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(54) Inkjet-printing sheet

(57) The inkjet-printing sheet has an ink-bearing layer made of an acrylic copolymer having (a) at least one structural unit having a hydrophilic group, (b) a structural unit having a quaternary ammonium group, and (c) a structural unit formed from a hydrophobic monomer or a monomer having a hydrophobic group having 4 or more carbon atoms. The structural unit (a) is constituted by (i) a structural unit formed from at least one monomer selected from the group consisting of aliphatic carboxylic acids or anhydrides thereof, acrylamides, acrylic monomers having phosphoric groups and vinylpyrrolidones, and optionally (ii) a structural unit having a hydroxyl group and/or an ether bond. When used as a transfer sheet, it has a support layer, a parting layer, an ultraviolet-absorbing layer and an ink-bearing layer in this order.

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Description

[0001] The present invention relates to an inkjet-printing sheet capable of providing inkjet print with excellent clarity, gloss, fixability, light resistance, etc., more particularly to an inkjet-printing sheet capable of forming inkjet print image on a surface which cannot easily be inkjet-printed.

[0002] Because an inkjet printing system is efficient and less costly in forming clear print on various media, it has become widely used recently. An aqueous color ink is usually used in the inkjet printing system, and dyes are used as colorants for the aqueous color ink. Print media are generally papers, plastic films, cloth, etc. To improve the clarity, gloss, fixability, rubbing-off resistance, etc. of inkjet print on such print media, it is a widely accepted practice to coat the print media with layers having affinity for inkjet-printing ink (generally referred to as "ink-bearing layers").

[0003] To form inkjet print including characters and designs on various surfaces which are not easily inkjet-printed, a transfer sheet may be used. The transfer sheet preferably has a support layer, a parting layer and an ink-bearing layer.

[0004] The inkjet print, however, has problems to be overcome in clarity, gloss, fixability and light resistance (discoloration resistance), requiring further improvement. Also, if there are transfer sheets capable of forming inkjet print on desired media surfaces, it may be expected to expand the varieties of surfaces on which inkjet printing can be carried out.

[0005] An object of the present invention, therefore, is to provide an inkjet-printing sheet capable of forming inkjet print with improved clarity, gloss, fixability and discoloration resistance.

[0006] Another object of the present invention is to provide an inkjet-printing transfer sheet capable of forming inkjet print with excellent clarity, gloss, fixability, discoloration resistance, etc. on any media surface.

[0007] As a result of research in view of the above objects, the inventor has found that an inkjet-printing sheet comprising an ink-bearing layer made of an acrylic copolymer having a plurality of structural units having desired hydroxyl groups makes it possible to form inkjet print with excellent clarity, gloss, fixability and discoloration resistance, and that by laminating an ultraviolet-absorbing layer, a parting layer and a support layer on such ink-bearing layer, it is possible to provide an inkjet-printing transfer sheet capable of forming inkjet print with excellent clarity, gloss, fixability and discoloration resistance on any media surface. The present invention has been made based on such findings.

[0008] Thus, the inkjet-printing sheet according to the present invention comprises an ink-bearing layer made of an acrylic copolymer having (a) at least one structural unit having a hydrophilic group, (b) a structural unit having a quaternary ammonium group, and (c) a structural unit formed from a hydrophobic monomer or a monomer having a hydrophobic group having 4 or more carbon atoms.

[0009] The inkjet-printing transfer sheet according to the present invention comprises a support layer, a parting layer, an ultraviolet-absorbing layer and a heat-sealable, ink-bearing layer, the ink-bearing layer being made of an acrylic copolymer having (a) at least one structural unit having a hydrophilic group, (b) a structural unit having a quaternary ammonium group, and (c) a structural unit formed from a hydrophobic monomer or a monomer having a hydrophobic group having 4 or more carbon atoms.

[0010] The inkjet-printing transfer sheet according to a preferred embodiment of the present invention comprises a support layer, a parting layer, an ultraviolet-absorbing layer and a heat-sealable, ink-bearing layer, the ink-bearing layer being made of an acrylic copolymer having (a) at least one structural unit having a hydrophilic group, (b) a structural unit having a quaternary ammonium group, and (c) a structural unit formed from a hydrophobic monomer or a monomer having a hydrophobic group having 4 or more carbon atoms, the structural unit (a) having a hydrophilic group being constituted by (i) a structural unit formed from at least one monomer selected from the group consisting of aliphatic carboxylic acids or anhydrides thereof, acrylamides, acrylic monomers having phosphoric groups and vinylpyrrolidones, and optionally (ii) a structural unit having a hydroxyl group and/or an ether bond.

Fig. 1 is a partial cross-sectional view showing the inkjet-printing transfer sheet according to one embodiment of the present invention; and

Fig. 2 is a partial cross-sectional view showing the transfer sheet adhered to a media surface with the support layer removed.

[0011] The inkjet-printing sheet of the present invention may be used as a recording sheet or a transfer sheet. To distinguish them, the recording sheet is herein called "inkjet-printing recording sheet," and the transfer sheet is herein called "inkjet-printing transfer sheet." Also, both of them are generally called "inkjet-printing sheet."

[1] Inkjet-printing recording sheet

[A] Ink-bearing layer

[0012] The inkjet-printing recording sheet of the present invention comprises an ink-bearing layer made of an acrylic copolymer formed on a support layer.

