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(54) Ink jet recording sheet

(57) An ink jet recording sheet comprising a substrate, and a layer of a polymer composition laminated on the substrate. The polymer composition comprises:

(A) 100 parts by weight of a water-soluble polymer,

(B) from 1.0 to 30 parts by weight of a polymer of a monomer which is sparingly soluble in water and which has at least three ethylenically unsaturated groups in the molecule, and

(C) from 0 to 20 parts by weight of a fluorine-containing surfactant or a silicone oil.

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Description

The present invention relates to an ink jet recording sheet, a polymerizable composition used in said sheet, and a process for production of said sheet.

Ink jet recording method has become popular rapidly in recent years because the method gives a small noise and can conduct high-speed printing and color printing easily. In the ink jet printer used in the method, it is preferable to use an ink of low drying property in order to prevent the jet nozzle from being plugged. Hence, there is generally used an ink which is an aqueous solution of a binder, a dye, a solvent, additives, etc. In this connection, the recording sheet used in the ink jet printer, i.e. the ink jet recording sheet is required to have high ink absorbability. In color printing which has come to be widely used recently, the ink jet recording sheet is required to have even higher ink absorbability because different color inks are injected in order and the drying of the injected inks is slower than in single-color printing. The ink jet recording sheet is further required not to become tacky at high humidities, or required to have water resistance (that is, the recorded image shows no blurring when waterdrops or sweat adheres thereto).

The ink jet recording sheet is also required to show no excessive blurring of printed image. However, when the ink printed on the recording layer of the sheet has insufficient spreadability, gaps appear between the dots constituting the intended line image, and consequently the line image actually obtained has a low density and is weak. Therefore, the recording layer of the ink jet recording sheet is required to allow adequate spreadability for applied ink dots.

In such a background, Japanese Patent Application Kokai (Laid-Open) No. 21796/1984 describes that a coated paper of good smoothness is obtained by (1) coating, on a paper, an aqueous composition for paper coating, composed of a pigment, an aqueous adhesive, and an unsaturated monomer and/or a polymerizable unsaturated group-containing prepolymer and then (2) irradiating the coated paper with a radiation. This publication describes that the coated paper obtained has improved smoothness and is superior in intaglio printability, but makes no mention on the use of the coated paper for ink jet recording. Generally, in intaglio printing wherein an oily ink is used, there is required no high ink absorbability such as required in ink jet printing wherein an aqueous ink is used. Therefore, the above publication does not at all anticipate any ink jet recording sheet.

Japanese Patent Application Kokai (Laid-Open) No. 155895/1994 discloses that an ink jet recording sheet is obtained by (1) coating, on a substrate, an aqueous coating composition composed of a polypyrrolidone and/or an acetoacetylated polyvinyl alcohol, a water-soluble and/or water-dispersible electron beam-curable compound, and a polyethylene glycol and then (2) irradiating the coated substrate with an electron beam. The publication, however, mentions no specific example of the water-dispersible electron beam-curable compound; therefore, it is impossible to anticipate, from the publication, the specific type of said compound to be used to obtain an ink jet recording sheet superior in ink absorbability and water resistance.

Conventional ink jet recording sheets such as mentioned above, obtained by coating, on a substrate, a polymerizable composition comprising a water-soluble polymer and a polymerizable monomer and then curing the coated composition, have ink absorbability and water resistance of certain levels or higher. They, however, have a problem in sheet transferability, i.e. the smoothness of sheet transfer from the setti ng of sheet in printer to the start of printing; therefore, there have often occurred printer blocking with sheet and manual correction of such blocking to make printing possible.

Japanese Patent Application Kokai (Laid-Open) No. 146389/1991 discloses an ink jet recording sheet of low blurring of printed image, having a recording layer comprising a water-soluble polymer and a fluorine-containing surfactant. In this recording sheet, however, the spreading of injected ink dots is too small, giving a weak line image; moreover, the ink absorbability and water resistance are insufficient.

Japanese Patent Application Kokai (Laid-Open) No. 146785/1989 shows that the intensity of line image can be improved by adding, to the above-mentioned recording layer comprising a water-soluble polymer and a fluorine-containing surfactant, an amphoteric surfactant. Even in the resulting recording sheet, however, the ink absorbability and water resistance are still insufficient. Further, the improvement in line image intensity is made possible only by the combination use of a fluorine-containing surfactant and an amphoteric surfactant.

