0.84	-

Transversal stretching was then performed on the longitudinally stretched films with a stretch time of 30 s and stretching speed of 1000 %/min under the conditions given in Table 7. The measured thickness and measured optical density with the MacBeth TR924 densitometer in transmission mode with a visible filter are also given in Table 7.

Table 7:

Comparative Example nr.	Stretch ratio	Stretch temperature [°C]	Thickness [µm]	OD TR924	OD [X-rite]

4/LS1/BS1	3.3	135	120	0.47	0.30
4/LS2/BS1	3.3	135	124	0.53	0.33

Since there is no contribution to the optical density from void-forming upon biaxial stretching for the composition of COMPARATIVE EXAMPLE 4 as can be seen from COMPARATIVE EXAMPLE 1 to 3, the dependence of optical density upon film thickness can be used to provide a baseline with which to assess the contribution of void-forming to the optical density for those compositions based upon aromatic polyesters with 2% by weight of the same titanium dioxide pigment which form voids upon biaxial stretching.

The Beer-Lambert relationship does not hold for pigmented films with light-scattering pigments such as titanium dioxide. If the film thickness is smaller than the average free path-length of the scattered light, light will escape after scattering otherwise the light does not escape and in fact interferes with further scattered light providing for a quasi-exponential dependence of optical density upon film thickness. The situation is too complex to be able to be described theoretically and hence the only possible approach is to measure the actual optical density observed at particular film thicknesses. The above-mentioned optical density appear to a fair approximation to bee linearly dependent upon the logarithm of the film thickness in the layer thickness range 1084 to 120 μm giving the following relationship:

$$\mathrm{OD} = 0.891 \log [\text{thickness in } \mu\mathrm{m}] - 1.3727$$

This relationship provides the optical density attributable to a 2% by weight concentration of the titanium dioxide pigment used as a function of film thickness.

COMPARATIVE EXAMPLE 5 and INVENTION EXAMPLES 1 to 17

The ca. 1100 μm thick extrudates of COMPARATIVE EXAMPLE 5 and INVENTION EXAMPLES 1 to 17 all with 2% by weight of titanium dioxide and 15% by weight of SAN 06 were produced by mixing the ingredients in Table 8 in the proportions given in Table 8 and then drying the mixture at 150°C for 4 hours under vacuum (< 100 mbar) before melting in a PET-extruder, extrusion through a sheet die and cooling to produce the extrudates of COMPARATIVE EXAMPLE 5 and INVENTION EXAMPLES 1 to 17 having a density of ca. 1.3 g/mL as summarized in Table 8 together with the isophthalate (IPA):terephthalate (TPA) ratio.

Table 8:

Comparative example nr.	PET02 [wt%]	PET04 [wt%]	PET05 [wt%]	IPA:TPA ratio	SAN type	SAN [wt%]	UVITEX OB-one [ppm]	TiO_2 [wt%]	Density [g/mL]
5	83	0	-	0	06	15	-	2.0	1.294
Invention example nr.									
1	58	25	-	0.0310	06	15	-	2.0	1.289
2	41.5	41.5	-	0.0526	06	15	100	2.0	1.284
3	33.35	49.7	-	0.0636	06	15	-	1.95	
4	33.3	49.7	-	0.0637	06	15	100	2.0	
5	32.3	50.7	-	0.0650	06	15	100	2.0	
6	32.3	50.7	-	0.0650	06	15	100	2.0	
7	26.29	56.71	-	0.0733	06	15	100	2.0	
8	25.25	57.75	-	0.0748	06	15	100	2.0	
9	25	58	-	0.0751	06	15	100	2.0	1.304
10	24.3	58.7	-	0.0761	06	15	100	2.0	
11	1.05	82.0	-	0.109	06	15	-	1.95	
12	-	83	-	0.111	06	15	-	2.0	1.299
13	-	83	-	0.111	06	15	100	2.0	
14	28.25	22.3	32.5	0.168	06	15	100	1.95	
15	14.85	22.3	45.9	0.239	06	15	-	1.95	
16	1.05	22.3	59.7	0.320	06	15	-	1.95	
17	1.05	-	82.0	0.421	06	15	-	1.95	

Longitudinal stretching was carried out for each extrudate as described in COMPARATIVE EXAMPLES 1 to 3 under the conditions given in Table 11. The expected thickness is the thickness based on the extrudate thickness and longitudinal as observed for non-voided films.

Longitudinal stretching was accompanied by a decrease in density due to void-forming, this decrease in density clearly increasing as the IPA:TPA ratio increases, surprisingly indicates that an increase in the IPA:TPA ratio favours increased void-forming in the film.

Table 11:

Comparative example nr	IPA: TPA ratio	Longitudinal stretch				Density [g/mL]	Thickness [μm]	
		temperature [°C]	ratio	V1 speed [m/min]	force [N/mm^2]		Measured	Expected
5/LS1	0		3.85	4.0	8	1.290	320	286
Invention example nr								
1/LS1	0.0310		3.85	4.0	8	1.264	325	286

1/LS2	0.0310		3.65	4.0	8		323	301
2/LS1	0.0526		3.85	4.0	8	1.251	318	286
3/LS1	0.0636	92	3.3	4.0	8.0		380	333
3/LS2	0.0636	80	3.3	4.0	9.0-9.5		380	333
3/LS3	0.0636	108	3.3	8.0	7.5		375	333
4/LS1	0.0637	101	3.3	4.0	8	1.216	350	333
4/LS2	0.0637	116	3.3	4.0	8	1.283	330	333
5/LS1	0.0650		3.3	4.0	8.6		365	333
6/LS1	0.0650	120	3.8	4.0	8		300	290
6/LS2	0.0650	96	3.6	4.0	8		335	305
6/LS3	0.0650	85	3.45	4.0	8		350	319
7/LS1	0.0733	92	3.3	4.0	8	1.229	360	333
8/LS1	0.0748	95	3.3	4.0	8	1.242	330	333
9/LS1	0.0751		3.85	4.0	8	1.217	330	286
10/LS1	0.0761	94	3.3	4.0	8	1.216	350	333
10/LS2	0.0761	110	3.3	4.0	7	1.258	333	333
11/LS1	0.109	96	3.3	4.0	8.0		370	333
11/LS2	0.109	84	3.3	4.0	9.0-9.5		385	333
12/LS1	0.111		3.85	4.0	8	1.125	345	286
12/LS2	0.111		3.65	4.0	8		380	301
13/LS1	0.111		3.85	4.0	8		320	286
13/LS2	0.111		3.85	4.0	5			286
13/LS3	0.111		3.85	4.0	6			286
14/LS1	0.168	85	3.3	4.0	8.2		393	333
15/LS1	0.239	86	3.3	4.0	6.0		390	333
16/LS1	0.320	79	3.3	4.0	8.0		392	327
16/LS2	0.321	85	3.3	4.0	7.0		400	327
17/LS1	0.421	82	3.3	4.0	6.0		375	333
17/LS2	0.421	87	3.3	4.0	5.0		380	333

Table 10 gives the measured thickness; the expected thickness i.e. thickness if no void-forming on the basis of the extrudate thickness and the longitudinal and transversal stretch ratios, the measured optical density with the MacBeth TR924 densitometer in transmission mode with a visible filter, the expected optical density, i.e. the optical density calculated using the relationship disclosed in COMPARATIVE EXAMPLE 4 using the theoretical layer thickness values, and the difference between the observed optical density and the optical density expected due to a 2% by weight concentration of the particular titanium dioxide pigment used, ΔOD.