(1) Acrylic copolymer

(I) Composition

[0013] The acrylic copolymer has (a) at least one

structural unit having a hydrophilic group, (b) a structural unit having a quaternary ammonium group, and (c) a structural unit formed from a hydrophobic monomer or a monomer having a hydrophobic group having 4 or more carbon atoms.

(a) Structural unit having a hydrophilic group

[0014] The structural unit (a) preferably has (i) a structural unit formed from at least one monomer selected from the group consisting of aliphatic carboxylic acids or anhydrides thereof, acrylamides, acrylic monomers having phosphoric groups and vinylpyrrolidones, and if desired, (ii) a structural unit having a hydroxyl group and/or an ether bond.

[0015] The structural unit (i) is a segment having a function of rapidly absorbing water and dyes dissolved or suspended therein, and materials for the structural unit (i) may be aliphatic carboxylic acids or anhydrides thereof such as acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, maleic anhydride, fumaric anhydride, itaconic anhydride, etc.; acrylamides such as (meth)acrylamide, dimethyl (meth)acrylamide, diethyl (meth)acrylamide, (meth)acryloyl morpholine, N,N-dimethylaminopropyl (meth)acrylamide, N,N-diethylaminopropyl (meth)acrylamide, (meth)acrylamide-*t*-butyl sulfonic acid, etc.; phosphoric group-containing acrylic monomers such as mono(2-methacryloyloxyethyl) acidic phosphate, mono(2-acryloyloxyethyl) acidic phosphate, etc.; vinylpyrrolidones such as N-vinyl-2-pyrrolidone, etc.

[0016] The structural unit (ii) is a segment mainly lowering the melting point of the acrylic copolymer, preferably formed from hydroxyl group-containing acrylic monomers such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, etc.; ether bond-containing monomers, etc.; acrylic monomers having both hydroxyl groups and ether bonds.

[0017] The ether bond-containing monomers include the following examples.

1. Acrylic monomers containing alkoxyl groups or alloxy groups

[0018] Methoxy (meth)acrylate, butoxyethyl (meth)acrylate, phenoxyethyl (meth)acrylate, nonylphenoxyethyl (meth)acrylate, etc.

2. Acrylic monomers containing polyoxyethylene groups

[0019] The acrylic monomers containing polyoxyethylene groups may be represented by the general formula:

$$R^1O(CH_2CH_2O)_nCOCR^2{=}CH_2,$$

wherein R^1 is an alkyl group, an aryl group, an aralkyl group or alkylaryl group each having 1-18 carbon atoms, R^2 is hydrogen or a methyl group, n is an integer from 2-30. The preferred examples of the acrylic monomers containing polyoxyethylene groups are methoxydiethylene glycol (meth)acrylate, methoxypolyethylene glycol (meth)acrylate (polymerization degree: 3-30), phethoxypolyethylene glycol (meth)acrylate (polymerization degree: 2-30), nonylphenoxypolyethylene glycol (meth)acrylate (polymerization degree: 2-30), etc.

[0020] Also, the hydroxyl group/ether bond-containing acrylic monomers may be 2-hydroxyl-3-methoxypropyl (meth)acrylate, etc.

[0021] The structural unit (a) may be constituted only by the structural unit (i), but it is preferable that the structural unit (a) contains both structural units (i) and (ii). In a case where both structural units (i) and (ii) are contained, a weight ratio of (i)/(ii) is preferably 97/3-50/50. When the weight ratio of (i)/(ii) is less than 50/50, the acrylic copolymer has too low a melting point, resulting in difficulty in molding. On the other hand, when the weight ratio of (i)/(ii) exceeds 97/3, in practice it is hard to fuse the acrylic copolymer onto the support layer. The more preferred weight ratio of (i)/(ii) is 90/10-70/30.

(b) Structural unit having quaternary ammonium group

[0022] The structural unit (b) is a segment contributing to fixing dyes. The term "quaternary ammonium group" used herein means a tertiary amino group coupled with a counter ion, which is represented by the formula: $-[NR^3R^4R^5]^+\text{-}X^-$, wherein R^3, R^4 and R^5 are alkyl groups, identical or different, X^- is a counter ion such as a halogen group. The quaternary ammonium group may be called a "quaternized amino group." The quaternary ammonium group is obtained by adding a haloalkyl, etc. to an alkylamino group. The structural unit (b) may preferably be formed from such monomers as N,N-dimethylaminoethyl (meth)acrylate • methyl chloride, N,N-dimethylaminopropyl (meth)acrylate • methyl chloride, N,N-dimethylaminoethyl (meth)acrylamide • methyl chloride, N,N-dimethylaminopropyl (meth)acrylamide • methyl chloride, etc. These monomers are represented by the formulae: $[CH_2{=}CHCOO\text{-}C_2H_4N(CH_3)_3]^+ \cdot Cl^-$, $[CH_2{=}C(CH_3)COO\text{-}C_2H_4N(CH_3)_3]^+ \cdot Cl^-$, $[CH_2{=}CHCOO\text{-}C_3H_6N(CH_3)_3]^+ \cdot Cl^-$, $[CH_2{=}C(CH_3)COO\text{-}C_3H_6N(CH_3)_3]^+ \cdot Cl^-$, $[CH_2{=}CHCONH\text{-}C_2H_4N(CH_3)_3]^+ \cdot Cl^-$, $[CH_2{=}C(CH_3)CONH\text{-}C_2H_4N(CH_3)_3]^+ \cdot Cl^-$, $[CH_2{=}CHCONH\text{-}C_3H_6N(CH_3)_3]^+ \cdot Cl^-$, and $[CH_2{=}C(CH_3)CONH\text{-}C_3H_6N(CH_3)_3]^+ \cdot Cl^-$, respectively.