Japanese Patent Publication No. 24908/1991 discloses an ink jet recording sheet obtained by coating or impregnating a substrate with a coating fluid comprising a pigment, a water-soluble polymer binder and a water-soluble silicone compound or a silicone emulsion. The publication mentions that the sheet is effective for the improvement of color aberration, but makes no mention on the addition of a polymerizable monomer to a coating fluid and the curing of the coating fluid. Further, this sheet has a certain level of transferability but the transferability is not satisfactory.

An object of the present invention is to provide an ink jet recording sheet which has sufficiently satisfactory ink absorbabili ty and water resistance, whose recording layer has excellent transparency, and which is suitable particularly as a light-permeable recording medium for use in, for example, overhead projector (hereinafter referred to as OHP).

Other object of the present invention is to develop an ink jet recording sheet wherein the injected ink dots spread favorably in the recording layer and give a distinct and strong line image and which has good ink absorbability and water resistance.

Still other object of the present invention is to develop an ink jet recording sheet which is superior in ink absorbability, water resistance and intra-printer transferability.

In order to achieve the above objects, the present inventors made a study. As a result, the present inventors found out that the above objects could be achieved by laminating, on a substrate, a layer of a polymer composition obtained by mixing a water-soluble polymer, a polymer of a particular sparingly-soluble-in-water monomer and, optionally, a fluorine-containing surfactant or a silicone oil at particular proportions.

The present invention provides an ink jet recording sheet comprising:

a substrate, and
a layer of polymer composition laminated thereon, composed of:

(A) 100 parts by weight of a water-soluble polymer,
(B) 1.0-30 parts by weight of a polymer of a sparingly-soluble-in-water monomer having at least three ethylenically unsaturated groups in the molecule, and
(C) 0-20 parts by weight of a fluorine-containing surfactant or a silicone oil, preferably 0.1-10 parts by weight of a fluorine-containing surfactant or 0.5-20 parts by weight of a silicone oil.

The present invention further provides a polymerizable composition used in production of the above ink jet recording sheet, which is an aqueous dispersion or solution of:

(a) 100 parts by weight of a water-soluble polymer,
(b) 1.0-30 parts by weight of a sparingly-soluble-in-water monomer having at least three ethylenically unsaturated groups in the molecule,
(c) 0-20 parts by weight of a fluorine-containing surfactant or a silicone oil, preferably 0.1-10 parts by weight of a fluorine-containing surfactant or 0.5-20 parts by weight of a silicone oil, and
(d) 0.0005-5 parts by weight of a radical polymerization initiator.

The present invention furthermore provides a process for production of the above ink jet recording sheet, which comprises coating a polymerizable composition on a substrate, drying the coated composition and then polymerizing the dried composition, said polymerizable composition being an aqueous dispersion or solution of:

(a) 100 parts by weight of a water-soluble polymer,
(b) 1.0-30 parts by weight of a sparingly-soluble-in-water monomer having at least three ethylenically unsaturated groups in the molecule,
(c) 0-20 parts by weight of a fluorine-containing surfactant or a silicone oil, preferably 0.1-10 parts by weight of a fluorine-containing surfactant or 0.5-20 parts by weight of a silicone oil, and
(d) 0.0005-5 parts by weight of a radical polymerization initiator.

The substrate used in the present invention is not particularly restricted. The substrate, however, is preferably a plastic film having flexibility and excellent transparency when it is used in production of a light-permeable recording medium for OHP, etc. The film is made of a plastic such as polyethylene terephthalate, polyvinyl chloride, polycarbonate, polypropylene or the like. The substrate may be an opaque substrate such as paper, synthetic paper, white film or the like. An ink jet recording layer may be formed on both sides of the substrate, but is preferably formed on one side in view of the cost of the resulting ink jet recording sheet.