Table 10:

Comparative example nr	IPA: TPA ratio	Thickness [μm]	V1 speed [m/	Expected thick-	OD TR924	Expected OD	ΔOD	ΔOD/ OD	OD [X-rite]

			min]	ness [µm]					
5/LS1	0	320	4.0	286	1.00	0.81	0.19	0.19	0.76
Invention example nr.									
1/LS1	0.0310	325	4.0	286	1.05	0.81	0.24	0.23	0.82
1/LS2	0.0310	323	4.0	301	1.00	0.83	0.17	0.17	0.78
2/LS1	0.0526	318	4.0	286	1.06	0.81	0.25	0.23	0.85
3/LS1	0.0636	380	4.0	333	1.17	0.87	0.30	0.26	0.96
3/LS2	0.0636	380	4.0	333	1.15	0.87	0.28	0.24	0.97
3/LS3	0.0636	375	8.0	333	1.12	0.87	0.25	0.22	0.92
4/LS1	0.0637	350	4.0	333	1.21	0.87	0.34	0.28	0.98
4/LS2	0.0637	330	4.0	333	1.02	0.87	0.15	0.15	0.80
5/LS1	0.0650	365	4.0	333		0.87			
6/LS1	0.0650	300	4.0	290					
6/LS2	0.0650	335	4.0	305					
6/LS3	0.0650	350	4.0	319					
7/LS1	0.0733	360	4.0	333	1.17	0.87	0.30	0.26	0.97
8/LS1	0.0748	330	4.0	333	1.08	0.87	0.21	0.19	0.90
9/LS1	0.0751	330	4.0	286	1.13	0.81	0.32	0.28	0.92
10/LS1	0.0761	350	4.0	333	1.18	0.87	0.31	0.26	1.00
10/LS2	0.0761	333	4.0	333	1.10	0.87	0.23	0.21	0.89
11/LS1	0.109	370	4.0	333	1.15	0.87	0.28	0.24	0.93
11/LS2	0.109	385	4.0	333	1.28	0.87	0.41	0.32	1.01
12/LS1	0.1111	345	4.0	286	1.20	0.81	0.39	0.32	1.02
12/LS2	0.1111	380	4.0	301	1.23	0.83	0.40	0.32	1.00
13/LS1	0.1111	320	4.0	286	1.24	0.81	0.43	0.35	1.00
13/LS2	0.1111		4.0	286	1.02	0.81	0.21	0.20	0.83
13/LS3	0.1111		4.0	286	1.10	0.81	0.29	0.26	0.83
14/LS1	0.168	393	4.0	333	1.15	0.87	0.28	0.24	0.97
15/LS1	0.239	390	4.0	333	1.12	0.87	0.25	0.22	0.91
16/LS1	0.320	392	4.0	327	1.37	0.87	0.50	0.36	1.10
16/LS2	0.320	400	4.0	327	1.10	0.87	0.23	0.21	0.89
17/LS1	0.421	375	4.0	333	1.13	0.87	0.26	0.23	0.76
17/LS2	0.421	380	4.0	333	0.97	0.87	0.10	0.10	0.89

The increase in optical density due to void forming was in the range of 17 to 36%. Moreover, the optical density values for INVENTION EXAMPLES 13/LS1, 13/LS2 and 13/LS3 clearly show the impact of the longitudinal stretching force with the highest optical density value of 1.24 being obtained with the film of INVENTION EXAMPLE 13/LS1 with the highest longitudinal stretching force of 8 N/mm^2 compared with 1.02 and 1.10 obtained with the films of INVENTION EXAMPLE 13/LS2 and 13/LS3 respectively with longitudinal stretching forces of 5 N/mm^2 and 6 N/mm^2 respectively.

Transversal stretching was then performed on the longitudinally stretched films with a stretch time of 30 s and stretching speed of 1000%/min under the conditions given in Table 11. The density, measured thickness and the expected thickness, i.e. thickness if no void-forming on the basis of the extrudate thickness and the longitudinal and transversal stretch ratios, are also given in Table 11.

Transversal stretching reduced the density of the films still further with again the density decrease being greater as the proportion of PET04 and PET05 increased. This again surprisingly indicates that an increase in the IPA:TPA ratio favoured increased void-forming in the film.

At an IPA:TPA ratio of 0.0650 transversal stretching was surprisingly not possible above 113°C, but was possible at as low temperatures as 85°C, which is less than 10°C above the glass transition temperature of the linear polyester matrix. This enables much higher optical densities to be realized by biaxial stretching.

Table 11:

Comparative Example nr	IPA: TPA ratio	Transversal stretch			Density [g/mL]	Measured thickness [µm]	Expected thickness [µm]
		temperature [°C]	ratio	speed [%/min]			
5/LS1/BS1	0	135	3.3	1000	1.284	101	87
Invention example nr							
1/LS1/BS1	0.031	134	3.3	1000	1.219	95	87
1/LS2/BS1	0.031	135	3.3	1000		102	91
2/LS1/BS1	0.0526	132	3.3	1000		100	87
2/LS1/BS2	0.0526			1000	1.234	97	87
3/LS1/BS1	0.0636	100	3.5	1000		145	95
3/LS2/BS1	0.0636	105	3.5	1000		150	95
3/LS3/BS1	0.0636	95	3.5	1000		126	95
4/LS1/BS1	0.0637	100	3.5	1000	1.074	140	95
4/LS1/BS2	0.0637	96	3.5	1000	1.002	135	95
4/LS2/BS1	0.0637	96	3.5	1000	1.158	116	95
5/LS1/BS1	0.0650	132	3.3	1000	1.228	140	101
6/LS1/BS1	0.0650	122	3.3	1000		110	88
6/LS2/BS1	0.0650	122	3.3	1000		135	93
6/LS3/BS1	0.0650	122	3.3	1000		150	97
7/LS1/BS1	0.0733	95	3.5	1000	1.071	145	95
8/LS1/BS1	0.0748	96	3.5	1000	1.070	138	95
9/LS1/BS1	0.0751	134	3.3	1000	1.195	105	87
10/LS1/BS1	0.0761	95	3.5	1000	1.055	147	95

10/LS2/BS1	0.0761	95	3.5	1000	1.140	112	95
11/LS1/BS1	0.109	92	3.5	1000		207	95
11/LS1/BS2	0.109	85	3.5	1000		199	95
11/LS1/BS3	0.109	83	3.5	1000		198	95
11/LS2/BS1	0.109	92	3.5	1000		205	95
11/LS2/BS2	0.109	85	3.5	1000		210	95
11/LS2/BS3	0.109	81	3.5	1000		214	95
12/LS1/BS1	0.1111	135	3.3	1000	0.990	169	87
12/LS2/BS1	0.1111	135	3.3	1000		185 156	91
12/LS1/BS1	0.1111	110	3.3	1000	1.121	130	86
13/LS2/BS1	0.1111	110	3.3	1000		125	86
13/LS3/BS1	0.1111	110	3.3	1000		120	86
14/LS1/BS1	0.168	89	3.5	1000		198	95
14/LS1/BS2	0.168	84	3.5	1000		201	95
14/LS1/BS3	0.168	78	3.5	1000		204	95
15/LS1/BS1	0.239	89	3.5	1000		191	95
15/LS1/BS2	0.239	84	3.5	1000		186	95
16/LS1/BS1	0.320	92	3.5	1000		211	95
16/LS1/BS2	0.320	86	3.5	1000		210	95
16/LS2/BS1	0.320	92	3.5	1000		190	95
16/LS2/BS2	0.320	86	3.5	1000		200	95
17/LS1/BS1	0.421	92	3.5	1000		190	95
17/LS1/BS2	0.421	90	3.5	1000		170	95
17/LS1/BS3	0.421	85	3.5	1000		170	95
17/LS2/BS1	0.421	92	3.5	1000		150	95
17/LS2/BS2	0.421	85	3.5	1000		150	95