(c) Structural unit formed from hydrophobic monomers or monomers having 4 or more carbon atoms

[0023] The structural unit (c) is a segment which imparts water resistance to the acrylic copolymer, and it should have a hydrophobic group. Accordingly, the structural unit (c) is constituted by a hydrophobic monomer or a monomer having a hydrophobic group having 4

or more carbon atoms. The hydrophobic monomers are not restrictive as long as they do not have hydrophilic groups. Also, even monomers having hydrophilic groups such as -OH, etc. or hydrophilic moieties such as -O-, etc. may be used to form hydrophobic moieties of the acrylic copolymer, as long as the monomers have hydrophobic moieties having 4 or more carbon atoms. Examples of such hydrophobic groups may be long-chain alkyl groups, long-chain alkylene groups, aromatic groups, etc. Such structural units are simply called "hydrophobic structural units."

[0024] Specific examples of the hydrophobic structural unit (c) are those formed from (meth)acrylate monomers such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, isononyl (meth)acrylate, isodecyl (meth)acrylate, n-dodecyl (meth)acrylate, tridecyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, 2-hydroxy-3-phenoxypropyl (meth)acrylate, etc.; carboxylate monomers such as dimethyl maleate, dibutyl maleate, di(2-ethylhexyl) maleate, dimethyl fumarate, dibutyl fumarate, di(2-ethylhexyl) fumarate, dimethyl itaconate, dibutyl itaconate, di(2-ethylhexyl) itaconate, etc.; vinyl monomers such as vinyl acetate, vinyl propionate, vinyl caproate, vinyl laurate, etc.; styrene monomers such as styrene, α-methyl styrene, *o*-methyl styrene, *m*-methyl styrene, *p*-methyl styrene, *p*-*t*-butyl styrene, etc.; (meth)acrylonitrile; vinyl chloride, etc.

(d) Percentage of each structural unit

[0025] The percentages of the structural unit (a), the structural unit (b), and the structural unit (c) are determined such that the structural unit (a) [(i)+(ii)] is 30-90 weight %, the structural unit (b) is 3-50 weight %, and the structural unit (c) is 3-50 weight %.

[0026] When the structural unit (a) [(i)+(ii)] is less than 30 weight %, the fixing of dyes and the hydrophilic properties of the acrylic copolymer are insufficient. On the other hand, when the structural unit (a) [(i)+(ii)] exceeds 90 weight %, the resultant ink-bearing layer has insufficient water resistance.

[0027] When the structural unit (b) is less than 3 weight %, the fixing of dyes is insufficient. On the other hand, when the structural unit (b) exceeds 50 weight %, the resultant ink-bearing layer has insufficient water resistance.

[0028] When the structural unit (c) is less than 3 weight %, the water resistance of the resultant ink-bearing layer is insufficient. On the other hand, when (c) exceeds 50 weight %, the fixing of dyes is insufficient.

[0029] The preferred percentages are that the structural unit (a) [(i)+(ii)] is 50-80 weight %, the structural unit (b) is 10-30 weight %, and the structural unit (c) is 5-20 weight %.

(e) Bonding of each structural unit

[0030] The bonding of each structural unit (a) [(i)+(ii)], (b), and (c) may be a random bonding because a mixture of monomers is copolymerized by a solution polymerization method.

(II) Production method

[0031] Monomers for the structural units (a)-(c) are uniformly dissolved in an organic solvent or a mixture of an organic solvent and water and copolymerized at 50-80°C for 4-10 hours. The organic solvents are preferably hydrophilic organic solvents such as methanol, ethanol, isopropanol, n-butanol, acetone, methyl ethyl ketone, etc. After the completion of the polymerization reaction, water or an organic solvent is added to adjust the viscosity of the polymerization product, if necessary, thus obtaining a uniform solution of the acrylic copolymer.

(iii) Properties

[0032] To provide inkjet print with excellent clarity, gloss, fixability, etc. and to impart excellent rubbing-off resistance to a surface of the ink-bearing layer, the acrylic copolymer preferably has a weight-average molecular weight of 5,000-1,000,000. When the weight-average molecular weight of the acrylic copolymer is less than 5,000, the inkjet print has insufficient clarity and rubbing-off resistance. On the other hand, when it exceeds 1,000,000, the solubility of the acrylic copolymer is not sufficient, resulting in difficulty in forming the ink-bearing layer. The more preferred weight-average molecular weight of the acrylic copolymer is 50,000-500,000.

[0033] The acrylic copolymer preferably has a melting point of 70-180°C. If the melting point is less than 70°C, blocking is likely to take place when a film formed with the ink-bearing layer is wound. On the other hand, if it exceeds 180°C, it is not easy to transfer the ink-bearing layer. The more preferred melting point of the acrylic copolymer is 100-150°C.

(2) Thickness of ink-bearing layer

[0034] The ink-bearing layer has a thickness of 1-50 μm, preferably 5-20 μm. When the thickness of the ink-bearing layer is less than 1 μm, the fixing of inkjet-printing ink is insufficient. On the other hand, when it exceeds 50 μm, inkjet print has blurred edges.

