

DESCRIPTION

Title of Invention: LAMINATED POLYESTER FILM

Technical Field

[0001]

The present invention relates to a laminated polyester film. More specifically, the present invention relates to a laminated polyester film suitable for use in ultrafine-line photoresist, the film exhibiting excellent transparency and slipperiness, being free of scratches, enabling the formation of a photoresist layer with excellent resolution and pattern formability on surfaces and edges, and exhibiting excellent abrasion resistance and antistatic properties, as well as high suitability for lamination processing.

Background Art

[0002]

Polyester films, represented by polyethylene terephthalate and polyethylene naphthalate, have been widely used in various applications due to their excellent properties, such as mechanical strength, dimensional stability, flatness, heat resistance, chemical resistance, and optical characteristics, as well as excellent cost efficiency.

[0003]

One example of an application of polyester films is their use as film in a dry film resist process, such as during the manufacturing of flexible printed circuit boards. A dry film resist typically has a three-layer structure composed of a substrate film, a photosensitive resin layer, and a protective film. As the substrate film, a polyester film with excellent mechanical properties, optical properties, chemical resistance, heat resistance, dimensional stability, flatness, etc., is used. An example of its use is briefly described. First, a protective film is peeled off, and an exposed photosensitive resin layer is brought into close contact with a conductive substrate attached

to a board. Subsequently, a glass plate or film on which a circuit pattern (referred to as a "photomask") is printed is brought into close contact with the substrate film side, and light is irradiated from the photomask side. Ultraviolet light is generally used as the exposure light. Light passes through the transparent portions of the circuit pattern printed on the photomask, and the photosensitive resin reacts only in the regions exposed to the ultraviolet light. The glass plate and the substrate film are removed, and the unexposed portions of the photosensitive resin layer, which have not been irradiated with ultraviolet light, are removed by using an appropriate solvent or the like. Further, by performing etching using an acid or the like, the photosensitive resin layer is removed, and a conductive substrate layer is formed into a circuit.

[0004]

Recently, due to increasing demand for high reproducibility and high resolution in circuit pattern formation, the circuits on printed wiring boards have become extremely complex, with finer wires and narrower spacing between the wires. When the photoresist layer in a photoresist film is exposed, the light passes through a support (substrate film) as stated above. Therefore, if the transparency of the support is low, problems arise, such as insufficient exposure of the photoresist layer or deterioration in resolution due to light scattering. Accordingly, it is important that the polyester film used as the support has low haze and excellent transparency. Further, if scratches are present on the film surface, transmitted light may be scattered, leading to problems such as lower resolution. Therefore, the film surface is required to be free of scratches.

[0005]

Polyester films with a smooth surface, high transparency, and low haze tend to exhibit poor handling properties in, for example, a film production step and a film winding step. When such film in the form of a roll is used, scratches are likely to occur on the surface, and air trapped

between the films during winding is difficult to release, leading to problems such as wrinkles.

[0006]

In order to improve the handling properties when a photoresist layer is formed on a support to produce a photoresist film, or to enhance the handling properties of the obtained photoresist film itself, it is important that the polyester film used as a support has appropriate slipperiness. Further, during the production of printed wiring boards, air releasability is also required in order to prevent problems, such as impaired reproducibility of the circuit pattern, due to the formation of air bubbles between the support and the glass plate having a circuit pattern formed thereon.

[0007]

To meet these market demands, a method comprising incorporating particles into a polyester film to form fine protrusions on the surface has been used. Many techniques, such as particle-blending techniques, multilayer film techniques, and their combinations, have been disclosed to form protrusions on the film surface (see, for example, Patent Literature (PTL) 1 to PTL 10). Further, PTL 3 and PTL 4 disclose techniques in which an antistatic agent is incorporated in order to improve handling properties during the production of a polyester film for photoresist and also to prevent the adhesion of dust and foreign matter, as well as to improve the handling properties of the photoresist film itself, which is produced using the polyester film.

[0008]

The techniques described above have been improving the handling properties of polyester film while maintaining transparency. In particular, the techniques disclosed in PTL 3 and PTL 4 teach incorporating particles only into a thin surface layer formed on a polyester film support, with the particle content being suppressed to a low level, and the obtained film exhibits excellent transparency and antistatic properties and has

excellent optical characteristics as a polyester film for ultrafine-line photoresist, thus attracting attention.

[0009]

However, the conventional techniques, including the techniques mentioned above, have been designed by focusing on handling properties, mainly on film slipperiness, and abrasion resistance of the film during film processing have not been taken into consideration. As a result, for example, the following problem has become apparent. In a process in which a composite film comprising a resist layer laminated on a photoresist film is laminated onto a wiring substrate, friction between the composite film and the film-holding device for cutting to match the wiring substrate's dimensions can cause scratches on the surface of the composite film opposite the resist layer. These scratches reduce the light transmittance of the composite film, thus leading to decreased resist resolution.

[0010]

Further, other problems have also become apparent. Specifically, in the lamination process, friction with the rolls used to press the composite film onto the wiring substrate causes scratches on the film surface, and contamination of the composite film occurs due to resin powder generated by the scratches. Accordingly, there has been a strong demand for the development of a polyester film for ultrafine-line photoresist that exhibits improved abrasion resistance while maintaining transparency and handling properties.

[0011]

In order to solve such problems, PLT 11 discloses a technique in which a resin composition layer containing silica particles is formed on the surface of a laminated polyester film opposite to the resist layer side and the thickness of the resin composition layer is increased to prevent particle detachment, thereby enhancing the abrasion resistance.

Citation List

Patent Literature

[0012]

PTL 1: JPH10-46012A

PTL 2: JPH10-128930A

PTL 3: JP2000-221688A

PTL 4: JP2001-117237A

PTL 5: JP2002-60598A

PTL 6: JP2002-62661A

PTL 7: JP2002-72486A

PTL 8: JP2002-278072A

PTL 9: JP2002-341546A

PTL 10: JP2003-43691A

PTL 11: JP2006-327158A

PTL 12: JP2019-143132A

Summary of Invention

Technical Problem

[0013]

As described above, further improvement in properties was required for the techniques disclosed in PTL 1 to PTL 10 to be usable as polyester films for ultrafine-line photoresist. To solve this problem, the techniques disclosed in PTL 11 and 12 were developed.

[0014]

However, the required level of abrasion resistance has become even higher, and further improvements are being required. Further, as shown in PTL 12, a polyester film for dry film resist substrates that substantially contains no particles with a size larger than 1 μm may be prone to film blocking under specific resist formation conditions, such as UV irradiation.

[0015]

The present invention has been made in view of such problems in the prior art. Specifically, an object of the present invention is to provide a laminated polyester film with excellent abrasion resistance and transparency, as well as excellent

suitability for processing, such as workability and ease of sliding, when the film is wound into a roll.

Solution to Problem

[0016]

As a result of a variety of study to achieve the above object, the present inventors found that the above problems can be solved by a film having a specific structure and components, and have accomplished the present invention.

[0017]

Specifically, the present invention includes the following.