Table 12 gives the measured thickness, the expected thickness, the measured optical density with the MacBeth TR924 densitometer in transmission mode with a visible filter, the expected optical density, i.e. the optical density calculated using the relationship disclosed in COMPARATIVE EXAMPLE 4 using the theoretical layer thickness values, and the difference between the observed optical density and the optical density expected due to a 2% by weight concentration of the particular titanium dioxide pigment used, ΔOD.

Table 12:

Comparative Example nr.	IPA: TPA ratio	V1 (LS) speed [m/min]	Thickness [µm]	Expected thickness [µm]	OD TR924	Expected OD	ΔOD	ΔOD/OD	OD [X-rite]
5/LS1/BS1	0	4.0	101	87	1.00	0.35	0.65	0.65	0.78
Invention example nr									

1/LS1/BS1	0.0310	4.0	95	87	1.01	0.35	0.66	0.65	0.78
1/LS2/BS1	0.0310	4.0	102	91	0.99	0.37	0.62	0.63	0.75
2/LS1/BS1	0.0526	4.0	100	87	1.04	0.35	0.69	0.66	0.80
2/LS1/BS2	0.0526	4.0	97	87	(1.04)	(0.35)	(0.69)	0.66	(0.80)
3/LS1/BS1	0.0636	4.0	145	95	1.02	0.39	0.63	0.62	0.85
3/LS2/BS1	0.0636	4.0	150	95	1.11	0.39	0.72	0.65	0.90
3/LS3/BS1	0.0636	8.0	126	95	1.03	0.39	0.64	0.62	0.77
4/LS1/BS1	0.0637	4.0	140	95	1.20	0.39	0.81	0.67	0.97
4/LS1/BS2	0.0637	4.0	135	95	1.25	0.39	0.86	0.69	1.00
4/LS2/BS1	0.0637	4.0	116	95	1.10	0.39	0.71	0.64	0.86
5/LS1/BS1	0.0650	4.0	140	101	1.10	0.41	0.69	0.63	0.85
6/LS1/BS1	0.0650	4.0	110	88	1.06	0.36	0.70	0.66	0.84
6/LS2/BS1	0.0650	4.0	135	93	1.18	0.38	0.80	0.68	0.94
6/LS3/BS1	0.0650	4.0	150	97	1.11	0.40	0.71	0.64	0.88
7/LS1/BS1	0.0733	4.0	145	95	1.21	0.39	0.82	0.68	0.94
8/LS1/BS1	0.0748	4.0	138	95	1.20	0.39	0.81	0.67	0.97
9/LS1/BS1	0.0751	4.0	105	87	1.10	0.35	0.75	0.68	0.90
10/LS1/BS1	0.0761	4.0	147	95	1.20	0.39	0.81	0.67	0.97
10/LS2/BS1	0.0761	4.0	112	95	1.05	0.39	0.66	0.63	0.82
11/LS1/BS1	0.109	4.0	207	95	1.26	0.39	0.87	0.69	1.04
11/LS1/BS2	0.109	4.0	199	95	1.28	0.39	0.89	0.69	1.04
11/LS1/BS3	0.109	4.0	198	95	1.27	0.39	0.88	0.69	1.03
11/LS2/BS1	0.109	4.0	205	95	1.34	0.39	0.95	0.71	1.12
11/LS2/BS2	0.109	4.0	210	95	1.34	0.39	0.95	0.71	1.08
11/LS2/BS3	0.109	4.0	214	95	1.35	0.39	0.96	0.71	1.11
12/LS1/BS1	0.111	4.0	169	87	1.32	0.35	0.97	0.73	1.06
12/LS2/BS1	0.111	4.0	185 156	91	1.26	0.37	0.89	0.71	1.00
12/LS1/BS1	0.111	4.0	130	86	1.24	0.35	0.89	0.72	1.00
13/LS2/BS1	0.111	4.0	125	86	0.95	0.35	0.60	0.63	0.74
13/LS3/BS1	0.111	4.0	120	86	0.98	0.35	0.63	0.64	0.74
14/LS1/BS1	0.168	4.0	198	95	1.30	0.39	0.91	0.70	1.05
14/LS1/BS2	0.168	4.0	201	95	1.28	0.39	0.89	0.69	1.04
14/LS1/BS3	0.168	4.0	204	95	1.30	0.39	0.91	0.70	1.08
15/LS1/BS1	0.239	4.0	191	95	1.20	0.39	0.81	0.67	0.99
15/LS1/BS2	0.239	4.0	186	95	1.19	0.39	0.80	0.67	0.97
16/LS1/BS1	0.320	4.0	211	95	1.26	0.39	0.87	0.69	1.00
16/LS1/BS2	0.320	4.0	210	95	1.30	0.39	0.91	0.70	1.08
16/LS2/BS1	0.320	4.0	190	95	1.19	0.39	0.80	0.67	0.95
16/LS2/BS2	0.320	4.0	200	95	1.21	0.39	0.82	0.68	0.98
17/LS1/BS1	0.421	4.0	190	95	1.14	0.39	0.75	0.66	0.91
17/LS1/BS2	0.421	4.0	170	95	1.14	0.39	0.75	0.66	0.90
17/LS1/BS3	0.421	4.0	170	95	1.16	0.39	0.77	0.66	0.91
17/LS2/BS1	0.421	4.0	150	95	1.03	0.39	0.64	0.62	0.81
17/LS2/BS2	0.421	4.0	150	95	1.07	0.39	0.68	0.63	0.83

The optical density values for INVENTION EXAMPLES 13/LS1/BS1, 13/LS2/BS1 and 13/LS3/BS1 clearly still show the impact of the longitudinal stretching force with the highest optical density value of 1.24 being obtained with the film of INVENTION EXAMPLE 13/LS1/BS1 with the highest longitudinal stretching force of 8 N/mm^2 compared with 0.95 and 0.98 obtained the films of INVENTION EXAMPLE 13/LS2/BS1 and 13/LS3/BS1 respectively with longitudinal stretching forces of 5 N/mm^2 and 6 N/mm^2 respectively.

The results of Table 12 show that at approximately the same stretching temperature the contribution to the optical density of biaxially stretched films of microvoiding increases to over 70% as the IPA:TPA ratio increases to 0.132. Above an IPA:TPA ratio of 0.132 there is a steady decrease to a still considerable contribution of 0.66 at an IPA:TPA ratio of 0.421, corresponding to 30 mole % isophthalate.