In the present invention, the water-soluble polymer (A or a), which is a component of the polymer composition to be laminated on the substrate, may be any known water-soluble polymer. Specific examples thereof are albumin, gelatin, casein, polyvinyl alcohol, polyacrylic acid, sodium polyacrylate, polyvinylpyrrolidone, methyl cellulose and hydropropyl methyl cellulose. These water-soluble polymers may be used singly or in combination of two or more kinds. A polyvinyl alcohol is particularly preferable.

In the present invention, the polymer (B) (which is also a component of the polymer composition) of a sparingl y-soluble-in-water monomer (b) having at least three ethylenically unsaturated groups in the molecule, may also be any known such polymer. The sparingly-soluble-in-water monomer (b) desi rably has a solubility in water, of 2% by weight or less, preferably 1% by weight or less at 20°C. The monomer (b) preferably has a molecular weight per one ethylenically unsaturated group, of 180 or less. Specific examples of the polymer (B) are polymers of a polyester [e.g. trimethylolpropane tri(meth)acrylate, pentaerythritol tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate or dipentaerythritol hexa(meth)acrylate] between (1) a polyol and (2) an ethylenically unsaturated carboxylic acid; and polymers of a urethane (meth)acrylate monomer [e.g. glycerine di(meth)acrylate isohexamethylene diisocyanate or pentaerythritol tri(meth)acrylate hexamethylene diisocyanate]. The polymer (B) may

be a copolymer of two or more of the above monomers.

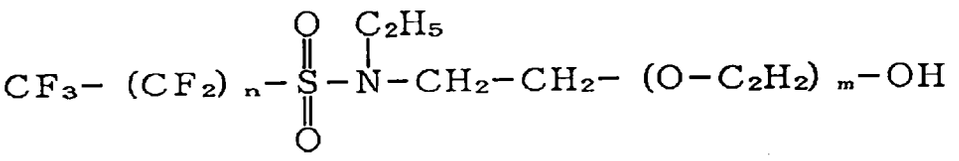
In the present invention, the polymer (B) of a sparingly-soluble-in-water monomer (b) having at least three ethylenically unsaturated groups in the molecule is used as a component of the recording layer of ink jet recording sheet, whereby the recording layer has greatly improved water resistance. When the monomer of the polymer has high solubility in water and yet it is intended to allow the recording layer to have sufficient water resistance, the polymer must be used in a large amount, which invites reduction in ink absorption speed and makes it impossible to obtain both of good water resistance and good ink absorption speed. When the monomer of the polymer has two or less ethylenically unsaturated groups (this leads to low crosslink density) and yet it is intended to allow the recording layer to have water resistance, the polymer must be used in a large amount, which invites reduction in ink absorption speed and nonuniformity in image density.

In the present invention, the polymer (B) may contain, in addition to the monomer (b), a small amount (preferably 30 mole % or less) of a sparingly-soluble-in-water monomer having one or two ethylenically unsaturated groups in the molecule, as long as the properties of the recording layer are not impaired thereby. (In this case, the polymer (B) is a copolymer.) The bifunctional monomer includes, for example, diesters [e.g. ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate or trimethylolpropane di(meth)acrylate] between a polyol and an ethylenically unsaturated carboxylic acid; and diesters (e.g. diallyl phthalate) between a polybasic acid and an unsaturated alcohol. The monofunctional monomer includes, for example, alkyl ethylenically unsaturated carboxylates such as methyl (meth)acrylate, ethyl (meth)acrylate and the like.

The proportions of the water-soluble polymer (A) and the polymer (B) of a sparingly-soluble-in-water monomer (b) having at least three ethylenically unsaturated groups in the molecule are such that the former is 100 parts by weight and the latter is 1.0-30 parts by weight, preferably 1.0-13.0 parts by weight, more preferably 2.0-12.0 parts by weight. When the proportion of the latter is smaller than 1.0 part by weight, there is seen no improvement in ink absorption speed or water resistance. When the proportion of the latter is larger than 30 parts by weight, no further improvement in ink absorption speed can be expected. An excessive amount of the latter causes reduction in the above properties and moreover invites increase in turbidity.