[0018]

[1]

A laminated polyester film comprising
a polyester film and
a functional layer formed on at least one surface of
the polyester film,
wherein

the air release index (mm H₂O) of the surface having
the functional layer is 493 mm H₂O or less, and

the number of coarse particles with a shortest diameter
of 3 μm or more present per 1 mm² on the surface having the
functional layer is 250 or fewer.

[0019]

[2]

The laminated polyester film according to [1], having a
haze of 1.0% or less.

[0020]

[3]

The laminated polyester film according to [1] or [2],
wherein at least one surface of the laminated polyester film has
a logarithm of surface resistivity ($\Omega/\square$) ($\log(\Omega/\square)$) of 13 or less
as measured at a temperature of 23°C and a humidity of 65% RH.

[0021]

[4]

The laminated polyester film according to any one of [1] to [3], wherein the functional layer contains particles, and the particles have a D50 of 1 μ m or less and have a D90/D50 ratio of 3 or less.

[0022]

[5]

The laminated polyester film according to any one of Items [1] to [4], which is for ultrafine-line photoresist.

[0023]

[6]

A support for ultrafine-line photoresist, comprising the laminated polyester film of any one of Items [1] to [4].

[0024]

[7]

An ultrafine-line photoresist film comprising the laminated polyester film of any one of Items [1] to [4].

Advantageous Effects of Invention

[0025]

The laminated polyester film of the present invention is suitable for use as a polyester film for ultrafine-line photoresist. This is because the polyester film of the present invention exhibits excellent transparency, slipperiness, antistatic properties, and abrasion resistance, has no scratches on its surface, and is thus suitable as a support for ultrafine-line photoresist films. A photoresist film using the polyester film for ultrafine-line photoresist of the present invention as a support exhibits excellent resolution of the photoresist layer, excellent pattern formability on surfaces and edges, and excellent adhesion of the photoresist layer. Furthermore, due to excellent handling properties and durability, such as blocking resistance and abrasion resistance, during the production of a photoresist film using the polyester film for ultrafine-line photoresist of the present invention as a support, the polyester

film also exhibits excellent suitability for processing, such as lamination processing, and is therefore useful for industrial applications.

[0026]

Furthermore, since the air release index of the surface having the functional layer satisfies the predetermined conditions, air entrapped when the film is wound into a roll can readily escape, allowing the film to be wound with rolls of the film in close contact with each other. Furthermore, for example, misalignment in the winding core direction during storage or transportation can be prevented, thereby preventing scratches caused by misalignment or the like.

Description of Embodiments

[0027]

In the present specification, the term "comprising" is used to include the meaning of "consisting essentially of" and "consisting of."

[0028]

In the present specification, the symbol "-" or the word "to" in a numerical range means "equal to or more than the left-end value" and "equal to or less than the right-end value." For example, "0.5-10 wt%" and "0.5 wt%-10 wt%" or "0.5 to 10 wt%" and "0.5 wt% to 10 wt%" all mean "0.5 wt% or more and 10 wt% or less." In terms of numerical ranges, "or more" means "equal to or more than," and "or less" means "equal to or less than."

[0029]

In the numerical ranges described stepwise in the present specification, the upper or lower limit of a numerical range of a certain stage may be freely combined with the upper or lower limit of a numerical range of another stage described in the same paragraph. Further, in the numerical ranges described in the present specification, the upper or lower limit of a given numerical range may be replaced with a value shown in the Examples or a value that can be unambiguously derived from the

Examples.

[0030]

Polyester Film Substrate

Preferable examples of the polyester film constituting the laminated polyester film of the present invention (preferably the polyester film for ultrafine-line photoresist) (which may be simply referred to below as "main-layer film") include biaxially oriented polyester films having a thickness of 12 to 25 μm , the films being mainly composed of a polyester-based resin comprising an aromatic linear polyester comprising an aromatic dicarboxylic acid and a diol, such as polyethylene terephthalate and polyethylene naphthalate, an aliphatic linear polyester comprising an aliphatic dicarboxylic acid and a diol, or a copolymer thereof. A film comprising an aromatic linear polyester resin, such as polyethylene terephthalate or polyethylene naphthalate, is preferred among such films. The main layer film of the present invention can be formed from one or a mixture of two or more of the aforementioned polyester resins. The main-layer film may be either a single-layer or a multilayer film composed of two or more layers. The film preferably has a thickness of 12 to 25 μm , more preferably 13 to 20 μm , and still more preferably within the range of 14 to 20 μm . When the film has a thickness of 12 to 25 μm , high resolution and excellent strength are achieved, and tearing is less likely to occur during peeling operations.

[0031]

The catalyst used for the polycondensation in the production of the polyester resin is not particularly limited. Antimony trioxide is preferred because it is inexpensive and exhibits excellent catalytic activity. It is also preferable to use a germanium compound or a titanium compound. More preferred polycondensation catalysts include catalysts containing aluminum and/or an aluminum compound and a phenolic compound, catalysts containing aluminum and/or an aluminum compound and a phosphorus compound, and catalysts containing an aluminum salt of a

phosphorus compound.

[0032]

The polyester film substrate used in the present invention is not particularly limited in its layer structure. The polyester film substrate may be a single-layer polyester film, a two-layer structure wherein the two layers are different in composition, or a polyester film substrate comprising at least three layers comprising outer layers and an inner layer.

[0033]

The air release index (mm H₂O) of at least one surface of the laminated polyester film of the present invention is 493 mm H₂O or less, more preferably 492 mm H₂O or less, still more preferably 490 mm H₂O or less, and particularly preferably 488 mm H₂O or less.

[0034]

When the air release index is 493 mm H₂O or less, air trapped during winding of the film into a roll can readily escape, allowing the films to be wound in close contact with each other. This can prevent misalignment in the winding core direction during storage or transport, thereby avoiding scratches caused by such misalignment or the like.

[0035]

The air release index is preferably 450 mm H₂O or more, for example, 460 mm H₂O or more, and may be 465 mm H₂O or more, for example, 470 mm H₂O or more. The air release index may be, for example, 450 to 493 mm H₂O, 460 to 493 mm H₂O, 465 to 493 mm H₂O, 470 to 493 mm H₂O, 450 to 492 mm H₂O, 460 to 492 mm H₂O, 465 to 492 mm H₂O, 470 to 492 mm H₂O, 450 to 490 mm H₂O, 460 to 490 mm H₂O, 465 to 490 mm H₂O, 470 to 490 mm H₂O, 450 to 488 mm H₂O, 460 to 488 mm H₂O, 465 to 488 mm H₂O, or 470 to 488 mm H₂O.

[0036]

Although a lower air release index is preferred, an index of 450 mm H₂O or higher can inhibit the complete release of air entrapped during film winding into a roll, thereby enhancing tight film-to-film contact and reducing the risk of blocking.

[0037]

The laminated polyester film of the present invention has an appropriate air release index. Therefore, the laminated polyester film can be transported and retained without collapsing the layer structure.

[0038]

The present invention can suppress the collapse of the layer structure during storage and transport as a film roll, and therefore can perform more uniform exposure in photoresist layer exposure. As a result, it becomes possible to form a photoresist layer that has excellent resolution and excellent pattern formability on surfaces and edges.