The presence of void-forming was demonstrated for several of the biaxially stretched films by clamping the films in an Instron 4411 apparatus and observing the changes in film thickness and optical density upon contacting the films with a soldering iron for 5s at 150°C. The results of these experiments are given in Table 13.

Table 13:

Comparative example nr.	IPA: TPA ratio	OD (TR924) before heating	Thickness before heating [µm]	after 5s heating at 150°C at a pressure of 0.5 N/mm^2		% decrease in OD	Change in thickness at 150°C [µm]
				OD (TR924)	Thickness [µm]		
5/LS1/BS1	0	1.03	103	0.62	94	40	9
Invention example nr.							
2/LS1/BS2	0.0526	1.05	97	0.58	87	45	10
9/LS1/BS1	0.0751	1.14	106	0.53	84	53	22
12/LS1/BS1	0.1111	1.34	168	0.83	110	38	58
12/LS2/BS1	0.1111	1.25	156	0.65	112	48	44

EXAMPLE 18

The 1100 µm thick extrudate of EXAMPLE 18 having a composition of 2% by weight of titanium dioxide, 100 ppm of UVITEX OB-one [ppm], 15% by weight of SAN 06 and 83% by weight of PET04 giving an IPA:TPA ratio of 0.0650 was produced as described for COMPARATIVE EXAMPLES 1 to 3. Stretching in the length direction was carried out for the extrudate as described in COMPARATIVE EXAMPLE 1 to 3 under four different sets of conditions as given in Table 14. The expected thickness is the thickness based on the extrudate thickness and longitudinal as observed for non-voided films.

Table 14:

Invention Example nr.	Longitudinal stretch			Thickness [μm]		OD
	ratio	force [N/mm^2]	temperature [°C]	measured	expected	X-rite
18/LS1	3.8	8.3	120	300	290	0.94
18/LS2	3.6	8.23	96	330	305	0.96
18/LS3	3.3	8.6	90	365	333	
18/LS4	3.1	8.2	80	380	355	

Transversal stretching was then performed on the longitudinally stretched films as described in COMPARATIVE EXAMPLES 1 to 3 under the conditions given in Table 15. The density, measured thickness and the expected thickness, i.e. thickness if no void-forming on the basis of the extrudate thickness and the longitudinal and transversal stretch ratios, are also given in Table 15.

Biaxial stretching reduced the density of the films with the density decrease being greater the lower the transversal stretching temperature. However, the decrease in density is smaller than would be expect simply based on the measured thicknesses compared with the expected thicknesses based on the extrudate thickness, longitudinal stretch ratio and transversal stretch ratio as observed for non-voided films, which can only be partly explained by the combination of two effects: the decrease in the density due to void forming on the one hand being to a degree compensated by the increase in the crystallinity of the polyester matrix due to biaxial stretching on the other.

Table 15:

Invention Example nr.	Transverse stretch				Density [g/mL]	Thickness	
	ratio	temper-ature [°C]	time [s]	speed [%/min]		Measured [μm]	Expected [μm]
18/LS3/BS1	3.3	86	30	1000	0.984	199	101
18/LS3/BS2	3.3	91	30	1000	0.978	185	101
18/LS3/BS3	3.3	98	30	1000	0.993	180,190	101
18/LS3/BS4	3.3	100	30	1000	1.117	165	101
18/LS3/BS5	3.3	100	30	1000		150	101
18/LS3/BS6	3.5	100	30	1000	1.080	175	95
18/LS3/BS7		101	30	1000		105	101
18/LS3/BS8		102	30	1000		135	101

18/LS2/BS1	3.3	106	30	1000		135	93
18/LS3/BS9	3.3	110	30	1000		150	101
18/LS4/BS1	3.3	110	30	1000		165	108
18/LS2/BS2	3.3	113	30	1000		135	93
18/LS1/BS1	3.3	114	30	1000		110	88
18/LS3/BS10	3.3	121	30	1000	1.199	150	101
18/LS2/BS3	3.3	123	30	1000		120	93
18/LS3/BS11	3.3	128	30	1000	1.221	140	101
18/LS3/BS12	3.3	132	30	1000	1.228	140	101
18/LS3/BS13	3.3	142	30	1000	1.242	140	101
18/LS4/BS2		150				162	108
18/LS3/BS14	3.3	153	30	1000	1.235	140	101
18/LS3/BS15	3.5	111	30	2000	1.132	140	95
18/LS3/BS16		110	10	1000		152	101
18/LS3/BS17	3.3	100	30	500	1.062	180	101
18/LS3/BS18	3.5	100	30	500	1.080	190	95

Table 16 gives the measured thickness, the expected thickness, i.e. thickness if no void-forming on the basis of the extrudate thickness and the longitudinal and transversal stretch ratios, the optical density measured with a MacBeth TR924 densitometer in transmission mode with a visible filter, the expected optical density, i.e. the optical density calculated using the relationship disclosed in COMPARATIVE EXAMPLE 4 using the theoretical layer thickness values, and the difference between the observed optical density and the optical density expected due to a 2% by weight concentration of the particular titanium dioxide pigment used, ΔOD, together with the temperature at which the transversal stretching was carried out.

Table 16:

Example nr.	Stretch temperature [°C]	Thickness [µm]	Expected thickness [µm]	OD (TR924)	Expected OD	ΔOD	ΔOD/ OD	OD (X-rite)
18/LS3/BS1	86	199	101	1.35	0.41	0.95	0.70	1.10
18/LS3/BS2	91	185	101	1.32	0.41	0.91	0.69	1.07
18/LS3/BS3	98	180 190	101	1.28 1.36	0.41	0.87 0.95	0.68 0.70	1.03
18/LS3/BS4	100	165	101	1.20	0.41	0.79	0.66	0.96
18/LS3/BS5	100	150	101	1.22	0.41	0.81	0.66	1.00
18/LS3/BS6	100*	175	95	1.22	0.39	0.83	0.68	0.98
18/LS3/BS7	101	105	101	1.15	0.41	0.75	0.65	0.90
18/LS3/BS8	102	135	101	1.08	0.41	0.67	0.62	0.81
18/LS2/BS1	106	135	93		0.38			1.005

Example nr.	Stretch temperature [°C]	Thickness [µm]	Expected thickness [µm]	OD (TR924)	Expected OD	ΔOD	ΔOD/ OD	OD (X-rite)
18/LS3/BS9	110	150	101		0.41			0.94
18/LS4/BS1	110	165	108	1.18	0.44	0.74	0.63	0.91
18/LS2/BS2	113	135	93	1.17	0.38	0.79	0.67	0.905
18/LS1/BS1	114	110	88	1.01	0.36	0.65	0.64	0.805
18/LS3/BS10	121	150	101	1.14	0.41	0.73	0.64	0.89
18/LS2/BS3	123	120	93		0.38			0.88
18/LS3/BS11	128	140	101	1.10	0.41	0.69	0.63	0.86
18/LS3/BS12	132	140	101	1.10	0.41	0.69	0.63	0.85
18/LS3/BS13	142	140	101	1.10	0.41	0.69	0.63	0.83
18/LS4/BS2	150	162	108		0.44			0.85
18/LS3/BS17	153	140	101	1.10	0.41	0.69	63	0.86

* stretch ratio = 3.5

It is clear from the results in Table 16 that the degree of void-forming, as indicated by the optical density not attributable to the 2% by weight of titanium dioxide present, increased up to 70% with decreasing transversal stretch temperature regardless of the other conditions pertaining during the transversal stretch process.

