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(72) Inventors:

- **MASUDA, Narihiro**
Santo-cho, Sakata-gun, Shiga 521-0234 (JP)
- **WATANABE, Shigeyuki**
Santo-cho, Sakata-gun, Shiga 521-0234 (JP)

(71) Applicants:

- **Mitsubishi Polyester Film Corporation**
Tokyo 108-0014 (JP)
- **DAI NIPPON PRINTING CO., LTD.**
Tokyo 162-8001 (JP)

(74) Representative:

ter Meer, Nicolaus, Dipl.-Chem., Dr.
TER MEER STEINMEISTER & PARTNER GbR,
Patentanwälte,
Mauerkircherstrasse 45
81679 München (DE)

(54) **BIAXIALLY ORIENTED POLYESTER FILM FOR THERMAL TRANSFER**

(57) A biaxially oriented polyester film for thermal transfer printing, which is obtained by applying a coating liquid containing a water-soluble or water-dispersible organic polymer to at least one surface of a polyester film prior to the completion of crystallization by orientation, drying said coating liquid, stretching said film and thermally treating said film, and which has a thickness of 20 µm or less, wherein a thickness fluctuation in any 15 meter interval in the machine direction of the coated film is 10 % or less. An ink ribbon, which is produced using this polyester film as a base film, can print images having less unevenness of color density with good reproducibility of color tone.

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Description

FIELD OF THE INVENTION

5 [0001] The present invention relates to a biaxially oriented polyester film for thermal transfer printing. In particular, the present invention relates to a biaxially oriented polyester film for thermal transfer printing, which causes less unevenness of print density and can print very precise images.

BACKGROUND ART

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[0002] Both melting type and sublimation type thermal transfer ink ribbons carry an ink layer on one surface of a polyester film as a base film. On transferring, the film is heated with a thermal head, etc. on an opposite surface to the ink layer, and the heat is transmitted to the ink layer to melt or sublimate the ink so that the ink is selectively transferred to a material to be printed. In this case, the heat applied to the opposite surface is transmitted across the thickness of the film and reaches the ink layer. Accordingly, heat is less transmitted when the film thickness is larger, while heat is more easily transmitted when the film thickness is small. That is, if a film thickness fluctuates, a print density is low at a part having a large thickness, while a print density is high at a part having a small thickness. Such a phenomenon is less troublesome in applications which do not require image quality, for example, the printing of characters or plain color images.

20 [0003] However, in the field of thermal transfer type printing, the quality of images has significantly been improved in connection with the recent spread of personal computers, digital cameras, etc. In particular, when it is required to produce highly precise full-color prints, for example, photographic images, the unevenness of a print density, which is caused by the thickness fluctuation of the base film of an ink ribbon, may cause various problems such that the color tones of images are unwillingly changed, or the reproducibility of color tones deteriorates. Thus, the unevenness of the print density is a serious problem.

25 [0004] The surfaces of polyester films, which are widely used as base films of thermal transfer ink ribbons, are often coated to impart special functions for thermal transfer printing. Such a coating is applied by a so-called in-line coating comprising applying a coating liquid containing organic polymer compounds in water as a medium to the film, drying the applied liquid, stretching the film, and then crystallizing the film. For in-line coating, a method is widely employed, which comprises applying a coating liquid containing water as a medium to a film which has been stretched in a machine direction and drying the applied liquid in the preheating zone of a transverse-stretching step, since such a method is preferable from the viewpoint of the simplicity of the process and thermal efficiency.

30 [0005] Since a coating liquid containing a large amount of water is applied onto a polyester film in such an in-line coating process, an amount of heat applied to the film for stretching is firstly consumed as the latent heat of water vaporization. After water is completely evaporated from the coating liquid, the temperature of the film rises. Accordingly, the temperature of a film is more easily fluctuated than a case where no in-line coating is employed. As a result, the thickness fluctuation of a film increases.

35 [0006] When a relatively thin film is produced for thermal transfer printing, the ratio of the thickness of a coating liquid to the thickness of a film, that is, the ratio of the amount of water to the weight of a polyester, unavoidably increases, and thus the thickness fluctuation of the film further increases.

40 [0007] Known measures to suppress the thickness fluctuation of polyester films which are not subjected to in-line coating include, for example, the improvement of polyethylene naphthalate films (JP-A-63-60730, JP-A-63-60731 and JP-A-63-60732), the improvement of shrinkable polyester films (JP-A-63-146940 corresponding to US-A-4,985,538), a production method in which a sound pressure level around a die is suppressed (JP-A-63-162215), a technique which defines the ratio of the sum of spectral intensities when a waveform of thickness fluctuation is Fourier transformed (JP-A-9-254254), and the like.

45 [0008] However, polyester films which are in-line coated and have less thickness fluctuation, and methods for the production of such polyester films are not known.

50 SUMMARY OF THE INVENTION

[0009] One object of the present invention is to provide a base film for the production of a thermal transfer ink ribbon which will print images while causing less unevenness of color density and achieving good reproducibility of color tone.

55 [0010] As a result of an extensive study to achieve the above object, it has been found that, if a thermal transfer ink ribbon is produced using a polyester film which has a thickness fluctuation in a specific range, the unevenness of a printing density can be suppressed, even when precise full-color images are printed, and thus the present invention has been completed.

[0011] Accordingly, the present invention provides a biaxially oriented polyester film for thermal transfer printing,

which is obtained by applying a coating liquid containing a water-soluble or water-dispersible organic polymer to at least one surface of a polyester film prior to the completion of crystallization by orientation, drying said coating liquid, stretching said film and thermally treating said film, and which has a thickness of 20 μm or less, wherein a thickness fluctuation in any 15 meter interval in the machine direction of the coated film is 10 % or less.

DETAILED DESCRIPTION OF THE INVENTION

[0012] Polyesters of polyester films used in the present invention mean polyesters at least 80 mole %, preferably at least 90 mole % of repeating units of which are derived from ethylene terephthalate, or at least one of ethylene-2,6-naphthalate and cyclohexanedimethylene terephthalate.

[0013] Polyesters may be copolyesters comprising other repeating units insofar as the percentage of the above repeating units is 80 mole % or larger. Examples of comonomers which form the other repeating units include, as glycol components, diols such as ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol, 1,4-butylene glycol, 1,4-cyclohexanedimethylene glycol, polyalkylene glycol, etc.; and as dicarboxylic acid components, terephthalic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, adipic acid, hydroxycarboxylic acids such as hydroxybenzoic acid, etc.

[0014] Among polyesters, polyethylene terephthalate is most preferable from an all-round view of quality and costs. The use of polyethylene naphthalate having good heat resistance can effectively reduce the corrugation of ink ribbons.

[0015] Polyester films used in the present invention may contain additives such as inorganic particles, organic lubricants, antistatic agents, stabilizers, dyes, pigments, organic polymers, etc. if necessary. In particular, to adjust the gloss of transfer printed images or to improve the running properties of the films during the production of polyester films or of ink ribbons, inorganic particles or organic particles are preferably compounded in the polyester films to roughen the surfaces of the film. When the average surface roughness of a film is from 0.03 to 0.2 μm , preferably from 0.04 to 0.1 μm , good running properties and highly precise images are both attained.

[0016] It does not matter if components of a coating layer on the film surface, which will be explained below, may be compounded, when scraps of films which are generated in the course of production are recycled.

[0017] Preferably, polyester films used in the present invention have an intrinsic viscosity of 0.45 to 1.20 dl/g, more preferably 0.50 to 0.80 dl/g, when it is measured using a mixed solvent of phenol and tetrachloroethane (weight ratio of 50:50) at 30°C, to maintain the continuity in the course of film production, and keep the thickness fluctuation in a specific range.