[0039]

In the present invention, the expression "can suppress the collapse of the layer structure" refers to, for example, a state in which deformation in the thickness direction of the laminated film is low, a state in which changes in film thickness unevenness before and after winding is minimal, a state in which the polyester film and the functional layer are uniformly adhered to each other without undergoing deformation, or a state in which deformation in the thickness direction of the functional layer is minimal and the number of coarse particles described in the present invention falls within a predetermined range.

[0040]

Although interpretation should not be limited to a specific theory, it is speculated, for example, that the present invention can suppress the localized presence of air in film rolls, thereby suppressing the collapse of the film's layer structure caused by uneven air distribution during winding.

[0041]

In this way, the layer structure can be maintained before and after winding the film, allowing for uniform exposure and avoiding exposure unevenness caused by thickness changes in the laminated film during the photoresist layer exposure. Therefore, the present invention is suitable for use in polyester

films for ultrafine-line photoresists.

[0042]

The air release index can be determined by the measurement method described in the Examples below.

[0043]

The means for obtaining the air release index of the present invention includes, for example, forming a resin composition layer on the surface of the film opposite to the surface on which the resist layer is laminated, wherein the resin composition layer contains 5 to 20 mass% of particles (a) having an average particle size of 0.01 to 0.1 μm and 0.1 to 1 mass% of particles (b) having a 50% volume particle size (D50) of 0.3 to 1 μm and producing the film in such a manner that, after coating with the resin composition by wet coating, the coated surface is transported directly into a drying oven without being brought into contact with the rolls, thereby suppressing the collapse of protrusions formed by the particles.

[0044]

The layer formed using the above resin composition layer is the functional layer of the present invention.

[0045]

Even after exposure of the photoresist layer, the present invention can suppress collapse of the layer structure during the storage or transportation of the film as a film roll. Therefore, since blocking of the film can be inhibited even after exposure, the laminated polyester film allows for easy separation of the functional layer from the polyester film using known techniques, and has excellent recyclability.

[0046]

The upper limit of the haze of the laminated polyester film of the present invention is preferably 1.0%, more preferably 0.9%, and still more preferably 0.8%. When the haze is 1.0% or less, good resolution tends to be obtained.

[0047]

Although a smaller haze is preferred, the haze is, from

a practical standpoint, 0.01% or more, and, for example, 0.05% or more. The haze may be, for example, 0.01 to 1.0%, 0.05 to 1.0%, 0.01 to 0.9%, 0.05 to 0.9%, 0.01 to 0.8%, or 0.05 to 0.8%.

[0048]

The logarithm of the surface resistivity ($\Omega/\square$) at 23°C and 65% RH on the surface of the film opposite to the surface on which the resist layer of the laminated polyester film of the present invention is laminated, that is, on the functional layer surface of the laminated polyester film, may be 13 or less. The logarithm of the surface resistivity is preferably 12 or less, and more preferably 11 or less.

[0049]

The logarithm of the surface resistivity ($\Omega/\square$) may be 7 or more, and, for example, 9 or more. The logarithm of the surface resistivity ($\Omega/\square$) may be, for example, 7 to 13, 9 to 13, 7 to 12, 9 to 12, 7 to 11, or 9 to 11.

[0050]

By setting the logarithm of the surface resistivity to 13 or less, excessive charging of the polyester film can be suppressed, resulting in good handling properties in the step of producing the main-layer film and during the production of a photoresist film using the polyester film as a support. For example, adhesion of dust and foreign matter can be reduced, and the handling properties of the photoresist film itself, which is produced using the polyester film for photoresist of the present invention as a support, can be maintained satisfactorily.

[0051]

The upper limit of the coefficient of static friction of one surface and the opposite surface of the laminated polyester film of the present invention is preferably 0.8, more preferably 0.7. By setting the coefficient of static friction to 0.8 or less, a laminated polyester film in which scratches are less likely to occur in the winding step can be obtained. As for the friction coefficient, addition of particles to the functional layer can impart slipperiness while maintaining transparency.

Although a smaller static friction coefficient is preferred, the friction coefficient of the laminated polyester film is usually 0.1 or more. The static friction coefficient may be, for example, 0.1 to 0.8 or 0.1 to 0.7. The static friction coefficient can be determined by the measurement method described in the Examples below.

[0052]

The number of coarse particles with a shortest diameter of 3 μm or more present per 1 mm^2 of the functional layer, i.e., on the surface of the laminated polyester film of the present invention opposite to the surface on which the resist layer is laminated, is 250 or less, more preferably 200 or less, still more preferably 150 or less, and particularly preferably 100 or less.

[0053]

When the number of coarse particles with a shortest diameter of 3 μm or more present per 1 mm^2 of the functional layer is 250 or less, the occurrence rate of poor exposure during photoresist layer exposure can be reduced. The number of coarse particles can be determined by the measurement method described in the Examples below.

[0054]

On the other hand, the number of coarse particles with a shortest diameter of 3 μm or more present per 1 mm^2 of the functional layer may be 0 or more, but is preferably 5 or more, and may be 10 or more in order to satisfy the air release index according to the present invention. By satisfying such conditions of the lower limit, blocking can be inhibited while enhancing tight film-to-film contact. The number of coarse particles with a shortest diameter of 3 μm or more present per 1 mm^2 of the functional layer can be, for example, 0 to 250, 0 to 200, 0 to 150, 0 to 100, 5 to 250, 5 to 200, 5 to 150, 5 to 100, 10 to 250, 10 to 200, 10 to 150, or 10 to 100.

[0055]

A preferred embodiment of the method of imparting the

properties described above is that a resin composition layer containing 5 to 20 wt% of particles (a) having an average particle size of 0.01 to 0.1 μm , 0.1 to 1 wt% of particles (b) having a 50% volume particle size (D50) of 0.3 to 1 μm , 1 to 3 wt% of a wax agent, and 1 to 10 wt% of an antistatic agent is laminated on the surface of the film opposite to the surface on which the resist layer is laminated. According to this embodiment, while maintaining high transparency, which is important for achieving high resolution expression of photoresist, handling properties and abrasion resistance of the polyester film for ultrafine-line photoresist and a composite film in which a resist layer is combined with the polyester film for ultrafine-line photoresist can be easily improved.

[0056]

For details on the 50% volume particle size D50, for example, the description in JP 2015-174383A can be referred to.

[0057]

The resin used to form the resin composition layer can be freely selected as long as it is transparent, capable of fixing the particles, wax, antistatic agent, etc. onto the polyester film surface, and resistant to abrasion. In a preferred embodiment, the resin to be used is at least one resin selected from the group consisting of polyester resins, polyurethane resins, acrylic resins, amino resins, epoxy resins, and oxazoline resins. The resin may be either a commercially available product or a custom-made product having a specific composition. Further, the resin may be a non-crosslinked product or a crosslinked product. The type of crosslinking agent is also not limited. Furthermore, the resin is used in the form of a solution or dispersion in an organic solvent or a solution or dispersion in an aqueous solvent. In particular, a dispersion in an aqueous solvent, that is, the form of a water-dispersed resin, is preferred from the viewpoints of working environment and coatability.

[0058]

In the present invention, two types of particles having different average particle sizes in the resin composition layer are preferably used as the particles contained in the resin composition layer because this enables improvement of slipperiness and abrasion resistance while maintaining transparency.