Table 17 summarizes the stretch conditions, the thickness, expected thickness based on the extrudate thickness, the longitudinal stretch ratio and the transversal stretch ratio, optical density, expected optical density and non-attibutable increase in optical density as a result of void-forming for different films obtained at a stretch temperature of approximately 110°C.

Table 17:

Invention example nr.	Transverse stretch			Thickness		OD TR924	Expected OD	ΔOD	ΔOD/ OD	OD (X-rite)
	temperature [°C]	time [s]	speed [%/min]	measured [µm]	Expected [µm]					
18/LS3/BS15	111	30	2000	140	95	1.20	0.39	0.81	0.67	0.95
18/LS3/BS9	110	30	1000	150	101		0.41			0.94
18/LS4/BS1	110	30	1000	165	108	1.18	0.44	0.74	0.63	0.91
18/LS3/BS16	110	10	1000	152	101	1.22	0.41	0.81	0.66	1.00
18/LS3/BS17	100	30	500	180	101	1.21	0.41	0.80	0.66	0.99
18/LS3/BS18*	100	30	500	190	95	1.23	0.39	0.84	0.68	1.01

* stretch ratio = 3.5

The data in Table 17 shows that reducing the stretching time from 30s to 10s and increasing the stretching speed from 1000%/min to 2000%/min also promote void-forming.

The presence of void-forming was demonstrated for the biaxially stretched film of EXAMPLE 18/LS1/BS1 by clamping the film in an Instron 4411 apparatus and observing the changes in film thickness and optical density upon contacting the film with a soldering iron for 5s at various temperatures. The results of these experiments are given in Tables 18 and 19.

A reduction in optical density at 150°C of 0.42 was observed for the film of EXAMPLE 18/LS1/BS1 corresponding to 25% accompanied by a reduction of 26% in layer thickness.

Table 18:

Invention Example nr	OD before heating	OD (TR924) after heating for 5s at a pressure of 0.5 N/mm^2 at					ΔOD at 150°C	% decrease in OD
		122°C	130°C	150°C	170°C	190°C		
18/LS3/BS1	1.36	1.18	1.12	1.02	0.82	0.72	0.42	25

Table 19:

EXAMPLE nr	Film thickness before heating [µm]	Film thickness [µm] after heating for 5s at a pressure of 0.5 N/mm^2 at				
		122°C	130°C	150°C	170°C	190°C
18/LS3/BS1	199	163	157	147	139	145

COMPARATIVE EXAMPLE 6 and INVENTION EXAMPLES 19 to 22

The ca. 1100 µm thick extrudates of COMPARATIVE EXAMPLE 6 and INVENTION EXAMPLES 19 to 22 all with 2% by weight of titanium dioxide and 15% by weight of SAN were produced as described for COMPARATIVE EXAMPLES 1 to 3 with 15% by weight of SAN or 15% by weight of ABS (MAGNUM 8391) and different weight ratios of PET02 and PET04 as summarized in Table 20.

Table 20:

Comparative example nr.	IPA: TPA ratio	PET02 [wt%]	PET04 [wt%]	MAGNUM 8391 [% by wt]	SAN 06 [wt%]	UVITEX OB-one [ppm]	TiO$_2$ [wt%]
6	0	83	0	15	-	-	2.0
Invention example nr.							
19	0.0401	32	51	-	15	100	2.0
20	0.0530	41.2	41.8	-	15	100	2.0

21	0.0650	32.3	50.7	-	15	100	2.0
22	0.1111	-	83	-	15	100	2.0

Stretching in the length direction was carried out for each extrudate as described in COMPARATIVE EXAMPLES 1 to 3 under the conditions given in Table 21. The expected thickness is the thickness based on the extrudate thickness and longitudinal as observed for non-voided films.

Table 21:

Comparative example nr.	IPA: TPA ratio	longitudinal stretch			Thickness		OD TR924	Expected OD	ΔOD	ΔOD/OD	OD [X-rite]
		ratio	force [N/mm^2]	temperature [°C]	Measured [µm]	Expected [µm]					
6/LS1	0	3.6	8	-	318	305	0.84	0.84	0.00		0.60
Invention example nr											
19/LS1	0.0401	3.6	8.23	114	330	305	1.26	0.84	0.42	0.33	0.96
20/LS1*	0.0530	3.3	7.97		375	333	1.08	0.87	0.21	0.19	0.96
20/LS2*	0.0530	3.3	7.14			333	0.948	0.87	0.078	0.08	0.86
20/LS3*	0.0530	3.3	9.67			333	1.19	0.87	0.32	0.27	1.09
21/LS1	0.0650	3.8	8.3	120	300	290		0.82			0.94
21/LS2	0.0650	3.6	8.23	96	330	305		0.84			0.96
21/LS3	0.0650	3.3	8.6	90	365	333		0.87			
21/LS4	0.0650	3.1	8.2	80	380	355		0.90			
22/LS1	0.1111	3.85	8	-	320	286	1.24	0.81	0.43	0.35	1.00

* stretching speed 4.0 m/min

Transversal stretching was then performed on the longitudinally stretched films with a stretch time of 30 s and stretching speed of 1000 %/min as under the conditions given in Table 22. The measured thickness, the expected thickness, i.e. thickness if no void-forming on the basis of the extrudate thickness and the longitudinal and transversal stretch ratios, the measured optical density with the MacBeth TR924 densitometer in transmission mode with a visible filter, the expected optical density, i.e. the optical density calculated using the relationship disclosed in COMPARATIVE EXAMPLE 4 using the theoretical layer thickness values, and the difference between the observed optical density and the optical density expected due to a 2% by weight concentration of the particular titanium dioxide pigment used, ΔOD, are also given in Table 22.

Table 22:

Comparative example nr.	IPA: TPA ratio	Transverse stretch		Density [g/mL]	Thickness		OD TR924	Expected OD	ΔOD	ΔOD/OD
		ratio	temperature °C		Measured [μm]	Expected [μm]				
6/LS1/BS1	0	3.3	112		65 85	88	0.73	0.36	0.37	0.50
Invention example nr										
19/LS1/BS1	0.0401	3.3	110		125	101	1.10	0.41	0.69	0.63
20/LS1/BS1	0.0530	3.5	115	1.19	140	95	0.925	0.39	0.535	0.58
20/LS1/BS2	0.0530	3.5	100	1.08	116	95	1.05	0.39	0.66	0.63
20/LS2/BS1	0.0530	3.5	100	1.17	123	95	1.01	0.39	0.62	0.61
21/LS1/BS1	0.0650	3.3	114		110	88	1.01	0.36	0.65	0.64
21/LS2/BS1	0.0650	3.3	113		135	93	1.17	0.38	0.69	0.59
21/LS3/BS1*	0.0650	3.5	111	1.132	140	95	1.20	0.39	0.81	0.67
21/LS4/BS1	0.0650	3.3	110		165	108	1.18	0.44	0.74	0.63
22/LS1/BS1	0.1111	3.3	110	1.121	100	87	1.20	0.35	0.85	0.71