[0018] The polyester films of the present invention are used as the base films of thermal transfer materials, and thus they are required to have good mechanical strength, thermal conductivity, or handling properties in the production of thermal transfer materials.

[0019] The total thickness of a coated film is preferably 20 μm or less, more preferably 10 μm or less particularly to obtain highly precise images. The lower limit of the total thickness is usually 0.5 μm , preferably 1 μm .

[0020] The biaxially oriented polyester film of the present invention is biaxially stretched and oriented in a machine direction and a transverse direction of the film. Unstretched or uniaxially stretched films have low mechanical strength or dimensional stability and thus cannot create highly precise transferred images.

[0021] The biaxially oriented polyester film of the present invention is a coated film, which is obtained by applying a coating liquid containing a water-soluble or water-dispersible organic polymer to at least one surface of a polyester film prior to the completion of crystallization by orientation, drying the coating liquid, stretching the coated film and thermally treating the film.

[0022] Water-soluble organic polymers are preferably polymers which are soluble in cold or warm water, or can be solubilized by the adjustment of pH. Specific examples of water-soluble polymers include polyalkylene glycol, polyvinyl alcohol, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylpyrrolidone, polystyrenesulfonic acid, gelatin, casein, dextran, cellulose, and their derivatives.

[0023] Water-dispersible organic polymers are polymers which are finely dispersed in water in a stable state. In the concrete, an average particle size of a suspension is preferably in the range between 0.001 and 50 μm , and a stability is such that the changing rate of the average particle size of a suspension is $\pm 10\%$, when the suspension is maintained at 25°C for 3 hours.

[0024] The fine dispersion of an organic polymer may be a dispersion obtained from emulsion polymerization, or a suspension which is prepared by dispersing a polymer in water by the application of strong shear or by adding water to a solution of an organic polymer and then removing a solvent. Dispersants may be used to disperse organic polymers in water.

[0025] Specific examples of organic polymers which can be finely dispersed in water include polystyrene, polypropylene, polybutadiene, polystyrene, polyacrylates, polymethacrylates, polyacrylonitrile, polyvinyl acetate, polyvinyl butyrate, polyvinyl chloride, polyvinylidene chloride, aromatic or aliphatic polyesters, aromatic or aliphatic polyamides, aromatic or aliphatic polyurethanes, aromatic or aliphatic polyethers, aromatic or aliphatic polyimides, polycarbonate,

polyarylketone, aromatic or aliphatic epoxy resins, phenol resins, urea resin, melamine resins, cyanate resins, polyfluoroethylene, polyorganosiloxanes, natural or synthetic waxes, polyamino acids, and their derivatives.

[0026] Such organic polymers may be homopolymers, or random, block or graft copolymers comprising two or more kinds of repeating units. Not only intended organic polymers are allowed to be present in water from the beginning, but also reactive monomers or polymers are contained in a dispersion and crosslinked or polymerized after the application of the dispersion. In this case, catalysts may be used in combination with reactive monomers or polymers.

[0027] A coating liquid which is applied to a biaxially oriented polyester film according to the present invention may contain necessary amounts of various additives such as inorganic fine particles, antistatic agents, fungicides, antioxidants, stabilizers, etc.

[0028] The medium of a coating liquid containing an organic polymer used in the present invention is preferably water, although water-soluble organic solvents may be used in combination with water to accelerate the dispersing of the organic polymer or improve the flexibility of a coated film (the following properties in the stretching step of a film). In such a case, the upper limit of the organic solvent is preferably adjusted such that the concentration of the used solvent in an environmental atmosphere is less than an explosion limit.

[0029] A coating liquid containing the above-described organic polymer is applied to at least one of the surfaces of a polyester film, and this coating step should be carried out in the process of the preparation of a polyester film. That is, one of the following methods should be used: a method comprising the steps of applying a coating liquid onto an unstretched polyester film and then biaxially stretching the film sequentially or simultaneously, a method comprising the steps of applying a coating liquid onto a uniaxially stretched polyester film and then stretching the film in the direction perpendicular to the direction of the previous uniaxial stretching, or a method comprising the steps of applying a coating liquid onto a biaxially stretched polyester film and further stretching the film in a machine direction and/or a transverse direction. Among these methods, the method comprising applying the coating liquid onto a uniaxially oriented polyester film is most preferable, since the fluctuation of a film thickness is suppressed, and the productivity is not decreased.

[0030] A coating liquid may be applied with any conventional coating apparatus, for example, a reverse roll coater, a gravure coater, a rod coater, an air doctor coater, etc.

[0031] The above-described coating layer containing an organic polymer is formed

1) as an interlayer between a polyester film and an ink layer to achieve:

- a) the improvement of adhesion properties with a binder in an ink layer for sublimation transfer printing, or
- b) the improvement of adhesion and releasing properties with an ink for melting transfer printing;

2) as an interlayer between a polyester film and a back layer to achieve the improvement of adhesion properties with the back layer of an ink ribbon;

3) as the back layer of an ink ribbon; or

4) to impart antistatic properties to an ink ribbon.

[0032] The biaxially oriented polyester film for thermal transfer printing of the present invention should have a thickness fluctuation of 10 % or less in any 15 meter interval in the machine direction of the coated film. The thickness fluctuation is a value obtained by dividing a difference between the maximum thickness and the minimum thickness by an average thickness of the film in a 15 m interval in the machine direction of the film.

[0033] When a thickness fluctuation exceeds 10 %, the difference of color tone due to the unevenness of a density can be observed with an eye, and image quality deteriorates, when highly precise full-color images are printed using an ink ribbon comprising such a film as a base film. A thickness fluctuation is preferably 7 % or less, more preferably 5 % or less, since the difference of color tone is negligibly small in such a thickness fluctuation range. The lower limit of a thickness fluctuation is ideally 0 %. However, the minimum thickness fluctuation is often about 2 % due to various factors.

[0034] It is preferable for a coated polyester film to have less thickness fluctuation also in the transverse direction of the film. In many cases, the effective width of a film cannot be as large as 15 m. Thus, a thickness fluctuation is measured in an interval of 3 m. Such a thickness fluctuation in the transverse direction of the coated film is preferably 10 % or less, more preferably 7 % or less, in particular 5 % or less.

[0035] The biaxially oriented polyester film for thermal transfer printing of the present invention is a laminate film prepared by a so-called in-line coating, which comprises applying a coating liquid containing water-soluble or dispersible organic polymer compounds in water as a medium to the film prior to the completion of crystallization by orientation, drying the applied liquid, stretching the film, and then thermally treating the film, and should have a small thickness fluctuation in its machine direction. However, as explained in the above, in the case of an in-line coating process, since a coating liquid containing a large amount of water is applied to the surface of a polyester film, the film more easily suffers from a temperature fluctuation in a subsequent stretching step than a film which has not been subjected to an in-line

coating process, and therefore, the thickness fluctuation of the film increases.

[0036] The present inventors have made a study to solve such a problem, and come to an conclusion that a coating liquid layer, which still has a flowability, has an uneven thickness distribution due to the vibration of a base film as a substrate, and as a result, the temperature distribution of the base film becomes uneven in the process comprising drying, preheating and transverse stretching, and such an uneven temperature distribution has a very large influence on the thickness fluctuation of a film in the machine direction. That is, it has been found that the thickness fluctuation of a film in its machine direction can be suppressed by decreasing such vibration of the film, or by avoiding the influence of the possible vibration.