It is more preferable that the particles (a) contain colloidal silica with an average particle size of 0.02 to 0.08 μm in an amount of 7 to 17 mass%, based on the amount of the resin component. It is even more preferable to incorporate colloidal silica with an average particle size of 0.03 to 0.06 μm in an amount of 5 to 14 mass%.

[0059]

The colloidal silica is usually a colloidal dispersion in which ultrafine particles of anhydrous silicic acid (silica) are stably dispersed in water. It is supplied to the market under brand names such as DuPont's Ludox and Nissan Chemical's Snowtex. Various methods for producing such colloidal silica are known, but the methods using ion exchange resins are generally used for the production. Specifically, colloidal silica is produced by a method in which an aqueous sodium silicate solution is passed through a cation exchange resin to form a sol, which is then heated and aged at 60°C or higher to grow into independently dispersed particles, to which a sol that has been newly passed through an ion exchange resin composition layer is added to cause polymerization and precipitation, thereby allowing for particle size growth and forming a stabilized sol. Such a colloidal silica sol may be either organic-solvent-based or water-dispersed, and it may be appropriately selected according to the solvent used for dissolving or dispersing the resin described above. In addition, such a sol may be in an alkali-stabilized form or an acid-stabilized form, and such selection may also be appropriately made depending on the type of resin or radiation crosslinking agent used.

[0060]

The upper limit of the 50% volume particle size D50 of the particles (b) is preferably 1 μm , more preferably 0.9 μm , and still more preferably 0.8 μm . When the 50% volume particle size D50 is 1 μm or less, the amount of coarse particles of 3 μm or larger per 1 mm^2 on the surface of the film opposite to the surface on which the resist layer of the laminated polyester film is laminated can be reduced, and abrasion resistance can also be improved. The lower limit of the 50% volume particle size D50 is preferably 0.35 μm , more preferably 0.4 μm , and still more preferably 0.5 μm . When the 50% volume particle size D50 is 0.5 μm or more, the air release index can be reduced. The 50% volume particle size D50 of the particles (b) may be, for example, 0.4 to 1 μm , 0.5 to 1 μm , 0.4 to 0.9 μm , 0.5 to 0.9 μm , 0.4 to 0.8 μm , or 0.5 to 0.8 μm .

[0061]

The upper limit of the ratio of the 90% volume particle size (D90) to the 50% volume particle size (D50) of the particles (b), D90/D50, is preferably 3. When the ratio of 90% volume particle size D90 to 50% volume particle size D50 is 3 or less, it is possible to achieve both a reduction in the amount of coarse particles of 3 μm or more per 1 mm^2 on the surface of the film opposite to the surface on which the resist layer of the laminated polyester film is laminated and a reduction in air release index. The ratio of 90% volume particle size D90 to 50% volume particle size D50 may be, for example, in the range of 1.0 to 3.0, or 1.0 to 2.0.

[0062]

Further, the particles (b) are preferably organic particles.

[0063]

The wax agent is not particularly limited as long as it does not impair transparency, and known wax agents may be used. However, it is more preferable to use a polymer-based wax component. Examples include polyethylene-based, polypropylene-based, and fatty acid-based waxes, with polyethylene-based wax

agents being particularly preferred. The weight average molecular weight of these wax components is preferably 1,000 to 10,000, and more preferably in the range of 1,500 to 6,000. If the molecular weight is less than 1,000, transfer contamination is likely to occur due to bleeding from the interior of the resin composition layer to the surface. If the molecular weight exceeds 10,000, the effect of improving slipperiness becomes insufficient. The amount of these wax components relative to the resin component is more preferably 1 to 10 mass%, even more preferably 1.2 to 8 mass%, and particularly preferably 2 to 5 mass%. By incorporating the two types of particles having different particle sizes and wax into the resin component at the blending ratio mentioned above, it is possible to maintain a high level of transparency and impart slipperiness and abrasion resistance, thereby easily imparting characteristics that should be possessed as the polyester film for ultrafine-line photoresist.

[0064]

The antistatic agent is a compound used for the purpose of imparting antistatic properties. Examples include polymeric antistatic agents composed of one or more polymers of unsaturated monomers having a sulfonate group (e.g., sodium vinylsulfonate, sodium methallylsulfonate, sodium styrenesulfonate, ammonium vinylsulfonate, potassium methacrylsulfonate, and lithium styrenesulfonate), and low-molecular-weight antistatic agents of the formula $R-SO_3X$ (wherein R represents an alkyl group, an aryl group, or an aromatic group having an alkyl group, and X represents a metal ion (such as Li, Na, or K), an ammonium ion, an amine ion, or a phosphate ester ion), as well as their dimers. However, the antistatic agent is not limited to these compounds, and any antistatic agent can be used as long as it possesses a sulfonate group having excellent heat resistance and functions to exhibit antistatic properties. Using a low-molecular-weight antistatic agent is more preferable to efficiently exhibit antistatic properties.

[0065]

Examples of alkyl sulfonates include sodium pentanesulfonate, sodium octanesulfonate, lithium octanesulfonate, potassium octanesulfonate, and sodium tetradecylsulfonate.

[0066]

Examples of aryl sulfonates include sodium benzylsulfonate, sodium toluenesulfonate, and sodium naphthylsulfonate. Examples of aromatic sulfonates having an alkyl group include metal salts (e.g., Li, K, or Na salts) of (C₈-C₂₀) alkyl benzenesulfonic acid, such as sodium dodecylbenzenesulfonate, as well as sodium alkyl naphthalenesulfonate and sodium alkylphenyl ether disulfonate.

[0067]

As the polymeric antistatic agent comprising a polymer of an unsaturated monomer having a sulfonate group, it is preferable to use, for example, a styrenic resin containing a sulfonate group component in the molecule, such as polystyrene sulfonate.

[0068]

A feature of the polymeric antistatic agent lies in high hydrophilicity of the sulfonic acid component. Examples of styrenic resins containing a sulfonate group component in the molecule include homopolymers, such as sodium salts, potassium salts, lithium salts, ammonium salts, and phosphonium salts of polystyrene sulfonic acid, and copolymers of an acrylic monomer, such as acrylic acid esters or methacrylic acid esters with a styrene sulfonic acid monomer. For example, it is preferable to use a styrenic resin containing a sulfonate group component in the molecule, such as polystyrene sulfonate. The polystyrene sulfonate preferably has a weight average molecular weight of 1,000 to 150,000, and more preferably 10,000 to 70,000. When the molecular weight is less than 1,000, it becomes difficult for the coating film to have sufficient water resistance. When the molecular weight exceeds 150,000, uniform mixing with the copolyester tends to become difficult.

[0069]

The amount of the antistatic agent relative to the resin component is preferably 2 to 9 mass%, and more preferably 3 to 8 mass%. Less than 1 mass% of the antistatic agent results in poor antistatic properties, thus being not preferable. On the other hand, if the amount of the antistatic agent exceeds 10 mass%, the effect of improving antistatic properties becomes saturated, and the antistatic agent contaminates rolls etc. used in the film production step and processing step, which is undesirable.