[B] Support layer

[0035] The materials of the support layer are not restrictive as long as the support layer has sufficient mechanical strength to support the ink-bearing layer. Specific examples of such materials for the support layer are papers, plastic films or cloth, etc. The plastic

films may be polyolefins such as polypropylene, polyethylene, etc.; polyesters such as polyethylene terephthalate, polyamides such as nylon, etc. To provide the inkjet print with excellent gloss, plastic films of polyethylene terephthalate, etc. having flat surfaces are preferable. The thickness of the support layer may change depending on materials thereof, but it is preferably 10-150 μm, more preferably 20-100 μm.

[C] Production method

[0036] The inkjet-printing sheet may be produced by the following method which is not restrictive: The ink-bearing layer is laminated on the support layer by coating the support layer with a uniform solution of the acrylic copolymer in a mixed solvent of an organic solvent and water by a gravure coating method, a roll-coating method, etc. and drying it at 50-150°C.

[2] Inkjet-printing transfer sheet

[0037] The transfer sheet preferably comprises a support layer 1, a parting layer 2, an ultraviolet-absorbing layer 3 and an ink-bearing layer 4 laminated in this order as shown in Fig. 1. The inkjet print 5 is also shown on the ink-bearing layer 4. The support layer 1 may be the same as used in the recording sheet. Thus, explanation will be made only on the parting layer 2, the ultraviolet-absorbing layer 3 and the ink-bearing layer 4.

[A] Layer structure

(1) Ink-bearing layer

[0038] The ink-bearing layer of the transfer sheet is made of an acrylic copolymer having (a) at least one structural unit having a hydrophilic group, (b) a structural unit having a quaternary ammonium group, and (c) a structural unit formed from a hydrophobic monomer or a monomer having a hydrophobic group having 4 or more carbon atoms.

[0039] In a case where the structural unit (a) comprises only (i) a structural unit formed from at least one monomer selected from the group consisting of aliphatic carboxylic acids or anhydrides thereof, acrylamides, acrylic monomers having phosphoric groups and vinylpyrrolidones, the composition of the acrylic copolymer is that the structural unit (i) is 30-96 weight %, the structural unit (b) is 3-50 weight %, and the structural unit (c) is 3-50 weight %.

[0040] When the structural unit (b) is less than 3 weight %, the fixing of ink dyes is insufficient. On the other hand, when the structural unit (b) exceeds 50 weight %, irregularities of inkjet print image such as blurring, etc. may take place. Further, when the structural unit (c) is less than 3 weight %, the water resistance of the acrylic copolymer is insufficient. On the other hand, when the structural unit (c) exceeds 50 weight %, the resulting ink-bearing layer cannot sufficiently absorb inkjet-printing ink.

[0041] In a case where the structural unit (a) further comprises (ii) a structural unit having a hydroxyl group and/or an ether bond in addition to the structural unit (i), the composition of the acrylic copolymer is that the structural unit (i) is 90 weight % or less, the structural unit (ii) is 3-70 weight %, the structural unit (b) is 3-50 weight %, and the structural unit (c) is 3-50 weight %. When the structural unit (i) exceeds 90 weight %, the acrylic copolymer is insufficient in water resistance. Also, when the structural unit (ii) is less than 3 weight %, the acrylic copolymer is insufficient in heat sealability. On the other hand, when the structural unit (ii) exceeds 70 weight %, the acrylic copolymer has low film-forming properties.

[0042] The preferred percentages are that the structural unit (i) is 10-70 weight %, the structural unit (ii) is 10-30 weight %, the structural unit (b) is 10-30 weight %, and the structural unit (c) is 10-30 weight %.

[0043] The thickness of the ink-bearing layer 4 is preferably 1-50 μm, preferably 5-20 μm. When the thickness of the ink-bearing layer 4 is less than 1 μm, the heat sealability is insufficient, making it likely that the ink-bearing layer peels off a print-receiving surface 6 (Fig. 2). On the other hand, when the thickness of the ink-bearing layer 4 exceeds 50 μm, the permeation of an inkjet-printing ink becomes insufficient, resulting in blurring in the edges of inkjet print. Though no adhesion is needed because the ink-bearing layer 4 has heat sealability, an adhesion layer may be formed to improve adhesion with the print-receiving surface 6.

(2) Ultraviolet-absorbing layer

[0044] The ultraviolet-absorbing layer 3 is made of a resin having excellent transparency, surface hardness and mechanical strength, which contains an ultraviolet-absorbing agent. Such resins are preferably acrylic resins. By using the acrylic resins for the ultraviolet-absorbing layer 3, inkjet print 5 such as characters and designs formed on the ink-bearing layer 4 is provided with excellent clarity, color and gloss. The ultraviolet-absorbing agent imparts good light resistance to the inkjet print.

[0045] The ultraviolet-absorbing agents may be benzophenone compounds such as 2-hydroxybenzophenone, 2,4-dihydroxybenzophenone, 2,2',4-trihydroxybenzophenone, etc.; salicylate compounds such as phenyl salicylate, 2,4-di-*t*-butylphenyl-3,5-di-*t*-butylphenyl-4-hydroxy benzoate, etc.; benzotriazole compounds such as 2'-hydroxyphenyl benzotriazole, 2'-hydroxy-5'-methylphenyl benzotriazole, etc.; acrylate compounds such as methyl-2-carbomethoxy-3-*p*-methoxy acrylate, etc.; hindered amine compounds such as bis(2,2,6,6-tetramethylpiperidinyl) sebacate, etc.; hindered phenol compounds such as tetrakis-[methylene-3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl) propionate] methane, 2,6-di-*t*-butyl-4-methylphenol, octadecyl-3-(3,5-di-

t-butyl-4-hydroxyphenyl) propionate, 2,2'-methylene-bis(4-methyl-6-*t*-butylphenol), 4,4'-butylidene-bis(6-*t*-butylphenol), etc.