[0037] The most of the vibration, which is generated in a film from the step of applying a coating liquid onto the film to the step of thoroughly evaporating off water (an aim being 1 wt. % of water in the layer) from the coated liquid after being supplied in a drying step, is caused by an impact generated when the edges of a film are clamped with tenter clips, and fluttering of the film generated by the blow of hot air from a tenter.

[0038] To suppress such vibration, the following methods can be employed: a method for suppressing pulsation of a hot air from a tenter by controlling the hot air with an inverter; a method for reducing an amount of a hot air; a method for preventing sagging at the center of a film the both edges of which are clamped with clips by gradually increasing the clip width as the film is expanded by heating; and a method providing tenter clips with cushioning materials to reduce an impact when the edges of a film are clamped with the tenter clips.

[0039] Even if a film is vibrated, the influence of vibration can be reduced by the following methods: a method for reducing the amplitude of vibration by reducing a distance from a coater to a position where the edges of a film are clamped with tenter clips as much as possible; and a method for blocking the propagation of vibration in a short distance by allowing one or more driving or free rolls in contact with the opposite surface of the film to the coated surface in a drying section when only one surface of the film is coated.

[0040] A combination of two or more of the above methods can be employed.

[0041] The vibration of a film, in particular, the vibration having a large amplitude, can be suppressed by the above-described method or methods. As a result, the generation of a thickness fluctuation in the machine direction of a film, which has been biaxially oriented and heat set, can be made small. In such a case, the amplitude of a film caused by the vibration in a drying zone depends on the width of a tenter, the thickness of the film and the thickness of a coated layer, and is 5 cm or less, preferably 3 cm or less.

[0042] In the present invention, it is possible to use any known method for suppressing a thickness fluctuation in addition to the above methods for suppressing the thickness fluctuation due to the in-line coating.

[0043] According to the experiences of the present inventors, the degree of the thickness fluctuation may be determined under the influence of a process which causes the worst results. Accordingly, even if the in-line coating process may be improved by this invention, the results may not be necessarily satisfactory, and a comprehensive countermeasure is necessary.

[0044] In the following, one preferred embodiment of a process, which can be desirably used to produce the film of the present invention, will be explained.

[0045] When a polyester raw material is melt extruded, a gear pump is preferably installed in the melt-line of an extruder to suppress the pulsation of discharge. In addition, it is preferable to install a static mixer to level a temperature distribution in a melt-line for a molten polyester.

[0046] A so-called electrostatic sticking method is preferably used in a process for casting and solidifying a molten polyester to obtain an unstretched film. The electrostatic sticking method is preferably carried out by allowing a molten polyester to be effectively in contact with a cooling drum using, as an electrode, an amorphous metal electrode having a thickness of 50 μm or less at its edge portion (JP-A-1-152031), or a laminated blade electrode having an electrically conductive thin film having a thickness of 0.01 to 10 μm on at least one surface of an insulating member.

[0047] To effectively perform an electrostatic sticking method, the melt of a polyester preferably has a resistivity of $1 \times 10^{10} \Omega \cdot \text{cm}$ or less, in particular, in a range between $1 \times 10^9 \Omega \cdot \text{cm}$ and $1 \times 10^6 \Omega \cdot \text{cm}$. For the same purpose, the methods may be used, which are described in JP-A-57-190040, JP-A-58-225123, JP-A-59-91121, JP-A-59-172542, JP-A-59-182840, JP-A-59-229314, JP-A-60-141751, JP-A-60-248737, JP-A-62-218416, JP-A-62-236722, JP-A-62-236722, etc.

[0048] When a molten polyester is discharged through an orifice, the thickness fluctuation of an unstretched film can be further reduced by adjusting a ratio of a slit distance of an orifice to a thickness of an unstretched film which has been cooled and solidified, in a range between 5 and 20, preferably between 8 and 15.

[0049] In addition, it is possible to use a countermeasure such that a molten polyester is allowed to be in contact with a cooling drum in a casting step while suppressing vibration as much as possible by reducing the rotational irregularity of a cooling drum, or screening a molten polyester from window.

[0050] When a sheet-form molten polyester touches a cooling drum while applying such a countermeasure, the amplitude of the drift of a touching part, which extends in a line form in a width direction on the surface of a cooling drum (hereinafter, referred to as a "touching line"), is preferably 1 mm or less, more preferably 0.5 mm or less, in an area cor-

responding to the width of an effective product.

[0051] Then, the unstretched film of a polyester formed by casting is preferably stretched in a machine direction by a roll stretching method. Stretching conditions in this step depend on the composition of used polyester. In the case of polyethylene terephthalate (PET), the stretching in the machine direction is preferably carried out in two steps, and a temperature in the second step is made lower than that in the first step. For example, an unstretched film is stretched in the first step at a temperature of 90 to 110°C at a draw ratio of 2.0 to 3.0, and then in the second step at a temperature of 70 to 90°C at a draw ratio of 1.2 to 2.0. In such a case, the film is preferably stretched by pressing the film against rolls using nip rolls or an electrostatic sticking method at a suitable position so that positions, at which the plastic deformation starts and ends, do not fluctuate in a stretching interval between a low speed roll and a high speed roll.

[0052] A polyester film, which has been uniaxially stretched in a machine direction, is then supplied to the above-described in-line coating process.

[0053] Thereafter, the film is stretched in a transverse direction with a tenter. Stretching conditions in the transverse direction also depend on the composition of polyester used. In the case of PET, a stretching temperature is from 85 to 130°C, and a draw ratio is from 3.0 to 5.0. In this step, the pulsation of an air blowing to heat or cool the film in the tenter is preferably suppressed as much as possible by controlling the air blowing with an inverter. It may be possible to use a method for improving the thickness fluctuation of a film in its transverse direction by changing the angle of a blowing outlet over time, as disclosed in JP-A-5-301284.

[0054] A biaxially oriented film after the transverse stretching may be restretched in a machine direction and/or a transverse direction. Preferably, restretching in a machine direction is carried out by roll stretching, while restretching in a transverse direction is carried out with a tenter. In the restretching step, it is possible to employ the same countermeasures against a thickness fluctuation as those employed in the above-described roll stretching and tenter stretching methods.

[0055] A biaxially oriented film, which has been subjected to all the stretching steps, is then supplied to a heat set step. The heat setting is preferably carried out by a tentering method. In this step, the same countermeasures against a thickness fluctuation as those used in the transverse stretching step may be used. In the heat setting step, a temperature is preferably from 180 to 240°C, and a time is from 0.5 to 60 seconds. In this step, a film may be relaxed by 1 to 10 % in a transverse direction in a region in which the maximum temperature is reached and/or a cooling region, to improve a thermal shrinkage factor in the transverse direction.

[0056] A biaxially oriented polyester film, which is produced by the above explained methods, preferably has a breaking strength of at least 25 kgf/mm² both in the machine and transverse directions, and a shrinking factor of 5 % or less both in the machine and transverse directions when the film is heated at 180°C for 3 minutes.

[0057] The laminate film of the present invention preferably has a bond strength of 100 gf/125 mm or less, more preferably 50 gf/125 mm, in particular 30 gf/125 mm, which is measured by a method described in the after-mentioned Examples. Such a bond strength means that, when a laminate film is once wound up in a roll form and then exposed to high-temperature and high humidity conditions in a pressurized state, one part of the laminate film does not bond to another part of the film, and thus the laminate film can be easily drawn when the film is unwound for further processing.

[0058] The bond strength of a film can be adjusted, for example, by adding a crosslinking agent or a crosslinkable polymer to a coating liquid, and effecting intermolecular or intramolecular crosslinking of the organic polymers in the above-described thermal treating step of the film. This will further increase an adhesive strength to an ink, when a coating layer is formed to increase the adhesive strength to a sublimation type ink. The bond strength can effectively be controlled by selecting the kind and amount of organic or inorganic particles contained in a base film and increasing the surface roughness of the base film.