* stretching speed of 2000 %/min

The increase in optical density due to void-forming clearly increased as IPA:TPA ratio in the linear polyester continuous phase increased from 0 for COMPARATIVE EXAMPLE 6/LS1/BS1 with a contribution of 50% to the optical density to 0.111 for INVENTION EXAMPLE 22/LS1/BS1 with a contribution of 71% to the optical density. The elasticity (Young's) modulus and yield stress of the biaxially stretched extrudates were measured for INVENTION EXAMPLES 20/LS1/BS1, 20/LS1/BS2 and 20/LS2/BS1 and the results are summarized in Table 23 below:

Table 23:

	Elasticity modulus [N/mm^2]		Yield stress [N/mm^2]	
	longitudinal direction	transversal direction	longitudinal direction	transversal direction
20/LS1/BS1	2908	4470	65.7	121
20/LS1/BS2	2594	3742	56.3	103.4
20/LS2/BS1	2965	4410	62.2	125.9

The presence of void-forming was demonstrated for the biaxially stretched film of COMPARATIVE EXAMPLE 6/LS1/BS1 by clamping the film in an Instron 4411 apparatus and observing the change in film thickness and optical density upon contacting the film with a soldering iron for 5s at 150°C. The results of these experiments are given in Table 24.

Table 24:

Comparative example nr	before heating		after heating at 150°C for 5s at pressure of 0.5 N/mm^2		ΔOD [%]	Change in thickness [μm]
	OD TR924	Thickness [μm]	OD (TR924)	thickness [μm]		
6/LS1/BS1	0.73	85	0.54	79	26	6

The presence of void-forming was demonstrated for the biaxially stretched films of INVENTION EXAMPLES 19/LS1/BS1 and 22/LS1/BS1 by clamping the films in an Instron 4411 apparatus and observing the changes in film thickness and optical density upon contacting the film with a soldering iron for 5s at various temperatures. The results of these experiments are given in Tables 25 and 26.

Reductions in optical density at 150°C of 0.19, 0.42 and 0.60 were observed for the films of COMPARATIVE EXAMPLE 6/LS1/BS1, INVENTION EXAMPLE 19/LS1/BS1 and 22/LS1/BS1 respectively corresponding to 26, 38 and 50%, again reflecting the impact of the IPA:TPA ratio being 0, 0.0401 and 0.111 respectively.

Table 25:

Invention example nr	OD before heating	OD (TR924) after heating for 5s at a pressure of 0.5 N/mm^2 at					ΔOD at 150°C	% decrease in OD
		122°C	130°C	150°C	170°C	190°C		
19/LS1/BS1	1.10	0.84	0.83	0.68	0.62	0.57	0.42	38
22/LS1/BS1	1.19	0.86	0.78	0.60	0.50	-	0.60	50

Table 26:

Invention example nr	Layer thickness before heating [μm]	Layer thickness [μm] after heating for 5s at a pressure of 0.5 N/mm^2 at				
		122°C	130°C	150°C	170°C	190°C
19/LS1/BS1	125	117	117	113	106	84
22/LS1/BS1	100	94	88	81	73	-

INVENTION EXAMPLES 23 to 25

The ca. 1100 μm thick extrudates of INVENTION EXAMPLES 23 to 25 of unpigmented dispersions of SAN 06 in aromatic polyester were produced as described for COMPARATIVE EXAMPLES 1 to 3 with different concentrations of SAN 06, TO4 and PET04 as summarized in Table 27.

Table 27:

Invention example nr	IPA:TPA ratio	PET02 [wt%]	PET04 [wt%]	SAN 06 [wt%]	Magnesium acetate [ppm]	UVITEX OB-one [ppm]
23	0.0314	57.7	25.3	17	-	100
24	0.0747	25.3	57.7	17	-	100
25	0.111	-	85.0	15	33	-

Stretching in the length direction was carried out for each extrudate as described in COMPARATIVE EXAMPLES 1 to 3 under the conditions given in Table 28. The expected thickness is the thickness observed for non-voided films.

Table 28:

Invention example nr.	IPA: TPA ratio	Longitudinal stretch			Thickness		OD TR924	Expected OD	ΔOD	ΔOD/ OD	OD [X-rite]
		ratio	force [N/mm^2]	temperature [°C]	Measured [µm]	Expected [µm]					
23/LS1	0.0314	3.8	8.21	175	301	289	0.80	0.05	0.75	0.94	0.47
23/LS2	0.0314	3.6	8.65	142	320	305	0.72	0.05	0.67	0.93	0.47
24/LS1	0.0747	3.8	8.44	116	298	289	0.97	0.05	0.92	0.95	0.77
24/LS2	0.0747	3.6	8.65	97	330	305	1.06	0.05	1.01	0.95	0.85
24/LS3	0.0747	3.35	6.36	119	320	328	0.78	0.05	0.73	0.93	0.60
25/LS1	0.1111	3.3	8.0	89			1.00	0.05	0.95	0.95	
25/LS2	0.1111	3.3	9.5	80			1.14	0.05	1.09	0.96	

The optical density values for INVENTION EXAMPLES 24/LS1, 24/LS2 and 24/LS3 clearly show the impact of the longitudinal stretching force with the highest optical density value of 1.06 being obtained with the film of INVENTION EXAMPLE 24/LS2 with the highest longitudinal stretching force of 8.65 N/mm^2 compared with 0.97 and 0.78 obtained with the films of INVENTION EXAMPLE 24/LS1 and 24/LS3 respectively with longitudinal stretching forces of 8.44 N/mm^2 and 6.36 N/mm^2 respectively.

The optical density values for INVENTION EXAMPLES 25/LS1 and 25/LS2 also show the impact of the longitudinal stretching force with the highest optical density value of 1.14 being obtained with the film of INVENTION EXAMPLE 25/LS2 with the higher longitudinal stretching force of 9.5 N/mm^2 compared with 1.00 obtained with the film of INVENTION EXAMPLE 25/LS2 with a longitudinal stretching force of 8.0 N/mm^2.

Transversal stretching was then performed on the longitudinally stretched films with a stretch time of 30s and stretching speed of 1000 %/min under the conditions given in Table 29. Table 29 also gives the measured thickness, the expected thickness, i.e. thickness if no void-forming on the basis of the extrudate thickness and the longitudinal and transversal stretch ratios, the measured optical density with the MacBeth TR924 densitometer in transmission mode with a visible filter, the expected optical density, i.e. 0.05 the optical density of polyethylene terephthalate being almost completely determined by refraction effects at the two sides of the film, and the difference between the observed optical density and the optical density expected due to the aromatic polyester, ΔOD.