[0046] The acrylic resins forming the ultraviolet-absorbing layer 3 may be either thermoplastic or thermosetting. In the case of thermosetting acrylic resins, they should be self-cross-linkable by containing unsaturated bonds or should contain cross-linking agents. To make the acrylic resins self-cross-linkable, cross-linkable monomers having 2 or more radically-polymerizable unsaturated bonds are added. Such cross-linkable monomers having 2 or more radically-polymerizable unsaturated bonds may be polymerizable unsaturated compounds such as ethylene glycol diacrylate, ethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, 1,4-butanediol diacrylate, neopentyl glycol diacrylate, 1,6-hexanediol diacrylate, pentaerythritol diacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, pentaerythritol dimethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, glycerol dimethacrylate, glycerol diacrylate, glycerol allyloxy dimethacrylate, 1,1,1-tris(hydroxymethylethane) diacrylate, 1,1,1-tris(hydroxymethylethane) triacrylate, 1,1,1-tris(hydroxymethylethane) dimethacrylate, 1,1,1-tris(hydroxymethylethane) trimethacrylate, 1,1,1-tris(hydroxymethylpropane) diacrylate, 1,1,1-tris(hydroxymethylpropane) triacrylate, 1,1,1-tris(hydroxymethylpropane) dimethacrylate, 1,1,1-tris(hydroxymethylpropane) trimethacrylate, diallyl terephthalate, diallyl phthalate, glycidyl acrylate, glycidyl methacrylate, triallyl cyanurate, triallyl isocyanurate, etc. The cross-linkable monomers may be up to 20 weight % of the acrylic copolymer.

[0047] The content of the ultraviolet-absorbing agent in the ultraviolet-absorbing layer 3 is preferably 0.0005-1.0 weight %. When the ultraviolet-absorbing agent is less than 0.0005 weight %, sufficient improvement in light resistance cannot be achieved. On the other hand, even though it exceeds 1.0 weight %, further effects cannot be achieved. The more preferred content of the ultraviolet-absorbing agent in the ultraviolet-absorbing layer 3 is 0.05-0.5 weight %.

[0048] The thickness of the ultraviolet-absorbing layer 3 is preferably 1-50 μm, more preferably 2-20 μm. When the thickness of the ultraviolet-absorbing layer 3 is less than 1 μm, sufficient effects of cutting ultraviolet rays cannot be achieved. On the other hand, when the thickness of the ultraviolet-absorbing layer 3 exceeds 50 μm, effects of cutting ultraviolet rays are saturated, failing to achieve further improvements.

(3) Parting layer

[0049] The parting layer 2 is a layer for making it easy to peel the ultraviolet-absorbing layer 3 and the ink-bearing layer 4 from the support layer 1. The parting layer 2 may be a coating layer of parting materials such as silicone resins which are widely used. The parting layer 2 may be as thin as possible as long as it has sufficient parting properties.

[B] Production method

[0050] The inkjet-printing transfer sheet of the present invention may be produced by the following method which is not restrictive: First, the support layer 1 coated with the parting layer 2 is laminated with the ultraviolet-absorbing layer 3 and the ink-bearing layer 4 in this order. The lamination of the ultraviolet-absorbing layer 3 and the ink-bearing layer 4 may preferably be carried out by coating a resin solution by a gravure coating method, a roll-coating method, etc., drying and, if necessary, heat-curing, or by the extrusion lamination of molten resins.

[C] Transfer method

[0051] The inkjet printing transfer sheet of the present invention is heat-transferable. The print-receiving surfaces 6 may be surfaces of films or moldings of papers; polyvinyl chloride resins; polyolefins such as polyethylene, polypropylene, ethylene-α-olefin copolymers, ethylene-vinyl acetate copolymers, ethylene-vinyl chloride copolymers, etc.; acrylic resins such as polymethyl methacrylate, methacrylate-styrene copolymers, etc.; polyester resins such as polyethylene terephthalate, polybutylene terephthalate, etc.; acrylonitrile resins; polystyrenes; ABS resins; polyamides; polycarbonates; phenol resins; polyphenylene oxide resins, etc. The transfer sheet of the present invention is particularly suitable for transferring the inkjet print onto surfaces of polyvinyl chloride resins, acrylic resins, etc. which cannot be printed by aqueous ink. The transferred ink print is shown in Fig. 2.

[0052] The present invention will be explained in further detail referring to the following Examples without intention of restricting it thereto.