[0059] The laminate film of the present invention preferably has a F5 value of at least 13.0 kgf/mm² both in the machine and transverse directions. When such conditions are met, the elongation of an ink ribbon both in the machine and transverse directions can additionally be reduced. As a result, the printing crimps and misprinting can be decreased. A method for measuring a F5 value will be described in the following Examples.

EXAMPLES

[0060] The present invention will be illustrated by the following Examples, which do not limit the scope of the invention in any way. In Examples, "parts" and "%" are "weight parts" and "weight %", respectively, unless otherwise indicated.

[0061] Physical properties and effects were measured and evaluated as follows:

(1) Film thickness

[0062] The total thickness of a laminate consisting of a base film and a coating layer containing an organic polymer was measured with a micrometer, and used as a "film thickness".

(2) Thickness fluctuation of film

[0063] Twenty regions each having a length of 15 m in a machine direction or a length of 3 m in a transverse direction were randomly selected from a biaxially oriented film. Then, the maximum thickness (μm) and the minimum thickness (μm) of each sample were measured using a continuous film thickness meter (manufactured by ANRITSU CORPORATION) which comprises an electronic micrometer. Separately, an average thickness (μm) in each region was calculated with the same region. Then, the fluctuation of a film thickness was calculated from the maximum and minimum thickness and average thickness according to the following formula:

$$\text{Thickness fluctuation (\%)} = [(\text{maximum thickness} - \text{minimum thickness}) / \text{average thickness}] \times 100$$

[0064] An average film thickness was calculated from the area, weight and density of a sample to be measured. Here, a density was 1.397 for polyethylene terephthalate, 1.354 for polyethylene naphthalate, and 1.270 for polycyclohexanedimethylene terephthalate.

(3) Average surface roughness

[0065] The surface roughness of a polyester base film was measured and used as an average surface roughness. When a base film had a coating layer on one surface, the surface roughness of the uncoated surface was measured. When a base film had coating layers on both surfaces, the coating layer was carefully removed with methyl ethyl ketone (MEK) or acetone so that the surface conditions of the base film did not change, and the surface roughness was measured on the exposed surface.

[0066] S_{Ra} was measured as a surface roughness with a two-beam interference type non-contact surface shape measuring system (Micromap 512 manufactured by MICROMAP; object lens of 20 times magnification). The measurement was carried out with 20 views, and an averaged value was used as an average surface roughness.

(4) Intrinsic viscosity of polyester film

[0067] The intrinsic viscosity of a polyester film was measured as follows:

[0068] Coating layers were completely removed from a base film with an organic solvent such as MEK or acetone, and the film was thoroughly dried. Then, the film was dissolved in a mixed solvent of phenol and tetrachloroethane (weight ratio of 50:50), and an intrinsic viscosity was measured at 30°C.

(5) Average particle size in suspension

[0069] A particle size distribution in a suspension containing an organic polymer was measured with a particle size analyzer (UPA 9340, laser Doppler/frequency analysis type, manufactured by NIKKISO Co., Ltd.), and then an average particle size was calculated.

(6) Degree of color density unevenness of printed images

[0070] An ink ribbon was produced by forming a sublimation type ink layer on an ink-receptive coating layer, which was formed on one surface of a biaxially oriented polyester film sample, and coating a back layer on the other surface of the film sample.

[0071] In the case of a film having no coating layer, an ink layer was formed on one surface of the film, while a back layer was coated on the other surface.

[0072] A sublimation type ink vehicle and a back layer vehicle, which had the following compositions, were successively gravure coated so that a dry coated weight was 1 g/m², and dried. The coated film was then cut to form an ink ribbon.

Compositions of ink vehicle and back layer vehicle

Yellow:

5 [0073]

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MIKELEX YELLOW 6G (Bayer AG)	2 parts
Polyvinylacetoacetal KS-5D (Sekisui Chemical Co., Ltd.)	3 parts
Toluene/MEK (1:1 by weight)	95 parts

15 Magenta:

[0074]

20

BAYMICRON VPSN2670 (Bayer AG)	3 parts
Polyvinylacetoacetal KS-5D (Sekisui Chemical Co., Ltd.)	4 parts
Toluene/MEK (1:1 by weight)	93 parts

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Cyan:

[0075]

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KAYASET BLUE 714 (NIPPON KAYAKU Co., Ltd.)	4 parts
Polyvinylacetoacetal KS-5D (Sekisui Chemical Co., Ltd.)	4 parts
Toluene/MEK (1:1 by weight)	92 parts

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Back layer:

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[0076]

45

Polyvinylbutyral, ESLECK BX-1 (Sekisui Chemical Co., Ltd.)	2 parts
Polyisocyanate, BARNOCK D 750-45 (DAINIPPON INK AND CHEMICALS, INC.)	9 parts
Phosphate ester lubricant, PLYSURF A208S (DAI-ICHI KOGYO SEIYAKU CO., LTD.)	2 parts
Talc, MICROACE L-1 (Nippon Talc Co., Ltd.)	0.3 part
Toluene/MEK (1:1 by weight)	86.7 parts

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[0077] Each ink ribbon was set in a marketed sublimation type color printer, and test printed in a sublimation transfer mode. A printing paper was a standard paper exclusive for the printer.

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[0078] In the test, a photograph of a human face was successively printed on five sheets of printing paper based on digital data (data size: about 32 Mb; A4 size image), and the reproducibility of color tone was evaluated. The evaluation was made visually by comparing the entire color tones of five printed pictures carefully, and by measuring the color of

the same skin-colored parts of the five printed pictures with a color analyzer (TC-1800 MKII manufactured by TOKYO DENSHOKU Co., Ltd.) and calculating the maximum value of color difference (ΔE).

[0079] With regards to the reproducibility of color tone, the results of visual evaluation were ranked according to the following three criteria:

- A: No difference of color tone was observed in the images, and the reproducibility was good.
- B: The difference of color tone was observed but only by the very careful observation.
- C: The difference of color tone was observed at a glance (disqualified)

(7) Breaking strength of film

[0080] A sample film of 50 mm in length and 15 mm in width was pulled at a rate of 200 m/min. with a tensile tester (Intesco Model 2001 manufactured by INTESCO) in a room which was conditioned at 23°C, 50 %RH. Then, a ratio of a load at break to an original cross sectional area (mm^2) of the sample was calculated from a tensile stress-strain curve, and used as a breaking strength.

(8) Thermal shrinkage factor of film

[0081] A sample film was heated at 180°C for 3 minutes with free ends using a hot air-circulation type oven, and the dimensional change (%) of the sample film between before and after the thermal treatment in the machine and transverse directions was calculated.

(9) Bond strength

[0082] Two test pieces of a laminate film were laminated with the coated surface of one piece contacting with the back surface of the other piece and maintained for 24 hours while pressing a rectangular area of 12.5 cm in width and 10.0 cm in length under a pressure of 10 kgf/cm^2 with a press in an air-conditioned room at 40°C, 80 %RH, and then the pressure was removed. After that, the conditions of the air-conditioned room were changed to 23°C and 50 %RH, and such conditions were maintained for 24 hours.

[0083] Thereafter, the test pieces were removed from the air-conditioned room. A strained piano wire having a diameter of 0.8 mm was inserted between the pair of laminated pieces and moved at a rate of 50 cm/min. while maintaining the piano wire in a parallel position with the side having a length of 1.5 cm of the pressed rectangular area. Thus, the pressed part was separated. An average line was drawn in the chart of peeling load (gf/125 mm), which was applied to the piano wire during the peeling procedure, and a load corresponding to the average line was used as a bond strength.