The ink jet recording sheet of the present invention comprising the substrate and a layer of the polymer composition laminated thereon, composed of the water-soluble polymer (A), the polymer (B) and a fluorine-containing surfactant (C or c) of an amount of 0-20 parts by weight, particularly 0.1-10 parts by weight per 100 parts by weight of the polymer (A), gives a distinct line image of high density because, in the recording sheet, injected ink dots spread favorably in the recording layer without causing excessive blurring and no gap is formed between the dots owing to the presence of the surfactant (C or c) in the polymer composition. This effect is enhanced by the presence, in the polymer composition, of the polymer (B) of a sparingly-soluble-in-water monomer (b) having at least three ethylenically unsaturated groups. The above effect (a distinct line image of high density) is not obtainable when a surfactant other than the fluorine-containing surfactant is used.

The fluorine-containing surfactant (C or c) may be any known fluorine-containing surfactant. It may be any of an anionic surfactant, a cationic surfactant and a nonionic surfactant. However, it is not preferable to use a surfactant having an ionicity opposite to the ionicity of the emulsifier used in dispersing the water-soluble polymer (A) and the sparingly-soluble-in-water monomer (b) in water. The fluorine-containing anionic surfactant includes, for example, salts (e.g. ammonium salt, sodium salt and potassium salt) of fluoroalkylsulfonic acids and salts (e.g. ammonium salt, sodium salt and potassium salt) of fluoroalkylcarboxylic acids. The fluorine-containing cationic surfactant includes, for example, fl uoroal kyl quaternary ammonium chlorides and fluoroalkyl quaternary ammoni um iodides. The fluorine-containing nonioni c surfactant includes, for example, polyoxyethylene fluoroalkyl ethers and perfluoroalkylsulfonamideethyl polyoxyethylenes represented by the following formula:



Examples of commercial fluorine-containing anionic surfactants are Fluorad FC-129 (a product of Sumitomo 3M Limited) and Ftergent 100 (a product of NEOS Company Limited). Examples of commercial fluorine-containing cationic surfactants are Fluorad FC-135 (a product of Sumitomo 3M Limited) and Ftergent 300 (a product of NEOS Company Limited). Examples of commercial fluorine-containing nonionic surfactants are Fluorad FC-170C (a product of Sumitomo 3M Limited) and Ftergent 251 (a product of NEOS Company Limited). These fluorine-containing surfactants may be used in combination of two or more kinds. It is also possible to use a fluorine-containing surfactant together with a

fluorine-free surfactant.

The fluorine-containing surfactant is more effective when it has a higher fluorination degree. A surfactant having a perfluoroalkyl group, such as Fluorad FC-170C or the like is particularly preferred. Generally, a nonionic surfactant is preferred.

The amount of the fluorine-containing surfactant used is 0-20 parts by weight, preferably 0.1-10 parts by weight, more preferably 0.2-9 parts by weight per 100 parts by weight of the water-soluble polymer (A).

The ink jet recording sheet of the present invention comprising the substrate and a layer of the polymer composition laminated thereon, composed of the water-soluble polymer (A), the polymer (B) and a silicone oil (C or c) of an amount of 0-20 parts by weight, particularly 0.5-20 parts by weight per 100 parts by weight of the polymer (A), has good intra-printer transferability because of the presence of the silicone oil (C or c) in the polymer composition. This effect is enhanced by the presence, in the polymer composition, of the polymer (B) of a sparingly-soluble-in-water monomer (b) having at least three ethylenically unsaturated groups in the molecule.

The silicone oil (C or c) may be any known silicone oil but is preferably dimethylsilicone oil, diphenylsilicone oil, methylphenylsilicone oil or the like. The silicone oil may also be a polyether-, alcohol- or carboxyl-modified silicone oil. The silicone oil, except when made water soluble by the above modification or the like, is preferably used generally in the form of an aqueous dispersion.

In the present invention, the amount of the silicone oil (C or c) used is 0-20 parts by weight, preferably 0.5-20 parts by weight, more preferably 1.0-18 parts by weight per 100 parts by weight of the water-soluble polymer (A).