Synthesis Example 1

[0053] 180 g of acrylic acid, 114 g of N,N-dimethylaminoethyl acrylate • methyl chloride ($[CH_2=CHCOO-C_2H_4N(CH_3)_3]^+ \cdot Cl^-$, 79% aqueous solution), 30 g of benzyl methacrylate and 1.5 g of azobisisobutyronitrile were introduced into a 2-liter flask equipped with a stirrer, a reflux condenser and a thermometer. After adding 676 g of methanol, stirring was carried out at 22°C to form a uniform solution. After a nitrogen gas was bubbled into the solution for 30 minutes to remove oxygen therefrom, the flask was heated in an oil bath. Copolymerization reaction was then carried out for 10 hours under the reflux of methanol while bubbling nitrogen in the solution. After the completion of the copolymeriza-

tion reaction, a solution of the resultant acrylic copolymer was transferred to a 3-liter beaker, and 1,000 ml of distilled water was added to obtain 1,980 g of a colorless, transparent solution. It was found by drying at 150°C that this solution contained 14.6 weight % of a solid component.

Synthesis Example 2

[0054] 125 g of acrylic acid, 100 g of N,N-dimethyl acrylamide, 32 g of N,N-dimethylaminoethyl methacrylate • methyl chloride ($[CH_2=C(CH_3)COOH-C_2H_4N(CH_3)_3]^+ \cdot Cl^-$, 78% aqueous solution), 37.5 g of cyclohexyl acrylate, 62.5 g of methoxypolyethylene glycol methacrylate (polymerization degree: 9.1) and 1.0 g of azobisisobutyronitrile were introduced into a 2-liter flask equipped with a stirrer, a reflux condenser and a thermometer. After adding 750 g of methanol, stirring was carried out at 22°C to form a uniform solution. After a nitrogen gas was bubbled into the solution for 2 hours to remove oxygen therefrom, the flask was heated in an oil bath. Copolymerization reaction was then carried out for 8 hours under the reflux of methanol at 58°C. After the completion of the copolymerization reaction, a solution of the resultant acrylic copolymer was transferred to a 3-liter beaker, and 500 g of distilled water and 500 g of isopropanol were added to obtain 1,995 g of a colorless, transparent solution. It was found by drying at 150°C that this solution contained 12.3 weight % of a solid component.

Synthesis Example 3

[0055] 225 g of N,N-dimethyl acrylamide, 60 g of N,N-dimethylaminoethyl acrylate • methyl chloride (79% aqueous solution) and 15 g of phenoxyethyl acrylate were introduced into a 2-liter flask equipped with a stirrer, a reflux condenser and a thermometer. After adding 850 g of water and 790 g of methanol, stirring was carried out at 22°C to form a uniform solution. After a nitrogen gas was bubbled into the solution for 30 minutes to remove oxygen therefrom, the flask was heated in an oil bath. 60 g of a 1%-solution of azobisisobutyronitrile in methanol was slowly added over 3 hours to carry out a copolymerization reaction under the reflux of methanol while bubbling nitrogen in the solution, and the reaction was continued for 7 hours to complete the copolymerization of the monomers.

[0056] After the completion of the copolymerization reaction, a solution of the resultant acrylic copolymer was cooled and transferred to a 3-liter beaker. 500 g of methanol was added to dilute the solution to obtain 2,500 g of a colorless, transparent, viscous solution. It was found by drying at 150°C that this solution contained 11.5 weight % of a solid component.

Synthesis Example 4

[0057] 150 g of N,N-dimethyl acrylamide, 76 g of N,N-dimethylaminoethyl acrylate • methyl chloride (79% aqueous solution), 30 g of 3-phenoxy-2-hydroxypropyl acrylate and 60 g of phenoxypolyethylene glycol acrylate (polymerization degree: 5) were introduced into a 2-liter flask equipped with a stirrer, a reflux condenser and a thermometer. After adding 494 g of water and 1130 g of methanol, stirring was carried out at 25°C to form a uniform solution. After a nitrogen gas was bubbled into the solution for 30 minutes to remove oxygen therefrom, the flask was heated in an oil bath. 60 g of a 1%-solution of azobisisobutyronitrile in methanol was slowly added over 3 hours to carry out a copolymerization reaction under the reflux of methanol while bubbling nitrogen in the solution, and the reaction was continued for 5 hours to complete the copolymerization of the monomers.

[0058] After the completion of the copolymerization reaction, a solution of the resultant acrylic copolymer was cooled and transferred to a 3-liter beaker. 500 g of isopropanol was added to dilute the solution to obtain 2,500 g of a colorless, transparent, viscous solution. It was found by drying at 150°C that this solution contained 12.0 weight % of a solid component.

Example 1

[0059] The acrylic copolymer solution obtained in Synthesis Example 1 was applied to a surface of a 12-μm-thick polyethylene terephthalate film as a support layer by a roll-coating method, and dried at 130°C to form a 10-μm-thick ink-bearing layer. The ink-bearing layer of an inkjet-printing recording sheet thus produced was inkjet-printed by an inkjet printer (MJ-500C, available from Epson). The resultant inkjet print had clear color and gloss.

Example 2

[0060] The acrylic copolymer solution obtained in Synthesis Example 2 was applied to a surface of the same polyethylene terephthalate film as in Example 1 by a roll-coating method, and dried at 110°C to form a 10-μm-thick ink-bearing layer. The ink-bearing layer of an inkjet-printing recording sheet thus produced was inkjet-printed by an inkjet printer (MJ-500C). The resultant inkjet print had clear color and gloss.

Example 3

[0061] The acrylic copolymer solution obtained in Synthesis Example 3 was applied to a surface of the same polyethylene terephthalate film as in Example 1 by a roll-coating method, and dried at 110°C to form a 10-μm-thick ink-bearing layer. The ink-bearing layer of an inkjet-printing recording sheet thus produced was

inkjet-printed by an inkjet printer (MJ-500C). The resultant inkjet print had clear color and gloss.