(10) F5 value

[0084] A sample film having a width of 15 mm was chucked with a chuck distance of 50 mm and pulled at a rate of 200 mm/min. with a tensile tester (Intesco Model 2001 manufactured by INTESCO) in a room conditioned at 23°C, 50 %RH. Then, a load (kgf) when the sample was stretched by 5 % of the original length was divided by the original cross sectional area (mm^2), which was calculated using the above-described total thickness of the laminate film. Such a load was measured at 5 points, and averaged to obtain a F5 value.

Example 1

[0085] Pellets of polyethylene terephthalate having an intrinsic viscosity of 0.66 and containing 0.3 % of silica particles with an average particle size of 1.2 μm was thoroughly dried by heating, and then supplied to an extruder and melt extruded at 290°C to obtain an unstretched film. In this case, the extruder was equipped with a filter of 10 μm cut to remove foreign materials and a gear pump to meter and discharge a melt while suppressing pulsation, and a static mixer was installed in a melt line to level the temperature distribution in the polyester melt.

[0086] The melt was extruded through a T die in the form of a film, and the film was wound around a cooling drum the surface temperature of which was kept at 40°C by an electrostatic sticking method, and cooled to solidify. The slit gap distance of a T die was 1.1 mm, and the thickness of the unstretched film, which had been cooled and solidified, was 91 μm . The ratio of the slit gap distance to the unstretched film which had been cooled and solidified was about 12.1. In the electrostatic sticking method, a voltage of 6 kV was applied using an amorphous metal blade made of cobalt-chromium-molybdenum-carbon having a thickness of 20 μm and a width of 2 mm. A zone in which the casting was carried out was surrounded by walls like a small room to avoid the influence of wind from an air conditioner, etc. As a result, the fluctuation of a touching line at which the molten polyester touched the cooling drum could be made sub-

stantially zero (0) in the full width of an effective product.

[0087] The obtained unstretched film was supplied to a stretching process in a machine direction. The film was stretched by a roll-stretching method in its machine direction at 100 °C at a draw ratio of 2.70 in the first stretching step, and then at 87°C at a draw ratio of 1.60 in the second stretching step. In this case, both the first and second stretching steps were carried out with supplying nip rolls to low speed and high speed rolls, which stretch the film using the difference of circumferential velocities, at positions where the film left the respective rolls and positions where the film firstly touched the rolls to press the film against the rolls so that positions, at which the plastic deformation of the film started and ended in the stretching region, did not fluctuate.

[0088] One surface of the obtained film, which had been uniaxially oriented, was treated by corona discharging in an air, and then a mixture, which had been prepared by mixing aqueous dispersions of components in the following composition, was applied to the treated surface by gravure coating. The coated amount of the aqueous dispersion was 6 g/m², and the solid content in the aqueous dispersion was 10 wt. %.

Composition of aqueous dispersion	
Polyester resin	40 parts (solid component)
Acrylic resin	40 parts (solid component)
Oxazoline crosslinking agent	20 parts (solid component)

[0089] The above dispersion of the polyester resin contained a polyester consisting of, as acid components, 55 mole % of terephthalic acid, 40 mole % of isophthalic acid and 5 mole % of 5-sodiumsulfoisophthalic acid, and as diol components, 60 mole % of ethylene glycol, 13 mole % of diethylene glycol and 27 mole % of 1,4-butanediol. The dispersion of the acrylic resin contained an acrylic resin consisting of 50 mole % of ethyl acrylate, 35 mole % of isobutyl methacrylate, 10 mole % of 2-hydroxyethylmethacrylate and 5 mole % of methacrylic acid. The dispersion of the oxazoline crosslinking agent contained a polymer consisting of 58.2 wt. % of styrene, 21.8 wt. % of butyl acrylate and 20 wt. % of 2-vinyl-2-oxazoline.

[0090] After the coating treatment, the film was supplied to a drying and preheating process. In this step, the following countermeasures were employed so as to suppress the vibration of the film carrying the coated aqueous dispersion as much as possible:

[0091] In a distance (2 m) from the gravure coater to the entrance of a tenter, two free rolls were set at equal intervals, and were allowed to be in contact with the opposite surface of the film to the coated surface at a wrap angle of the film of 2 degrees. Then, the both edges of the film were clamped with tenter clips. A hot air, the pulsation of which was suppressed by inverter controlling, was blown onto the film to remove water from the aqueous dispersion. The temperature of the film gradually rose as the water was removed from the coated layer, and as a result, the film was thermally expanded and thus the center part of the film sagged. Thus, the clip distance of the tenter was slightly widened towards the end of the tenter to remove the sagging of the center part of the film.

[0092] Because of the above countermeasures, the maximum amplitude of vibration of the film was 1.5 cm in the drying zone from the exit of the coater for a coating liquid to the position where water in the coated layer was fully evaporated.

[0093] Next, the film was stretched in its transverse direction at 105°C at a draw ratio of 4.5, and then heat treated in a subsequent tenter at 230°C for 2 seconds. Thereafter, the film was relaxed at 210°C by reducing the clip distance by 5 %, and passed through a cooling zone to obtain a biaxially oriented polyester film having a total thickness of 4.5 µm, which carried a laminated coating layer having a thickness of 0.1 µm.

[0094] The properties of the obtained polyester film are listed in Table 1.

[0095] The obtained film carried, on one surface, a coating layer to which a sublimation type ink is easily adhered and which was formed by in-line coating, and had less thickness fluctuation. Thus, an ink ribbon, which was prepared using this film, could print images having less unevenness of color density.

Comparative Example 1

[0096] The same polyester as that used in Example 1 was extruded, casted, stretched in a machine direction, and subjected to the corona discharge treatment, in the same ways as in Example 1. Furthermore, the same aqueous dispersion was applied in the same manner as in Example 1.

[0097] Thereafter, the edges of the film were clamped with tenter clips while providing the same countermeasures as those used in Example 1 to suppress the film vibration in the drying zone except that no free roll was provided in the

distance from the gravure coater to the entrance of the tenter. After that, a hot air, the pulsation of which was suppressed by inverter controlling, was blown onto the film to remove water from the aqueous dispersion. In this step, the clip distance of the tenter was not widened towards the end of the tenter, and therefore the film, the center of which sagged, was passed through a drying zone. The maximum amplitude of vibration of the film in the drying zone was 7 cm.

[0098] Thereafter, the film was stretched in a transverse direction, heat set, and relaxed in the transverse direction in the same ways as in Example 1 to obtain a biaxially oriented polyester film having a total thickness of 4.5 μm , which carried a laminated coating layer having a thickness of 0.1 μm .

[0099] The properties of the obtained polyester film are listed in Table 1.

[0100] The obtained film carried, on one surface, a coating layer to which a sublimation type ink is easily adhered but had a large thickness fluctuation. Thus, an ink ribbon, which was prepared using this film, could print images having a large unevenness of color density, and was not suitable for printing full-color images.

Comparative Example 2

[0101] The same polyester as that used in Example 1 was extruded, casted, stretched in a machine direction, and subjected to the corona discharge treatment, in the same ways as in Example 1. Then, the film was passed through a gravure coater without applying any aqueous dispersion unlike Example 1.

[0102] Thereafter, the edges of the film were clamped with tenter clips while providing the same countermeasures as those used in Example 1 to suppress the film vibration in the drying zone except that no free roll was provided in the distance from the gravure coater to the entrance of the tenter, like Comparative Example 1. After that, a hot air, the pulsation of which was suppressed by inverter controlling, was blown onto the film to remove water from the aqueous dispersion. In this step, the clip distance of the tenter was not widened towards the end of the tenter, and therefore the film, the center of which sagged, was passed through a drying zone. The maximum amplitude of vibration of the film in the drying zone was 7 cm.