Table 29:

Invention example nr.	IPA:TPA ratio	Transverse stretch		Thickness		OD TR924	Ex-pec-ted OD	ΔOD	ΔOD/ OD
		ratio	temper-ature [°C]	Meas ured [µm]	Expec-ted µm]				
23/LS2/BS1	0.0314	3.3	124	82	92	0.83	0.05	0.78	0.94
24/LS1/BS1	0.0747	3.3	120	97	88	0.99	0.05	0.94	0.95
24/LS2/BS1	0.0747	3.3	120	123	92	1.04	0.05	0.99	0.95
25/LS1/BS1	0.111	3.5	90	165	95	1.08	0.05	1.03	0.95
25/LS1/BS2	0.111	3.5	88	175	95	1.10	0.05	1.05	0.95
25/LS1/BS3	0.111	3.5	85	172	95	1.15	0.05	1.10	0.96
25/LS1/BS4	0.111	3.5	82	195	95	1.20	0.05	1.15	0.96
25/LS2/BS1	0.111	3.5	94	227	95	1.22	0.05	1.17	0.96
25/LS2/BS2	0.111	3.5	85	228	95	1.30	0.05	1.25	0.96
25/LS2/BS3	0.111	3.5	81	227	95	1.30	0.05	1.25	0.96
25/LS2/BS4	0.111	3.5	77	235	95	1.34	0.05	1.29	0.96
25/LS2/BS5	0.111	3.5	75	232	95	1.33	0.05	1.28	0.96

The results in Table 29 show strongly increased opacification optical densities of 1.28 and 1.29 due to void-forming for the films of INVENTION EXAMPLES 25/LS2/BS4 and 25/LS2/BS5 with a linear polyester matrix with an IPA:TPA ratio of 0.111 compared with an opacification optical density of 0.78 due to void forming for the film of INVENTION EXAMPLE 23/LS2/BS1 with a linear polyester matrix with an IPA:TPA ratio of 0.0314.

The presence of void-forming was demonstrated for the biaxially stretched films of INVENTION EXAMPLES 23/LS2/BS1, 24/LS1/BS1 and

24/LS2/BS1 and the INVENTION EXAMPLE 25 series by clamping the films in an Instron 4411 apparatus and observing the changes in film thickness and optical density upon contacting the film with a soldering iron for 5s at various temperatures. The results of these experiments are given in Tables 30 and 31.

Table 30:

Invention Example nr	OD before heating	OD (TR924) after heating for 5s at a pressure of 0.5 N/mm^2 at					ΔOD at 170°C	% decrease in OD
		122°C	130°C	150°C	170°C	190°C		
23/LS2/BS1	0.83	0.45	0.38	0.19	0.16	0.18	0.67	81
24/LS1/BS1	0.99	0.49	0.42	0.22	0.14	0.13	0.85	86
24/LS2/BS1	1.04	0.67	0.44	0.22	0.16	0.13	0.88	85
25/LS1/BS1	1.10 1.08	-	-	-	0.23 0.17	0.17 0.14	0.87 0.91	79 84
25/LS1/BS2	1.11	-	-	-	0.18	0.17	0.93	84
25/LS1/BS3	1.12	-	-	-	0.25	0.19	0.87	78
25/LS1/BS4	1.10	-	-	-	0.23	0.22	0.87	79
25/LS2/BS1	1.29	-	-	-	0.30	0.19	0.99	77
25/LS2/BS2	1.32 1.12	-	-	-	0.32 0.17	0.16 0.20	1.00 0.92	76 82
25/LS2/BS3	1.33	-	-	-	0.32	0.22	1.01	76
25/LS2/BS4	1.32	-	-	-	0.48	0.16	0.84	64
25/LS2/BS5	1.32	-	-	-	0.35	-	0.97	72

Table 31:

Invention Example nr	Film thickness before heating [µm]	Film thickness [µm] after heating for 5s at a pressure of 0.5 N/mm^2 at					Δ thickness at 170°C	% decrease in thickness
		122°C	130°C	150°C	170°C	190°C		
23/LS2/BS1	82	83	80	74	71	76	11	13
24/LS1/BS1	97	97	91	87	81	67	16	16
24/LS2/BS1	123	118	114	105	99	74	24	19
25/LS1/BS1	164 163	-	-	-	118 122	118 98	46 41	28 25
25/LS1/BS2	170	-	-	-	121	91	49	29
25/LS1/BS3	158	-	-	-	119	101	39	25
25/LS1/BS4	194	-	-	-	140	140	54	28
25/LS2/BS1	209	-	-	-	142	135	67	32
25/LS2/BS2	220	-	-	-	141	104	79	36
25/LS2/BS3	216	-	-	-	138	111	78	36
25/LS2/BS4	219	-	-	-	148	92	71	32
25/LS2/BS5	216	-	-	-	139	-	77	36

A reduction in optical density at 190°C of 0.67 was observed for the film of INVENTION EXAMPLE 23/LS2/BS1 corresponding to 81%, whereas reductions in optical density of 0.85 and 0.88 were observed for the films of INVENTION EXAMPLES 24/LS1/BS1 and 24/LS2/BS1 corresponding to 86 and 85% respectively. In the INVENTION 24 series the reduction in optical density at 190°C varied between 0.84 and 1.01 corresponding to 64 to 84%.

These reductions in optical density were accompanied by a reduction in layer thickness of 13% for the film of INVENTION EXAMPLE 23/LS2/BS1 and reductions of 16 and 19% in layer thickness for the films of INVENTION EXAMPLES 24/LS1/BS1 and 24/LS2/BS1 with 25 to 36% reduction in thickness being observed for the INVENTION EXAMPLE 25 series. These results show an extremely large reduction in optical density of up to 1.01 upon transparentizing polyester layers with 15 or 17 wt% SAN 06.

EXAMPLE 26

The ca. 1100 µm thick extrudate of EXAMPLE 26 with 2% by weight of titanium dioxide, 15% by weight of TPX® DX820, poly(4-methyl-pentene), 33.3% by weight of PET02 and 49.7% by weight of PET04 having an IPA:TPA molar ratio of 0.0636 was produced as described for EXAMPLES 1 to 58. Stretching in the length direction was carried out for each extrudate as described in EXAMPLES 1 to 58 under the conditions given in Table 32. The expected thickness is based on the extrudate thickness observed for non-voided films.

Table 32:

Example nr.	Longitudinal stretch			Density [g/mL]	Thickness		OD TR924	Expected OD	ΔOD	ΔOD/OD	OD [X-rite]
	Ratio	Force [N/mm^2]	Speed [m/min]		Measured [µm]	Expected [µm]					
26/BS1	3.3	5.21	4.0	1.147	500	333	1.10	0.87	0.23	0.21	0.96

Transversal stretching was then performed on the longitudinally stretched film with a stretch time of 30 s and stretching speed of 1000 %/min under the conditions given in Table 33. Table 33 also gives the measured thickness, the expected thickness, i.e. thickness if no void-forming on the basis of the extrudate thickness and the longitudinal and transversal stretch ratios, the measured optical density with the MacBeth TR924 densitometer in transmission mode with a visible filter, the expected optical density and the difference between the observed optical density and the optical density expected due to the aromatic polyester, ΔOD.

Table 33:

Example nr.	Transversal stretch		Density [g/mL]	Thickness		OD TR924	Expected OD	ΔOD	ΔOD/OD
	ratio	temperature [°C]		Measured [µm]	Expected [µm]				
26/LS1/BS1	3.5	100	0.64	270	95	1.08	0.39	0.69	0.64

The results in Table 33 clearly show very substantial opacification, 64% of the optical density realized being due to void-forming with a matrix of PET04 with TPX as crystalline dispersed phase with a particle size of ca. 10 µm. However, the elasticity (Young's) modulus in the longitudinal direction at 1258 N/mm^2 and the yield stress in the longitudinal direction at 26.4 N/mm^2 were substantially lower than for materials using SAN as opacity-producing agent, see results for INVENTION EXAMPLES 20/LS1/BS1, 20/LS1/BS2 and 20/LS2/BS1.