[0070]

Since the wax agent and antistatic agent tend to segregate on the film surface, their blending ratio affects antistatic properties, slipperiness, and abrasion resistance. When the total amount of the wax agent and the antistatic agent is defined as 100 mass%, the upper limit of the amount of the wax agent is preferably 80 mass%, more preferably 70 mass%, and particularly preferably 60 mass%. By setting the amount of the wax agent to 80 mass% or less, slipperiness and abrasion resistance derived from the wax agent can be exhibited. When the total amount of the wax agent and the antistatic agent is defined as 100 mass%, the lower limit of the amount of the antistatic agent is preferably 10 mass%, more preferably 20 mass%, particularly preferably 30 mass%, and most preferably 40 mass%. Setting the amount of the antistatic agent to 10 mass% or more is preferable because it can improve the antistatic performance.

[0071]

In a more preferable embodiment of the present invention, a silicone-based and/or fluorine-based surfactant is incorporated in an amount of 0.1 to 10 mass% into the resin composition layer. Examples of silicone-based surfactants include dimethyl silicone, aminosilane, acrylsilane, vinylbenzylsilane, vinylbenzylaminosilane, glycidiosilane, mercaptosilane, dimethylsilane, polydimethylsiloxane, polyalkoxysiloxane, hydrogen-modified siloxane, vinyl-modified siloxane, vitrox-

modified siloxane, amino-modified siloxane, carboxyl-modified siloxane, halogenated-modified siloxane, epoxy-modified siloxane, methacryloxy-modified siloxane, mercapto-modified siloxane, fluorine-modified siloxane, alkyl group-modified siloxane, phenyl-modified siloxane, and alkylene oxide-modified siloxane.
[0072]

Examples of fluorine-based surfactants include tetrafluoroethylene, perfluoroalkyl ammonium salts, perfluoroalkyl sulfonic acid amide, perfluoroalkyl sodium sulfonate, perfluoroalkyl potassium salts, perfluoroalkyl carboxylates, perfluoroalkyl sulfonates, perfluoroalkyl ethylene oxide adducts, perfluoroalkyl trimethylammonium salts, perfluoroalkyl aminosulfonates, perfluoroalkyl phosphate esters, perfluoroalkyl alkyl compounds, perfluoroalkyl alkyl betaines, and perfluoroalkyl halides.
[0073]

The amount of the surfactant is more preferably 0.1 to 9 mass%, and even more preferably 0.3 to 8 mass%. By incorporating the surfactant, the affinity of the resin composition layer to the main material film during coating is improved, and a coating film with good appearance is obtained.
[0074]

It is more preferable to add a crosslinking agent to the resin composition layer in order to suppress particle detachment. Preferable examples of the crosslinking agent include blocked isocyanate-based crosslinking agents and oxazoline-based crosslinking agents. A polyisocyanate having three or more functional groups, which is a precursor of the blocked isocyanate, can be suitably obtained by introducing an isocyanate monomer. Examples include biurets, nurates, and adducts obtained by modifying an isocyanate monomer, such as aromatic diisocyanate, aliphatic diisocyanate, aromatic aliphatic diisocyanate, or alicyclic diisocyanate, having two isocyanate groups. Among these, it is more preferable to use a biuret.
[0075]

A biuret is a self-condensate having a biuret bond formed by self-condensation of an isocyanate monomer. Examples include a biuret of hexamethylene diisocyanate.

[0076]

A nurate is a trimer of an isocyanate monomer. Examples include a trimer of hexamethylene diisocyanate, a trimer of isophorone diisocyanate, and a trimer of tolylene diisocyanate.

[0077]

An adduct is a trifunctional or higher functional isocyanate compound obtained by reacting an isocyanate monomer with a trifunctional or higher functional low-molecular-weight active hydrogen-containing compound. Examples include a compound obtained by reacting trimethylolpropane with hexamethylene diisocyanate, a compound obtained by reacting trimethylolpropane with tolylene diisocyanate, a compound obtained by reacting trimethylolpropane with xylylene diisocyanate, and a compound obtained by reacting trimethylolpropane with isophorone diisocyanate.

[0078]

The resin composition layer may contain known additives, such as antioxidants, heat stabilizers, weathering stabilizers, and organic lubricants, as long as the effects of the present invention are not impaired.

[0079]

In the present invention, it is important to impart slipperiness and abrasion resistance while maintaining high transparency. Accordingly, in a preferable embodiment, when a coating liquid is prepared, the temperature of the raw materials before preparation is controlled in order to prevent particle aggregation caused by temperature differences between the materials during liquid material mixing. In a more preferable embodiment, each material is added while continuously stirring the coating liquid tank used for preparation. In a further preferable embodiment, a filter is provided upstream of the coating apparatus for removing microaggregates that were

contained in the raw materials before preparation or that were generated by component aggregation during preparation.

[0080]

In the present invention, the method for laminating the resin composition layer is not limited. However, in a preferred embodiment, the resin composition layer is laminated on an unstretched film or a uniaxially stretched film in a polyester film production process, that is, the resin composition layer is formed using a "in-line coating" method. The inline coating method improves the adhesion between the main-material film and the resin composition layer and adhesion durability. It is also excellent in terms of economic efficiency and therefore suitable.

[0081]

As the method for providing the resin composition layer, a commonly used method, such as gravure coating, kiss coating, dipping, spray coating, curtain coating, air knife coating, blade coating, or reverse roll coating, can be used.

[0082]

In the present invention, it is important to impart slipperiness and abrasion resistance while maintaining high transparency. To achieve this, it is important to minimize particle aggregation in the coating liquid for forming the resin composition layer. For example, a lower liquid temperature of the coating liquid increases aggregation of the particles, whereas a higher liquid temperature of the coating liquid results in poor wettability. Therefore, in another preferred embodiment, the liquid temperature is maintained under extremely strict control, within a range of $\pm 1^{\circ}\text{C}$. By introducing such an embodiment, the high quality of the laminated polyester film of the present invention can be stably maintained.

[0083]

The thickness of the resin composition layer is not particularly limited, but in the present invention, the final thickness after drying is preferably 0.01 to 0.2 μm , more preferably 0.015 to 0.16 μm , and still more preferably 0.02 to

0.12 μm . When the thickness is 0.01 μm or more, the effect of improving slipperiness and abrasion resistance is enhanced, whereas when the thickness exceeds 0.2 μm , transparency decreases, which is not preferable.

[0084]

In the present invention, when the resin composition layer is laminated, slipperiness and abrasion resistance are imparted to the laminated polyester film. Therefore, there is no need to incorporate particles into the main-layer film from the viewpoint of transparency.

[0085]

Note that the phrase "there is no need to incorporate particles into the main-layer film" means that particles do not need to be incorporated intentionally, and does not mean that the resulting film contains absolutely no particles. This is because even if particles are not intentionally added into the film, contaminant components from foreign matter, or dirt that adheres to lines or equipment in the raw material production step or the film production step may peel off and become mixed into the film. As for the particle content of the obtained film, for example, the inorganic particle content as determined by quantifying inorganic elements using fluorescent X-ray analysis is 50 ppm or less, preferably 10 ppm or less, and most preferably below the detection limit, it is regarded as substantially containing no particles.