[0103] Thereafter, the film was stretched in a transverse direction, heat set, and relaxed in the transverse direction in the same ways as in Example 1 to obtain a biaxially oriented polyester film having a total thickness of 4.4 μm but carrying no coating layer.

[0104] The properties of the obtained polyester film are listed in Table 1.

[0105] The level of thickness fluctuation was good, but the film carried no coating layer to which a sublimation type ink is easily adhered. Therefore, when an ink ribbon was produced using this film, an ink layer was peeled off from the film, and thus the ink ribbon could not be used in printing.

Example 2

[0106] Pellets of polyethylene naphthalate (PEN) having an intrinsic viscosity of 0.55 and containing 0.3 % of silica particles with an average particle size of 1.2 μm was thoroughly dried by heating, and then supplied to an extruder and melt extruded at 305°C to obtain an unstretched film. In this case, the extruder was equipped with the same filter and gear pump as those used in Example 1, and the static mixer as that used in Example 1 was installed in a melt line.

[0107] The melt was extruded through a T die in the form of a film, and the film was wound around a cooling drum the surface temperature of which was kept at 60°C by an electrostatic sticking method, and cooled to solidify. The slit gap distance of a T die was 1.1 mm, and the thickness of the unstretched film, which had been cooled and solidified, was 107 μm . The ratio of the slit gap distance to the unstretched film which had been cooled and solidified was about 10.3. In the electrostatic sticking method, the same voltage was applied using the same amorphous metal blade as in Example 1. A zone in which the casting was carried out was surrounded by walls like a small room to avoid the influence of wind from an air conditioner, etc. like Example 1. As a result, the fluctuation of a touching line at which the molten polyester touched the cooling drum could be made substantially zero (0) in the full width of an effective product.

[0108] The obtained unstretched film was supplied to a stretching process in a machine direction. The film was stretched by a roll-stretching method in its machine direction at 130°C at a draw ratio of 2.70 in the first stretching step, and then at 123°C at a draw ratio of 1.80 in the second stretching step. In this case, both the first and second stretching steps were carried out with supplying nip rolls to the low speed and high speed rolls at the same positions as those in Example 1 to press the film against the rolls so that positions, at which the plastic deformation of the film started and ended in the stretching region, did not fluctuate.

[0109] One surface of the uniaxially stretched film was treated by corona discharging in an air, and then an aqueous dispersion having the same composition as that used in Example 1 was applied in the same amount to the treated surface by gravure coating to suppress the film fluctuation as much as possible.

[0110] After the coating treatment, the film was supplied to a drying and preheating process. In this step, the same countermeasures as those employed in Example 1 were also employed. Because of such countermeasures, the max-

imum amplitude of vibration of the film was 1.5 cm in the drying zone from the exit of the coater for a coating liquid to the position where water in the coated layer was fully evaporated.

[0111] Next, the film was stretched in its transverse direction at 135°C at a draw ratio of 4.7, and then heat treated in a subsequent tenter at 230°C for 2 seconds. Thereafter, the film was relaxed at 210°C by reducing the clip distance by 5 %, and passed through a cooling zone to obtain a biaxially oriented polyester film having a total thickness of 4.5 μm , which carried a laminated coating layer having a thickness of 0.1 μm .

[0112] The properties of the obtained polyester film are listed in Table 1.

[0113] In this Example using PEN, the obtained film carried, on one surface, a coating layer to which a sublimation type ink is easily adhered and which was formed by in-line coating, and had less thickness fluctuation, like Example 1.

Thus, an ink ribbon, which was prepared using this film, could print images having less unevenness of color density.

Comparative Example 3

[0114] The same polyester as that used in Example 2 was extruded, casted, stretched in a machine direction, and subjected to the corona discharge treatment, in the same ways as in Example 2. Furthermore, the same aqueous dispersion was applied in the same manner as in Example 2.

[0115] Thereafter, the edges of the film were clamped with tenter clips while providing the same countermeasures as those used in Example 2 to suppress the film vibration in the drying zone except that no free roll was provided in the distance from the gravure coater to the entrance of the tenter. After that, a hot air, the pulsation of which was suppressed by inverter controlling, was blown onto the film to remove water from the aqueous dispersion. In this step, the clip distance of the tenter was not widened towards the end of the tenter, and therefore the film, the center of which sagged, was passed through a drying zone. The maximum amplitude of vibration of the film in the drying zone was 7 cm.

[0116] Thereafter, the film was stretched in a transverse direction, heat set, and relaxed in the transverse direction in the same ways as in Example 2 to obtain a biaxially oriented polyester film having a total thickness of 4.5 μm , which carried a laminated coating layer having a thickness of 0.1 μm .

[0117] The properties of the obtained polyester film are listed in Table 1.

[0118] The obtained film carried, on one surface, a coating layer to which a sublimation type ink is easily adhered but had a large thickness fluctuation and which was formed by in-line coating. Thus, an ink ribbon, which was prepared using this film, printed images having a large unevenness of color density, and was not suitable for printing full-color images.

Table 1

	Ex. 1	C. Ex. 1	C. Ex. 2	C. Ex. 3	Ex. 2
In-line coating	Yes	Yes	No	Yes	Yes
Thickness fluctuation					
-Machine direction	4 %	12 %	3 %	4 %	12 %
-Transverse direction	3 %	11 %	3 %	3 %	11 %
Maximum color difference at skin-colored parts (ΔE)	0.6	1.8	---	0.6	1.8
Reproducibility of color tone by visual inspection	A	C	---	A	C
Bond strength (g/125 mm)	18	18	0	18	18
F5 (kgf/mm ²)					
-Machine direction	12.8	12.8	12.8	13.8	13.8
-Transverse direction	12.0	12.0	12.0	13.2	13.2

[0119] The following coating liquids were used in following Examples 3-6 and Comparative Example 4:

(Polyester polymer: A)

[0120] Polyester polymer consisting of 90 mole % of terephthalic acid and 10 mole % of 5-sodiumsulfoisophthalic acid as dicarboxylic acid components, and 73 mole % of ethylene glycol and 27 mole % of diethylene glycol as glycol components.

(Acrylic polymer: B)

[0121] Acrylic polymer consisting of 35 mole % of methacrylic acid, 35 mole % of alkyl methacrylate and 30 mole % of styrene.

(Crosslinking agent or crosslinkable polymer: C1)

[0122] A water-soluble epoxy compound comprising tetraglycerol tetraglycidyl ether.

(Crosslinking agent or crosslinkable polymer: C2)

[0123] A water-soluble melamine compound comprising mononucleic, dinucleic and trinucleic materials of substantially tetrafunctional methylol- and methoxymethylolmelamine.

Example 3

[0124] Pellets of polyethylene naphthalate having an intrinsic viscosity of 0.55 and containing 0.7 % of silica particles with an average particle size of 1.2 μm was thoroughly dried by heating, and then supplied to an extruder and melt extruded at 305°C to obtain an unstretched film. In this case, the extruder was equipped with a filter of 10 μm cut to remove foreign materials and a gear pump to meter and discharge a melt while suppressing pulsation, and a static mixer was installed in a melt line to level the temperature distribution in the polyester melt.

[0125] The melt was extruded through a T die in the form of a film, and the film was wound around a cooling drum the surface temperature of which was kept at 60°C by an electrostatic sticking method, and cooled to solidify. The slit gap distance of a T die was 1.1 mm. In the electrostatic sticking method, a voltage of 6 kV was applied using an amorphous metal blade made of cobalt-chromium-molybdenum-carbon having a thickness of 20 μm and a width of 2 mm. A zone in which the casting was carried out was surrounded by walls like a small room to avoid the influence of wind from an air conditioner, etc. As a result, the fluctuation of a touching line at which the molten polyester touched the cooling drum could be made substantially zero (0) in the full width of an effective product.