The present invention may include any feature or combination of features disclosed herein either implicitly or explicitly or any generalisation thereof. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

CLAIMS

1. A process for producing a non-transparent microvoided self-supporting film comprising the steps of: i) mixing at least one linear polyester having together monomer units consisting essentially of terephthalate, isophthalate and aliphatic dimethylene with the molar ratio of isophthalate monomer units to terephthalate monomer units being at least 0.02 to provide a linear polyester matrix; at least one amorphous high polymer with a higher glass transition temperature than the glass transition temperature of said linear polyester matrix and/or at least one crystalline high polymer having a higher melting point than the glass transition temperature of said linear polyester matrix; and optionally at least one ingredient from the group of ingredients consisting of inorganic opacifying pigments, whitening agents, UV-absorbers, light stabilizers, antioxidants, flame retardants and colorants in a kneader or an extruder; ii) forming the mixture produced in step i) in a thick film followed by quenching; iii) longitudinally stretching the thick film at a stretching force of > 4 N/mm^2 to at least twice the initial length; and iv) transversly stretching the longitudinally stretched film from step (iii) to at least twice the initial width.

2. The process according to claim 1, wherein said longitudinal stretching force is > 5 N/m^2.

3. The process according to claim 1 or 2, wherein said transverse stretching is performed with a force > 4 N/m^2.

4. The process according to any one of claims 1 to 3, wherein said transverse stretching temperature is no more than 40°C above the glass transition temperature of the linear polyester matrix.

5. The process according to any one of claims 1 to 4, wherein said molar ratio of isophthalate monomer units to terephthalate monomer units is at least 0.065.

6. The process according to any one of claims 1 to 5, wherein said molar ratio of isophthalate monomer units to terephthalate monomer units is at least 0.11.

7. The process according to any one of claims 1 to 6, wherein said molar ratio of isophthalate monomer units to terephthalate monomer units is 0.50 or less.

8. The process according to any one of claims 1 to 7, wherein the concentration of said uniformly dispersed amorphous high polymer or said crystalline high polymer in said film is 5 to 35% by weight.

9. The process according to any one of claims 1 to 8, wherein said uniformly dispersed amorphous high polymer is crosslinked or non-crosslinked.

10. The process according to any one of claims 1 to 9, wherein said amorphous high polymer comprises at least one chain-polymerized block.

11. The polymeric film according to claim 10, wherein said at least one chain-polymerized block is selected from the group consisting of polystyrene, styrene copolymers, SAN-polymers, polyacrylates, acrylate-copolymers, polymethacrylates and methacrylate-copolymers.

12. The process according to claim 11, wherein said styrene copolymers are selected from the group consisting of SAN-polymers and ABS-polymers.

13. The process according to claim 12, wherein the concentration of AN-monomer units in said SAN-polymer is 15 to 35% by weight.

14. The process according to claim 12 or 13, wherein the weight ratio of said linear polyester to said SAN-polymer is in the range of 2.0:1 to 9.0:1.

15. The process according to any one of claims 1 to 14, wherein said amorphous high polymer is exclusive of a cellulose ester.

16. The process according to any one of claims 1 to 15, wherein said at least one inorganic opacifying pigment is selected from the group consisting of silica, zinc oxide, zinc sulphide,

lithopone, barium sulphate, calcium carbonate, titanium dioxide, aluminium phosphate and clays.

17. The process according to any one of claims 1 to 16, wherein said film comprises ≤ 5% by weight of inorganic opacifying pigment.

18. The process according to any one of claims 1 to 17, wherein said linear polyester matrix comprises at least two linear polyester resins.

19. A process for obtaining a transparent pattern comprising the step of: image-wise application of heat optionally supplemented by the application of pressure to a non-transparent microvoided biaxially stretched self-supporting film produced by a process comprising the steps of: i) mixing at least one linear polyester having together monomer units consisting essentially of terephthalate, isophthalate and aliphatic dimethylene with the molar ratio of isophthalate monomer units to terephthalate monomer units being at least 0.02 to provide a linear polyester matrix; at least one amorphous high polymer with a higher glass transition temperature than the glass transition temperature of said linear polyester matrix and/or at least one crystalline high polymer having a higher melting point than the glass transition temperature of said linear polyester matrix; and optionally at least one ingredient from the group of ingredients consisting of inorganic opacifying pigments, whitening agents, UV-absorbers, light stabilizers, antioxidants, flame retardants and colorants in a kneader or an extruder; ii) forming the mixture produced in step i) in a thick film followed by quenching; iii) longitudinally stretching the thick film at a stretching force of > 4 N/mm^2 to at least twice the initial length; and iv) transversly stretching the longitudinally stretched film from step (iii) to at least twice the initial width.

20. Use of the non-transparent microvoided self-supporting film produced according to any one of claims 1 to 18 as a synthetic paper.

21. Use of the non-transparent microvoided self-supporting film produced according to any one of claims 1 to 18 in image recording elements.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/060373

A. CLASSIFICATION OF SUBJECT MATTER
INV. G03C1/795 B41M5/41 B41M5/50 C08J5/18 C08L67/02

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G03C B41M C08J C08L B29C

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 457 018 A1 (SOMMER KLAUS [US] ET AL) 10 October 1995 (1995-10-10) cited in the application abstract column 1, line 48 - line 52 column 3, line 54 - line 60 column 4, line 66 - column 5, line 55 claims 1-10; examples 7-10 -----	1-18,20, 21
A	JP 09 255806 A (TOYO BOSEKI) 30 September 1997 (1997-09-30) paragraph [0005] - paragraph [0006] abstract -----	1-18,20, 21
A	JP 2004 196951 A (MITSUBISHI ENG PLASTIC CORP) 15 July 2004 (2004-07-15) paragraphs [0001], [0006], [0007], [0015], [0020] ----- -/--	1-18,20, 21

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Date of the actual completion of the international search 29 February 2008	Date of mailing of the international search report 06/03/2008
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Bolger, Walter

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004/167022 A1 (LANEY THOMAS M [US] ET AL) 26 August 2004 (2004-08-26) abstract paragraphs [0001], [0031], [0032], [0075], [0076] -----	1-18,20, 21

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2007/060373

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US 5457018	A1		NONE			
JP 9255806	A	30-09-1997	NONE			
JP 2004196951	A	15-07-2004	NONE			
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			EP	1452336	A1	01-09-2004
			JP	2004255882	A	16-09-2004

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INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. G03C1/795 B41M5/41 B41M5/50 C08J5/18 C08L67/02

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G03C B41M C08J C08L B29C

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

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

EPO-Internal, WPI Data

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A	JP 09 255806 A (TOYO BOSEKI) 30 September 1997 (1997-09-30) paragraph [0005] - paragraph [0006] abstract	1-18,20, 21
A	JP 2004 196951 A (MITSUBISHI ENG PLASTIC CORP) 15 July 2004 (2004-07-15) paragraphs [0001], [0006], [0007], [0015], [0020]	1-18,20, 21

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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Bolger, Walter

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004/167022 A1 (LANEY THOMAS M [US] ET AL) 26 August 2004 (2004-08-26) abstract paragraphs [0001], [0031], [0032], [0075], [0076] -----	1-18,20, 21

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2007/060373

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