[0086]

Accordingly, in a preferred embodiment of the present invention, in order to make the haze of the laminated film 1.0% or less, the polyester film as a support has a laminate structure in which a biaxially stretched polyester film as the main layer substantially contains no particles, whereas particles are contained only in a resin composition layer laminated on the surface of the main-layer film on the side opposite to the surface on which a resist layer is laminated.

[0087]

Therefore, in the preferred embodiment described above,

Therefore, in the preferred embodiment described above, it is not necessary to form a functional layer for imparting slipperiness or the like on the surface of the main-layer film where the resist layer is laminated. While omitting such measures is recommended, as it allows the effects of the present invention to be more remarkably exhibited, a method of incorporating particles into the film serving as the main layer of the support, or a method of laminating a functional layer on the surface where the resist layer is formed, are not excluded as long as they do not impair the effects of the invention.

[0088]

Regarding scratches on the film surface, in addition to taking measures to prevent scratches from occurring in the steps of processing described above, sufficient consideration must also be given to the occurrence of scratches in the main-layer film production step. For example, if the surface roughness of rolls, such as applicator rolls, in the coating step is high, it leads to the occurrence of scratches; therefore, in a preferred embodiment, the surface roughness of such rolls is set to 0.2S or less. In addition, in another preferred embodiment, in order to prevent the sedimentation of deposits, adherents, foreign matter, or like substances that cause scratches on the roll surface, roll cleaners are disposed at the preheating inlet and cooling rolls in the longitudinal stretching step.

[0089]

Further, there is a method of controlling the cleanliness level in the film production step to Class 1,000 or lower (i.e., 1,000 particles with a particle size of 0.5 μm or larger per cubic foot of volume). In another preferred embodiment, air with a clean level of Class 100 or higher is particularly used around the rolls, and also used in the air cooling unit for cooling the reverse-roll surface in the casting step.

[0090]

In another preferred embodiment, the speed of the rolls through which the film passes in the film production step is individually and precisely controlled to minimize the speed difference between the film and the rolls and take measures to prevent the occurrence of scratches due to friction.

[0091]

Further, a method of cleaning rolls, for example, by scraping off defects on the rolls using an abrasive material before film production is also usable. In order to prevent the film from attracting dust and other particles due to generation of static electricity and causing defects, a method of installing a device to reduce the amount of charge of the film to ± 1500 V or less throughout all the steps is also usable. The steps from film casting, which forms the main layer of the support, to the tenter processing, described below, are processes in which scratches are most likely to occur. Therefore, it is also preferable to design these sections in a compact layout and keep the passage time within 5 minutes, because this can contribute to suppressing the occurrence of defects.

Examples

[0092]

Next, the present invention is described in detail with reference to Examples and Comparative Examples. However, the present invention is not limited to these Examples. First, the evaluation methods used in the present invention are described below.

[0093]

The effectiveness of the present invention is illustrated below with Examples. However, the present invention is not limited to the Examples. The methods for evaluating the physical properties in the following Examples are as described below.

[0094]

(1) D50 and D90 of the Particles

A measurement was performed using a laser diffraction particle size analyzer (SALD-7500nano, produced by Shimadzu Corporation). Before measurement, the particles were weighed and dispersed in ion-exchanged water as a solvent to prepare a slurry with a concentration equivalent to 0.2 wt%. The mixture was stirred for 10 minutes using a mixer (e.g., National MXV253 kitchen mixer), then cooled to room temperature, and measured using a high-concentration measurement unit. The refractive index of the inorganic particle with the highest mass percentage among the inorganic particles used was taken from the database built in the device, and the particle size was calculated.

The refractive index used for particle size calculation was taken from the instrument's built-in database, corresponding to the type of inorganic particle with the highest mass percentage among the inorganic particles used, and the particle size was calculated. From the particle size distribution measurement results, the 50% volume particle size (D50) and 90% volume particle size (D90) were determined, and the D90/D50 ratio was calculated.

[0095]

(2) Thickness of the Resin Composition Layer

The cross-section of each film was cut into ultrathin sections, and the obtained sections were observed and photographed under a transmission electron microscope (TEM) by a stained ultrathin section method with RuO₄ staining, OsO₄ staining, or double staining using both RuO₄ and OsO₄. The thickness of the resin composition layer was measured from the obtained photographs of the film's cross-section. The average of 30 measurement points within the measurement field of view was taken as the thickness of the resin composition layer.

[0096]

(3) Air Release Index

The measurement was conducted in accordance with JIS P

8155: 2010 "Paper and board - Determination of smoothness - Oken method." An Oken-type smoothness tester, produced by Kumagai Riki Kogyo Co., Ltd. (production number: No. 2040-C), was used. The pressure applied to the test piece described in JIS is specified as 98.1 ± 1.0 kPa. However, when this pressure was applied directly to the film, it was difficult to reproduce the air-release behavior during film roll winding. Through diligent investigation, the present inventors confirmed that the air-release properties during film roll winding can be accurately reproduced by applying a pressure of $48 \text{ kPa} \pm 1.0 \text{ kPa}$ to the test piece and setting the measurement time to 150 seconds. The water column level (mm H₂O) obtained from measurement was defined as the air-release index and measured.

[0097]

(4) Static Friction Coefficient

The measurement was conducted in accordance with JIS K 7125. The load cell and the sample were directly connected without using a spring. The sliding block had a mass of 4.4 kgf, and the test speed was set to 200 mm/min. Each sample was measured 3 times. The average of the three measurements was taken as the static friction coefficient.

[0098]

(5) Amount of Coarse Particles with a Shortest Diameter of 3 μm or Larger

6 cm $\times$ 6 cm samples were taken from laminated polyester films. For each sample, using a scanning white-light interference microscope (device: VertScan (registered trademark) VS1540, produced by Hitachi High-Tech Science Corporation), the surface of the laminated polyester film opposite to the surface on which the resist layer was laminated was measured in 36 fields of view with a measurement area of $936 \mu\text{m} \times 702 \mu\text{m}$ using a 10 $\times$ objective lens. The sample set was measured by setting each sample on the stage such that the measurement Y-axis was aligned with the longitudinal direction of the sample film (the direction in which the film was wound). For samples whose longitudinal direction was

not known, the measurement was first performed with the measurement Y-axis being aligned with an arbitrary direction of the sample film. The sample was then rotated by 120° and measured again. Subsequently, the sample was further rotated by 120° and measured again. The average of the measurement results was taken as the number of protrusions present in the sample. Further, the sample film to be measured was placed between two metal frames containing rubber packing so that the film in the frames was in a taut state (a state in which sagging or curling of the sample was eliminated), and the sample surface was measured.

[0099]

The obtained microscopic images were subjected to image processing under the following conditions using the surface analysis software VS-Viewer Version 10.0.3.0 built into the microscope to determine the number of protrusions at each height.

[0100]

Image Processing Conditions

Image processing was performed in the following order.

- Interpolation: Full interpolation
- Filtering: Gaussian (cutoff: 100)
- Surface correction: 4th order

Subsequently, particle analysis processing was carried out under the conditions described below, and the number of particles displayed in the "particle analysis" window detected at a height threshold of 25 nm (height threshold setting: 0.025 μm) (particles) was used as the amount of coarse particles having a shortest diameter of 3 μm or larger.