Example 4

[0062] The acrylic copolymer solution obtained in Synthesis Example 4 was applied to a surface of the same polyethylene terephthalate film as in Example 1 by a roll-coating method, and dried at 110°C to form a 10-μm-thick ink-bearing layer. The ink-bearing layer of an inkjet-printing recording sheet thus produced was inkjet-printed by an inkjet printer (MJ-500C). The resultant inkjet print had clear color and gloss.

Example 5

[0063] A 12-μm-thick polyethylene terephthalate film as a support layer was coated with a parting agent ("L-70," available from Daicel Chemical Industries, Ltd.) to form a 1-μm-thick parting layer. An acrylic resin ("S-1030," available from Toagosei Chemical Industry Co., Ltd.), to which 0.2 weight % of a benzotriazole ultraviolet-absorbing agent ("Tynubin P," available from Ciba-Geigy) was blended, was applied to a surface of the parting layer by a roll-coating method to form a 3-μm-thick ultraviolet-absorbing layer. The acrylic copolymer solution obtained in Synthesis Example 2 was applied to a surface of the ultraviolet-absorbing layer by a roll-coating method to form a 10-μm-thick ink-bearing layer.

[0064] A transfer sheet thus obtained was inkjet-printed on the ink-bearing layer by an inkjet printer (MJ-500C), and transferred to a surface of a 200-μm-thick polyvinyl chloride film by a heat roll (surface temperature: 75°C). The support layer was then removed.

[0065] The inkjet print transferred to the polyvinyl chloride film had clear color and gloss. The transferred inkjet print was subjected to a light resistance test by a dew-cycle sunshine super-long-life weatherometer ("WEL-SUN-DC," available from Suga Shikenki K. K.), under the conditions of no rainfall and 240-hour exposure. As a result, a retention ratio of reflection intensity of the transferred inkjet print was 80% or more, proving that the transferred inkjet print had excellent light resistance.

Example 6

[0066] An acrylic resin ("S-4090," available from Toagosei Chemical Industry Co., Ltd.), to which 0.2 weight % of a benzophenone ultraviolet-absorbing agent ("UVINUL D-49," available from BASF) was blended, was applied by a roll-coating method to a surface of the parting layer formed on the support layer in the same manner as in Example 3, to form a 3-μm-thick ultraviolet-absorbing layer. The acrylic copolymer solution obtained in Synthesis Example 2 was applied to a surface of the ultraviolet-absorbing layer by a roll-coating method to form a 10-μm-thick ink-bearing layer.

[0067] A transfer sheet thus obtained was inkjet-printed on the ink-bearing layer by an inkjet printer in the same manner as in Example 3, and heat-transferred to a surface of a 200-μm-thick polyvinyl chloride film. The support layer was then removed. The inkjet print transferred to the polyvinyl chloride film had clear color and gloss. As a result of the light resistance test under the same conditions as in Example 3, a retention ratio of reflection intensity of the transferred inkjet print was 80% or more, proving that the transferred inkjet print had excellent light resistance.

Example 7

[0068] The acrylic copolymer solution obtained in Synthesis Example 3 was applied by a roll-coating method to a surface of the ultraviolet-absorbing layer formed on the support layer in the same manner as in Example 5, to form a 10-μm-thick ink-bearing layer.

[0069] A transfer sheet thus obtained was inkjet-printed by an inkjet printer and heat-transferred to a surface of a 200-μm-thick polyvinyl chloride film in the same manner as in Example 5. The inkjet print transferred to the polyvinyl chloride film had clear color and gloss. As a result of the light resistance test under the same conditions as in Example 5, a retention ratio of reflection intensity of the transferred inkjet print was 80% or more, proving that the transferred inkjet print had excellent light resistance.

Example 8

[0070] The acrylic copolymer solution obtained in Synthesis Example 4 was applied by a roll-coating method to a surface of the ultraviolet-absorbing layer formed on the support layer in the same manner as in Example 5, to form a 10-μm-thick ink-bearing layer.

[0071] A transfer sheet thus obtained was inkjet-printed by an inkjet printer and heat-transferred to a surface of a 200-μm-thick acrylic film in the same manner as in Example 5. The inkjet print transferred to the polyvinyl chloride film had clear color and gloss. As a result of the light resistance test under the same conditions as in Example 5, a retention ratio of reflection intensity of the transferred inkjet print was 80% or more, proving that the transferred inkjet print had excellent light resistance.

Comparative Example 1

[0072] A solution of a polyethylene oxide-polypropylene oxide copolymer cross-linked with urethane (molecular weight: 200,000) was applied to a surface of the same support layer as in Example 1 to form an ink-bearing layer. The resultant inkjet-printing recording sheet was subjected to inkjet printing in the same manner as in Example 1. The resultant inkjet print was slightly blurred with ink.

Comparative Example 2

[0073] A transfer sheet was produced in the same manner as in Example 3 except for forming a 15-μm-thick ink-bearing layer by linear low-density polyethylene. Inkjet printing was carried out on this transfer sheet in the same manner as in Example 3. As a result, an aqueous inkjet-printing ink was repelled, failing to achieve clear ink print on the ink-bearing layer.