[0126] The obtained unstretched film was supplied to a stretching process in a machine direction. The film was stretched by a roll-stretching method in its machine direction at 130°C at a draw ratio of 2.70 in the first stretching step, and then at 123°C at a draw ratio of 1.90 in the second stretching step. In this case, both the first and second stretching steps were carried out with supplying nip rolls to low speed and high speed rolls, which stretch the film using the difference of circumferential velocities, at positions where the film left the respective rolls and positions where the film firstly touched the rolls to press the film against the rolls so that positions, at which the plastic deformation of the film started and ended in the stretching region, did not fluctuate.

[0127] One surface of the uniaxially stretched film was treated by corona discharging in an air, and then a mixture, which had been prepared by mixing aqueous dispersions or solutions of components to attain the solid contents shown in Table 2, was applied to the treated surface by gravure coating.

[0128] After the coating treatment, the film was supplied to a drying and preheating process. In this step, the following countermeasures were employed so as to suppress the vibration of the film carrying the applied coating liquid as much as possible:

[0129] In a distance (2 m) from the gravure coater to the entrance of a tenter, two free rolls were set at equal intervals, and were allowed to be in contact with the opposite surface of the film to the coated surface at a wrap angle of the film of 2 degrees. Then, the both edges of the film were clamped with tenter clips. A hot air, the pulsation of which was suppressed by inverter controlling, was blown onto the film to remove water from the aqueous dispersion. The temperature of the film gradually rose as the water was removed from the coated layer, and as a result, the film was thermally expanded and thus the center part of the film sagged. Thus, the clip distance of the tenter was slightly widened towards the end of the tenter to remove the sagging of the center part of the film.

[0130] Because of the above countermeasures, the maximum amplitude of vibration of the film was 1.5 cm in the drying zone from the exit of the coater for a coating liquid to the position where water in the coated layer was fully evaporated.

[0131] Next, the film was stretched in its transverse direction at 135°C at a draw ratio of 4.8, and then heat treated in a subsequent tenter at 230°C for 2 seconds. Thereafter, the film was relaxed at 180°C by reducing the clip distance by 3 %, and passed through a cooling zone to obtain a biaxially oriented polyester film, which carried a laminated coating layer having a thickness of 0.09 μm . This coating layer improved the adhesion strength to a sublimation type ink.

[0132] Thirty thousand (30,000) meters of this laminate film was wound in a roll form around a core having an inner diameter of 6 inch and a wall thickness of 10 mm at a suitable tightness such that no weaving occurred, while trimming the film to a width of 500 mm.

[0133] The properties of the obtained laminate film were measured, and the results are listed in Table 3.

[0134] After the roll-form film was treated at high temperature and high humidity as described below, a sublimation type thermal transfer printing ribbon was produced from the treated rolled film, and its properties were evaluated.

5 (Production of sublimation type thermal transfer printing ribbon after high temperature/high humidity treatment)

[0135] The roll-form laminate film was treated in an air-conditioned room at 40°C, 80 %RH for 24 hours. After the treatment, the conditions of the air-conditioned room were changed to 23°C, 50 %RH, and the film was maintained under such conditions for 24 hours. Then, the laminate film was unwound and traveled over a plurality of rotating rolls, and the opposite surface of the film to the coated surface was gravure coated with a coating liquid, which contained 2 parts of polyvinylbutyral, ESLECK BX-1 (manufactured by Sekisui Chemical Co., Ltd.), 9 parts of polyisocyanate, BARNOCK D 750-45 (manufactured by DAINIPPON INK AND CHEMICALS, INC.), 2 parts of a phosphate ester lubricant, PLYSURF A208S (manufactured by DAI-ICHI KOGYO SEIYAKU CO., LTD.), 0.3 part of talc, MICROACE L-1 (manufactured by Nippon Talc Co., Ltd.), and 86.7 parts of toluene/MEK (1:1 by weight). The coated liquid was dried to form a heat-resistant easy-slipping layer having a thickness of 1.0 μm.

[0136] Next, the film carrying the heat-resistant easy-slipping layer was traveled over a plurality of rotating rolls, and then each of ink coating liquids having the following compositions was applied onto the coated layer opposite to the heat-resistant easy-slipping layer by gravure coating, and dried to form a sublimation type ink layer having a final thickness of 1.0 μm. Thus, an ink ribbon was obtained. Compositions of ink coating liquids:

20

Yellow:

[0137]

25

MACROLEX YELLOW 6G (Bayer AG)	2 parts
Polyvinylacetoacetal KS-5D (Sekisui Chemical Co., Ltd.)	3 parts
Toluene/MEK (1:1 by weight)	95 parts

30

Magenta:

35 [0138]

BAYMICRON VPSN2670 (Bayer AG)	3 parts
Polyvinylacetoacetal KS-5D (Sekisui Chemical Co., Ltd.)	4 parts
Toluene/MEK (1:1 by weight)	93 parts

40

45 Cyan:

[0139]

50

KAYASET BLUE 714 (NIPPON KAYAKU Co., Ltd.)	4 parts
Polyvinylacetoacetal KS-5D (Sekisui Chemical Co., Ltd.)	4 parts
Toluene/MEK (1:1 by weight)	92 parts

55

Example 4

[0140] A laminate film was prepared in the same manner as in Example 3 except that the thickness of an unstretched film was changed so that the thickness of a polyethylene naphthalate film as a final substrate was the same as that of Example 3, the draw ratio in the second step of the stretching in the machine direction was changed to 1.6, the solid content of a coating liquid was adjusted so that the final thickness of the coating layer was the same as that of Example 3, and the draw ratio of the stretching in the machine direction was changed to 4.3. The properties of this laminate film were measured. The results are listed in Table 3.

[0141] Furthermore, a sublimation type thermal transfer printing ribbon was prepared after the treatment at high temperature and high humidity in the same manner as in Example 3, and its properties were measured. The results are also listed in Table 3.

Comparative Example 4

[0142] The same polyester as that used in Example 3 was extruded, casted, stretched in a machine direction, and subjected to the corona discharge treatment, in the same ways as in Example 3. Furthermore, the same aqueous dispersion was applied in the same manner as in Example 3.

[0143] Thereafter, the edges of the film were clamped with tenter clips while providing the same countermeasures as those used in Example 3 to suppress the film vibration in the drying zone except that no free roll was provided in the distance from the gravure coater to the entrance of the tenter. After that, a hot air, the pulsation of which was suppressed by inverter controlling, was blown onto the film to remove water from the aqueous dispersion. In this step, the clip distance of the tenter was not widened towards the end of the tenter, and therefore the film, the center of which sagged, was passed through a drying zone. The maximum amplitude of vibration of the film in the drying zone was 7 cm.

[0144] Thereafter, the film was stretched in a transverse direction, heat set, and relaxed in the transverse direction in the same ways as in Example 3 to obtain a laminate film. The properties of the this laminate film are listed in Table 3.

[0145] Furthermore, a sublimation type thermal transfer printing ribbon was prepared after the treatment at high temperature and high humidity in the same manner as in Example 3, and its properties were measured. The results are also listed in Table 3.

Example 5

[0146] Pellets of polyethylene terephthalate having an intrinsic viscosity of 0.66 and containing 0.7 % of silica particles with an average particle size of 1.2 μm was thoroughly dried by heating, and then supplied to an extruder and melt extruded at 290°C to obtain an unstretched film. In this case, the extruder was equipped with the same filter and gear pump as those used in Example 3, and the static mixer as that used in Example 3 was installed in a melt line.