[0101]

Particle Analysis Conditions

Protrusion analysis processing was performed under the following conditions.

[0102]

- Type of analysis: Protrusion analysis
- Image correction: None
- Processing:

- Height threshold: 0.025 μm
- Reference height: Zero plane (mean plane)

The same operation was performed for all 36 measured fields of view, and the total number of particles having a shortest diameter of 3 μm or more was calculated and divided by the measurement area for 36 fields of view (0.657 mm^2) to determine the number of coarse particles of 3 μm or more (particles/ mm^2).

[0103]

(6) Antistatic Properties (Surface Resistivity)

The film was cut into pieces with a dimension of 5 cm $\times$ 10 cm and conditioned at a temperature of 23°C and a humidity of 65% RH for 24 hours. The antistatic properties of the surface of the film on which the resin composition layer was laminated was then evaluated by measuring the surface resistivity ($\Omega/\square$) using a surface resistivity meter (a surface resistivity meter, produced by Mitsubishi Yuka K.K.) in an environment at an applied voltage of 500 V, a temperature of 23°C, and a humidity of 65% RH, and showing the value as a logarithm ($\log (\Omega/\square)$). Five randomly selected samples were used for the measurement, and the average of the five obtained measurements was calculated.

[0104]

(7) Abrasion Resistance (Abrasion Resistance Index)

Friction was applied using a Gakushin (JIS) rubbing fastness tester (produced by Yamaguchi Scientific Industrial Co., Ltd.) to the resin-laminated surface of a specimen measuring 3 cm in width and 20 cm in length, under a load of 500 gf for 40 reciprocating cycles. Aluminum foil was used as the friction counterpart, and the abrasiveness of the resin composition layer was evaluated on three levels by observing the surface of the aluminum foil after the friction loading.

[0105]

◎: No particle transfer observed on the aluminum foil.

[0106]

○: Slight particle transfer observed on the aluminum foil.

[0107]

×: Significant particle transfer observed on the aluminum foil.

[0108]

(8) Film Roll Misalignment

A 1000-meter length of each sample film was wound into a roll. The obtained film rolls were visually inspected and evaluated based on the degree of winding misalignment as follows:

○: No noticeable misalignment observed.

△: Slight misalignment observed.

×: Significant misalignment observed.

[0109]

(9) Haze

The haze was measured in accordance with JIS K 7136-2000 "Plastics - Determination of haze for transparent materials" using a haze meter (NDH-2000, produced by Nippon Denshoku Industries Co., Ltd.).

[0110]

Preparation of the Aqueous Dispersion (C-1WD) of the Blocked Isocyanate Crosslinking Agent (C-1)

125.2 parts by mass of a polyisocyanate compound with a biuret structure produced using hexamethylene diisocyanate (Duranate 24A-100, produced by Asahi Kasei Chemicals, NCO concentration: 23.1%) as a starting material, 50.0 parts by mass of dipropylene glycol dimethyl ether, and 68.8 parts by mass of 3,5-dimethylpyrazole were added to a flask equipped with a stirrer, a thermometer, and a reflux condenser. The resulting mixture was maintained at 70°C under a nitrogen atmosphere with stirring for 2 hours. The infrared spectrum of the reaction mixture was then measured, and the absorption of the isocyanate group was confirmed to have disappeared. Subsequently, after the reaction mixture was cooled to room temperature, 6 parts by mass of polyethylene glycol (n = 12) monolaurate was added. While the resulting mixture was mixed by stirring at 2000 rpm, water was added. The concentration was adjusted with water to thereby obtain an aqueous dispersion (C-1WD) of a blocked isocyanate-

based crosslinking agent (C-1) having a solids content of 30.0 mass%.

[0111]

Example 1

(1) Preparation of Coating Liquid

The coating agent materials listed below were mixed in a mixed solvent of water and isopropanol to obtain a coating liquid.

- Polyester aqueous dispersion: 8.00 parts by mass

(Bylonal MD1200, produced by Toyobo Co., Ltd., solids content: 30 wt%)

- Particles (a): 1.00 part by mass

(Snowtex OL, produced by Nissan Chemical Corporation; colloidal silica with an average particle size of 0.045 μm , solids content: 20 wt%)

- Particles (b): 1.50 parts by mass

(acrylic particles with D50 = 0.57 μm and D90/D50 = 1.3; solids content: 2 wt%)

- Surfactant: 0.50 parts by mass

(silicone-based; solids content 10 wt%)

- Wax agent: 0.80 parts by mass

(High-Tech E9015, produced by Toho Chemical Co., Ltd.; solids content: 20 wt%)

- Antistatic agent: 0.80 parts by mass

(alkylsulfonate TB214; solids content: 16.7 wt%)

[0112]

(2) Production of the Laminated Polyester Film

As the film-forming polymer, PET resin pellets having an intrinsic viscosity of 0.62 dL/g (solvent: phenol/tetrachloroethane = 60/40) and substantially free of particles were dried at 135°C under reduced pressure of 133 Pa for 6 hours. The dried pellets were then fed into an extruder, melt-extruded into a sheet at approximately 280°C, and quenched and brought into close contact with a rotating cooled metal roll maintained at a surface temperature of 20°C to solidify the

sheet, thereby obtaining an unstretched PET sheet.

[0113]

The unstretched PET sheet was heated to 100 °C using a combination of heated rolls and an infrared heater, and then uniaxially stretched 3.5 times in the machine direction using a series of rolls with different peripheral speeds to obtain a uniaxially stretched PET film.

[0114]

Subsequently, the coating liquid, which had been allowed to stand at room temperature for 5 hours or longer, was applied to one surface of the PET film by a roll coating method. Subsequently, the film was stretched 4.0 times in the width direction at 120°C using a tenter. While maintaining the stretched width, the film was heat-treated at 230°C for 5 seconds, followed by a 3% relaxation treatment in the width direction at 100°C for 10 seconds, thereby obtaining a 16 µm-thick laminated polyester film. Table 1 shows the evaluation results of this film. The coating amount was adjusted so that the final (after biaxial stretching) coating amount after drying would be 0.05 g/m² (functional layer thickness after drying: 50 nm).

[0115]

Example 2

A laminated polyester film was obtained in the same manner as in Example 1 except that particles (b) were changed to polystyrene particles having a D50 of 0.70 µm and a D90/D50 ratio of 1.3 (solids content: 2%), and the amount of particles (b) added was changed to 1.25 parts by mass.

[0116]

Example 3

A laminated polyester film was obtained in the same manner as in Example 1 except that particles (b) were changed to acrylic particles having a D50 of 0.73 µm and a D90/D50 ratio of 1.2 (solids content: 2%), and the amount of particles (b) added was changed to 0.75 parts by mass.

[0117]

Example 4

A laminated polyester film was obtained in the same manner as in Example 1, except that the coating agent materials listed below were mixed into a mixed solvent of water and isopropanol.