[0074] As described in detail above, inkjet print with excellent clarity, gloss, fixability, etc. can be formed on the inkjet-printing sheet of the present invention. When the inkjet-printing sheet of the present invention is used as a transfer sheet, inkjet print with excellent light resistance (discoloration resistance) can be obtained.

Claims

1. An inkjet-printing sheet comprising an ink-bearing layer made of an acrylic copolymer having (a) at least one structural unit having a hydrophilic group, (b) a structural unit having a quaternary ammonium group, and (c) a structural unit formed from a hydrophobic monomer or a monomer having a hydrophobic group having 4 or more carbon atoms.

2. The inkjet-printing sheet according to claim 1, wherein the amount of said structural unit (a) is 30-90 weight %, the amount of said structural unit (b) is 3-50 weight %, and the amount of said structural unit (c) is 3-50 weight %.

3. The inkjet-printing sheet according to claim 1, wherein said structural unit (a) comprises (i) a structural unit formed from at least one monomer selected from the group consisting of aliphatic carboxylic acids or anhydrides thereof, acrylamides, acrylic monomers having phosphoric groups and vinylpyrrolidones.

4. The inkjet-printing sheet according to claim 3, wherein said structural unit (a) further comprises (ii) a structural unit having a hydroxyl group and/or an ether bond, a weight ratio of (i)/(ii) being 97/3-50/50.

5. An inkjet-printing transfer sheet comprising a support layer, a parting layer, an ultraviolet-absorbing layer and a heat-sealable, ink-bearing layer laminated in this order, said ink-bearing layer being made of an acrylic copolymer having (a) at least one structural unit having a hydrophilic group, (b) a structural unit having a quaternary ammonium group, and (c) a structural unit formed from a hydrophobic monomer or a monomer having a hydrophobic group having 4 or more carbon atoms.

6. The inkjet-printing transfer sheet according to claim 5, wherein said structural unit (a) comprises (i) a structural unit formed from at least one monomer selected from the group consisting of aliphatic carboxylic acids or anhydrides thereof, acrylamides, acrylic monomers having phosphoric groups and vinylpyrrolidones.

7. The inkjet-printing transfer sheet according to claim 6, wherein said structural unit (a) further comprises (ii) a structural unit having a hydroxyl group and/or an ether bond.

8. The inkjet-printing transfer sheet according to claim 7, wherein the amount of said structural unit (i) is 90 weight % or less, the amount of said structural unit (ii) is 3-70 weight %, the amount of said structural unit (b) is 3-50 weight %, and the amount of said structural unit (c) is 3-50 weight %.

9. The inkjet-printing sheet according to claim 5, wherein said ultraviolet-absorbing layer has a thickness of 1-50 μm, and said ink-bearing layer has a thickness of 1-50 μm.

FIG. 1

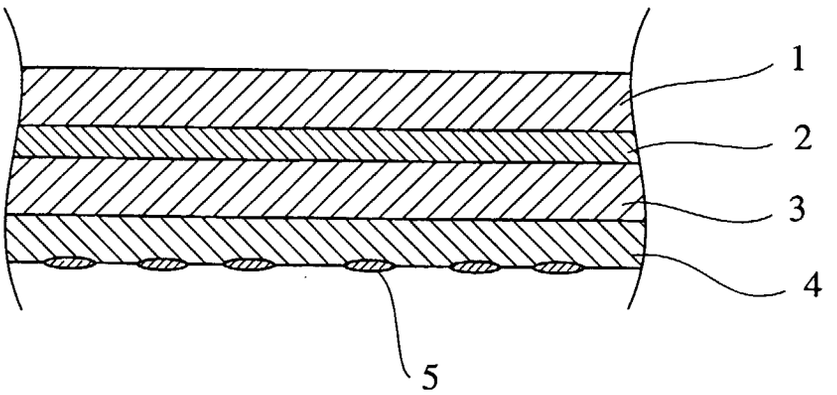
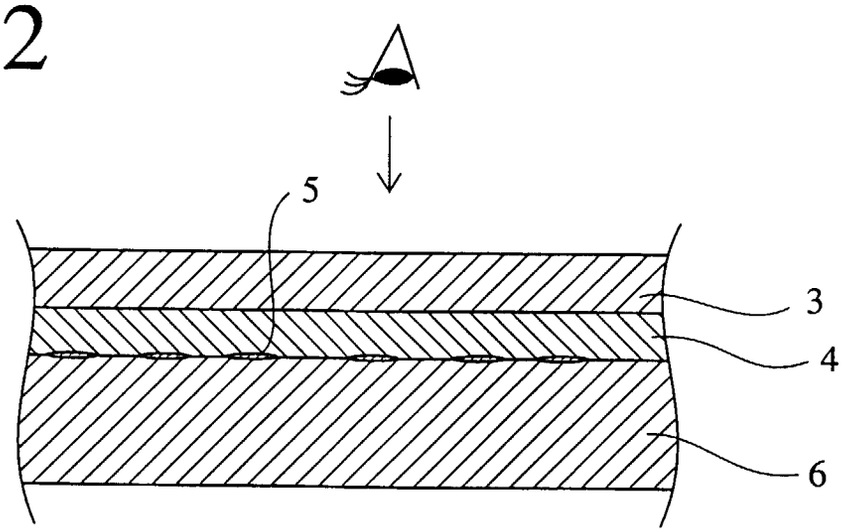


FIG. 2



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EUROPEAN SEARCH REPORT

Application Number
EP 98 30 3171

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	2 September 1998	Markham, R

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