[0147] The melt was extruded through a T die in the form of a film, and the film was wound around a cooling drum the surface temperature of which was kept at 40°C by an electrostatic sticking method, and cooled to solidify. The slit gap distance of a T die was 1.1 mm. In the electrostatic sticking method, the same voltage was applied using the same amorphous metal blade as in Example 3. A zone in which the casting was carried out was surrounded by walls like a small room to avoid the influence of wind from an air conditioner, etc. like Example 3. As a result, the fluctuation of a touching line at which the molten polyester touched the cooling drum could be made substantially zero (0) in the full width of an effective product.

[0148] The obtained unstretched film was supplied to a stretching process in a machine direction. The film was stretched by a roll-stretching method in its machine direction at 100°C at a draw ratio of 2.70 in the first stretching step, and then at 87°C at a draw ratio of 1.60 in the second stretching step. In this case, both the first and second stretching steps were carried out with supplying nip rolls to the low speed and high speed rolls at the same positions as those in Example 3 to press the film against the rolls so that positions, at which the plastic deformation of the film started and ended in the stretching region, did not fluctuate.

[0149] One surface of the uniaxially stretched film was treated by corona discharging in an air, and then a coating liquid was applied to the treated surface in the same manner as in Example 3 except that the composition was changed as shown in Table 2 and the solid content of the coating liquid was changed so that the final thickness of the coating layer was the same as that of Example 3.

[0150] After the coating treatment, the film was supplied to a drying and preheating process. In this step, the same countermeasures as those employed in Example 3 were also employed so as to suppress the vibration of the coated film as much as possible. Because of such countermeasures, the maximum amplitude of vibration of the film was 1.5 cm in the drying zone from the exit of the coater for a coating liquid to the position where water in the coated layer was fully evaporated.

[0151] Next, the film was stretched in its transverse direction at 105°C at a draw ratio of 4.4, and then heat treated in a subsequent tenter at 220°C for 2 seconds. Thereafter, the film was relaxed at 180°C by reducing the clip distance by 3 %, and passed through a cooling zone to obtain a biaxially oriented polyester film, which carried a laminated coating layer having a final thickness of 0.09 μm .

[0152] The properties of the laminate film are listed in Table 3.

[0153] Furthermore, a sublimation type thermal transfer printing ribbon was prepared after the treatment at high temperature and high humidity in the same manner as in Example 3, and its properties were measured. The results are also listed in Table 3.

Example 6

[0154] A laminate film was prepared in the same manner as in Example 3 except that the composition of a coating liquid was changed as shown in Table 2. The properties of the laminate film are listed in Table 3.

[0155] When a sublimation type thermal transfer printing ribbon was prepared from this laminate film in the same manner as in Example 3, it was difficult to peel off one turn of the wound film from the next turn in the course of unwinding the film to prepare an ink ribbon, and the yield slightly decreased.

[0156] The total thickness of each of the laminate films obtained in Examples 3-6 and Comparative Example 4 was 2.8 μm .

Table 2

Solid compositions of coating liquids (wt. %) and final coating thickness (μm)					
	Ex. 3	Ex. 4	Ex. 5	C. Ex. 4	Ex. 6
Polyester polymer A	50	50	50	50	60
Acrylic polymer B	30	30	30	30	40
Crosslinking agent or crosslinkable polymer					
-C1	20	20	0	20	0
-C2	0	0	20	0	0
Final coating thickness (μm)	0.09	0.09	0.09	0.09	0.09

Table 3

	Ex. 3	Ex. 4	Ex. 5	C. Ex. 4	Ex. 6
In-line coating	Yes	Yes	Yes	Yes	Yes
Thickness fluctuation					
-Machine direction	7 %	8 %	7 %	19 %	7 %
-Transverse direction	5 %	6 %	5 %	17 %	5 %
Maximum color difference at skin-colored parts (ΔE)	0.8	0.9	0.8	2.5	0.8
Reproducibility of color tone by visual inspection	A	A	A	C	A
Bond strength (g/125 mm)	12	12	7	12	130
F5 (kgf/mm^2)					
-Machine direction	14.0	12.0	13.2	14.0	14.0
-Transverse direction	13.5	11.0	13.1	13.5	13.5

EFFECTS OF THE INVENTION

[0157] The biaxially oriented polyester film for thermal transfer printing of the present invention carries a coating layer which imparts special functions for thermal transfer printing, and has less thickness fluctuation, although such a coating layer is laminated by the application of a coating liquid comprising water as a medium in the course of film production. As a result, an ink ribbon prepared using the film of the present invention can print images having less unevenness of color density with good reproducibility of color tone.

Claims

1. A biaxially oriented polyester film for thermal transfer printing, which is obtained by applying a coating liquid containing a water-soluble or water-dispersible organic polymer to at least one surface of a polyester film prior to the completion of crystallization by orientation, drying said coating liquid, stretching said film and thermally treating said film, and which has a thickness of 20 μm or less, wherein a thickness fluctuation in any 15 meter interval in the machine direction of the coated film is 10 % or less.
2. A polyester film according to claim 1, wherein a thickness fluctuation in any 15 meter interval in the machine direction of the coated film is 7 % or less.
3. A polyester film according to claim 1, wherein a thickness fluctuation in any 15 meter interval in the machine direction of the coated film is 5 % or less.
4. A polyester film according to claim 1, wherein a thickness fluctuation in any 3 meter interval in the transverse direction of the coated film is 10 % or less.
5. A polyester film according to claim 1, wherein a thickness fluctuation in any 3 meter interval in the transverse direction of the coated film is 7 % or less.
6. A polyester film according to claim 1, wherein a thickness fluctuation in any 3 meter interval in the transverse direction of the coated film is 5 % or less.
7. A polyester film according to any one of claims 1 to 6, wherein said polyester has an intrinsic viscosity of 0.45 to 1.20 dl/g, when it is measured using a mixed solvent of phenol and tetrachloroethane (weight ratio of 50:50) at 30°C.
8. A polyester film according to any one of claims 1 to 7, wherein the total thickness of the coated film is 20 μm or less.
9. A polyester film according to any one of claims 1 to 8, wherein a bond strength of the coated layer is 100 gf/125 mm or less.
10. A polyester film according to any one of claims 1 to 9, which has a F5 value of at least 13.0 kgf/mm² in the machine and transverse directions.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP98/05431

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁶ B41M5/40, B32B27/36		
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) Int.Cl ⁶ B41M5/38-5/40		
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 practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E, X	JP, 10-329292, A (Toray Industries, Inc.), 15 December, 1998 (15. 12. 98), Pages 3, 4 (Family: none)	1-6, 10
X Y	JP, 9-239931, A (Daifol Hoechst Co., Ltd.), 16 September, 1997 (16. 09. 97), Pages 3, 5 (Family: none)	1-6, 8, 9 7, 10
X Y	JP, 5-77374, A (Toray Industries, Inc.), 30 March, 1993 (30. 03. 93), Pages 3, 5 (Family: none)	1-9 10
Y	JP, 4-10985, A (Mitsubishi Paper Mills Ltd.), 16 January, 1992 (16. 01. 92), Page 5, lower left column & DE, 4113581, A	7, 8
Y	JP, 4-41297, A (Toray Industries, Inc.), 12 February, 1992 (12. 02. 92), Page 1, lower left column; page 3, lower right column (Family: none)	7, 10
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 2 February, 1999 (02. 02. 99)		Date of mailing of the international search report 16 February, 1999 (16. 02. 99)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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