Aqueous polyester dispersion: 8.00 parts by mass

(produced by Toyobo Co., Ltd., Bylonal MD1200, solids content: 30 wt%)

Crosslinking agent C-1WD: 0.80 parts by mass

(solids content: 30 wt%)

Particles (a): 1.00 part by mass

(Snowtex OL, produced by Nissan Chemical, colloidal silica with an average particle size of 0.045 μm , solids content: 20 wt%)

Particle (b): 1.50 parts by mass

(acrylic particles with D50 of 0.57 μm and a D90/D50 ratio of 1.3, solids content: 2 wt%)

Surfactant: 0.50 parts by mass

(silicone-based, solids content: 10 wt%)

Wax agent: 0.80 parts by mass

(Hi-Tech E9015, produced by Toho Chemical Co., solids content: 20%)

Antistatic agent: 0.80 parts by mass

(alkyl sulfonate TB214, solids content: 16.7%)

[0118]

Example 5

A laminated polyester film was obtained in the same manner as in Example 1 except that particles (b) were changed to polystyrene particles having a D50 of 0.31 μm and a D90/D50 ratio of 1.5 (solids content: 2%).

[0119]

Example 6

A laminated polyester film was obtained in the same manner as in Example 1 except that particles (b) were changed to silica particles with a D50 of 0.80 μm and a D90/D50 ratio of 2.8

(solids content: 2%) and the amount of particles (b) added was changed to 0.75 parts by mass.

[0120]

Comparative Example 1

A laminated polyester film was obtained in the same manner as in Example 1 except that particles (b) were changed to silica particles having a D50 of 0.28 μm and a D90/D50 ratio of 1.7 (solids content: 2%).

[0121]

Comparative Example 2

A laminated polyester film was obtained in the same manner as in Example 1 except that particles (b) were changed to silica particles having a D50 of 0.93 μm and a D90/D50 ratio of 3.2 (solids content: 2%) and the amount of particles (b) added was changed to 0.75 parts by mass.

[0122]

Comparative Example 3

A laminated polyester film was obtained in the same manner as in Example 1 except that particles (b) were changed to silica particles having a D50 of 1.46 μm and a D90/D50 ratio of 3.8 (solids content: 2%) and the amount of particles (b) added was changed to 0.75 parts by mass.

[0123]

Comparative Example 4

A laminated polyester film was obtained in the same manner as in Example 1 except that particles (b) were changed to silica particles having a D50 of 2.36 μm and a D90/D50 ratio of 2.2 (solids content: 2%), and the amount of particles (b) added was changed to 0.75 parts by mass.

[0124]

Table 1 summarizes the evaluation results of each Example and Comparative Example.

[0125]

Table 1

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4
Particle (b)	D50 (μm)	0.57	0.70	0.73	0.57	0.31	0.80	0.28	0.93	1.46	2.36
	D90 (μm)	0.74	0.91	0.91	0.74	0.45	2.20	0.49	2.99	5.52	5.30
	D90/D50	1.3	1.3	1.2	1.3	1.5	2.8	1.7	3.2	3.8	2.2
Crosslinking agent		—	—	—	C-1WD	—	—	—	—	—	—
Film	Air release index (mmH ₂ O)	487.4	486.6	487.9	483.0	492.0	484.0	495.0	484.0	489.9	485.0
	Static friction coefficient	0.43	0.44	0.45	0.42	0.46	0.49	0.43	0.48	0.47	0.45
	Number of coarse particles with a particle size of ≥ 3 μm (particles /mm ²)	61	33	78	78	20	122	10	266	350	1242
	Antistatic properties (log (Ω/□))	10.5	10.9	10.4	10.9	10.5	10.6	10.7	10.4	10.4	10.9
	Abrasion resistance	◎	◎	◎	◎	◎	△	○	×	×	×
Film winding misalignment		○	○	○	○	△	○	×	○	○	○
Haze (%)		0.6	0.5	0.4	0.9	0.5	0.4	0.5	0.3	0.2	0.6

[0126]

The present invention exhibited favorable results in all of the following properties: air-release index, static friction coefficient, amount of coarse particles with a shortest diameter of 3 μm or more (number of coarse protrusions), antistatic properties, abrasion resistance, and film winding misalignment. Accordingly, the present invention is suitable as a support for ultrafine-line photoresist films.

[0127]

Further, a photoresist film produced using a polyester film for ultrafine-line photoresist of the present invention as a support exhibits excellent resolution of the photoresist layer, superior pattern formability on surfaces and edges, and outstanding adhesion of the photoresist layer. Furthermore, the photoresist film has excellent handling properties and durability, such as blocking and abrasion resistance, when a photoresist film is produced using the polyester film for ultrafine-line photoresist of the present invention as a support. Therefore, the photoresist film has excellent suitability for processing, such as lamination processing, and is useful for industrial applications.

[0128]

In contrast, in Comparative Example 1, the air-release index was outside the range of the present invention, and film winding misalignment occurred. In Comparative Examples 2 and 3, the number of coarse particles of 3 μm or larger was outside the range of the present invention, and the obtained films did not satisfy the required abrasion resistance.

[0129]

In Comparative Example 4, the number of coarse particles of 3 μm or larger was outside the range of the present invention, and the obtained film did not satisfy the required abrasion resistance. In addition, the film had much surface roughness, thus being unsuitable for use in producing ultrafine-line photoresist.

Industrial Applicability

[0130]

Since the polyester film for ultrafine-line photoresist of the present invention has excellent transparency, slipperiness, antistatic properties, and abrasion resistance, it can be suitably used as a support for ultrafine-line photoresist films. A photoresist film produced using the polyester film of the present invention as a support exhibits excellent resolution of the photoresist layer, superior pattern formability on surfaces and edges, and excellent adhesion to the photoresist layer. Further, when the polyester film of the present invention for ultrafine-line photoresist is used as a support, excellent handling properties and durability, such as blocking resistance and abrasion resistance, during the production of photoresist film, are provided. Therefore, the polyester film for ultrafine-line photoresist of the present invention can be used in applications such as lamination processing, and exhibit excellent suitability for processing. Accordingly, the polyester film of the present invention is particularly suitable as a support for ultrafine-line photoresist. The technical concept of the present invention can also be applied to other industrial films, such as substrate films for optical functional films that require high transparency. Accordingly, the present invention offers significant benefits to industry.

CLAIMS

[Claim 1]

A laminated polyester film comprising
a polyester film and
a functional layer formed on at least one surface of
the polyester film,
wherein

the air-release index (mm H₂O) of the surface having
the functional layer is 493 mm H₂O or less, and

the number of coarse particles with a shortest diameter
of 3 µm or more present per 1 mm² on the surface having the
functional layer is 250 or fewer.

[Claim 2]

The laminated polyester film according to claim 1,
having a haze of 1.0% or less.

[Claim 3]

The laminated polyester film according to claim 1,
wherein at least one surface of the laminated polyester film has
a logarithm of surface resistivity ($\Omega/\square$) ($\log(\Omega/\square)$) of 13 or less
as measured at a temperature of 23°C and a humidity of 65% RH.

[Claim 4]

The laminated polyester film according to claim 1,
wherein the functional layer contains particles, and the
particles have a D50 of 1 µm or less and have a D90/D50 ratio of
3 or less.