The ink jet recording sheet of the present invention can be produced by any process. It can be produced preferably by coating a polymerizable composition on a substrate, drying the coated composition and then polymerizing the dried composition, said polymerizable composition being an aqueous dispersion or solution of:

(a) 100 parts by weight of a water-soluble polymer,
(b) 1.0-30 parts by weight of a sparingly-soluble-in-water monomer having at least three ethylenically unsaturated groups in the molecule, and
(c) 0-20 parts by weight of a fluorine-containing surfactant or a silicone oil, preferably 0.1-10 parts by weight of a fluorine-containing surfactant and 0.5-20 parts by weight of a silicone oil, and
(d) 0.0005-5 parts by weight of a radical polymerization initiator.

The amount of the water used for di spersi ng or dissolving the above components (a) to (d) is not particularly restricted, but is generally 700-1,700 parts by weight per 100 parts by weight of the water-soluble polymer (A). In preparation of the polymerizable composition, which is an aqueous dispersion of solution of the above components, it is generally preferable to first prepare an aqueous dispersion or solution of the sparingly-soluble-in-water monomer (b), or of the sparingly-soluble-in-water monomer (b) and the radical polymerization initiator (d) and then adding thereto the water-soluble polymer (a) in an aqueous solution form and, optionally, the fluorine-containing surfactant (c) or the silicone oil (c). In preparation of the aqueous dispersion of the sparingly-soluble-in-water monomer (b), a water-soluble polymer, a surfactant or the like may be used as an emulsifier.

The radical polymerization initiator (d) is not particularly restricted and it includes, for example, benzoins such as benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether and the like; acetophenones such as di-ethoxyacetophenone, 4-phenoxydichloroacetophenone and the like; and thioxanthones such as thioxanthone, 2-chlo-rothioxanthone and the like. The amount of the radical polymerization initiator (d) used is 0.0005-5 parts by weight, preferably 0.005-3 parts by weight per 100 parts by weight of the water-soluble polymer (A) so that the sparingly-soluble-in-water monomer (b) can be polymerized sufficiently.

The polymerizable composition can comprise, besides the above components, various additives such as film-forming auxiliary, plasticizer, defoamer, surfactant, antifungal agent, antiseptic agent, thickening agent, aqueous emul-sion, PH-controlling agent, organic solvent and the like. The polymerizable composition can further comprise various fillers as long as the transparency of the recording layer of the present recording sheet is not impaired, in order to eliminate the tackiness and blocking property of the surface of said recording layer and/or to control the blurring of printed i nk on said surface. The fillers include, for example, silica, colloidal silica, clay, talc, diatomaceous earth, calcium carbonate, calcium sulfate, aluminum silicate, synthetic zeolite, alumina and zinc oxide.

The coating of the polymerizable composition on the substrate can be conducted by any method. However, it is generally preferable to coat the polymerizable composition of aqueous dispersion form on the substrate by a known method (e.g. roll coating, bar coating, gravure coating or air knife coating) and drying the coated composition. The amount of the composition coated is generally 1-30 g/m^2, preferably 3-10 g/m^2 in terms of solid content, in view of the absorption speed of ink and economy, the uniformity of film formed, etc.

The polymerization of the coated polymerizable composi tion may be conducted by an ordinary method such as thermal polymerization or the like, but is generally conducted by using a radiation. As the radiation, an electron beam or an ultraviolet light is ordinarily used. The ultraviolet light is obtained from a mercury lamp, a xenon lamp, a metal

halide lamp or the like; and the electron beam is obtained from an electron accelerator. In conducting polymerization using an electron beam, the radical polymerization initiator may not be used and, even if it is used, the amount may be small.

The thus-obtained ink jet recording sheet is superior in transparency of recording layer. Therefore, when a substrate of excellent transparency is used, the recording layer has a cloudiness of 20% or less as measured by JIS K 6714. A recording layer having such a cloudiness is superior in distinctness of image when projection is made using an OHP.

The ink jet recording sheet of the present invention has quick ink absorbability and good water resistance. Further, the present ink jet recording sheet gives a distinct and strong line image because printed ink dots spread favorably in the recording layer; has excellent intra-printer transferability; and is low in cloudiness of recording layer. Therefore, the ink jet recording sheet of the present invention is suited for use as an ink jet recording sheet of color printing type, or as an optical recording medium in OHP, etc.

The present invention is hereinafter described specifically by way of Examples. However, the present invention is not restricted to these Examples. In the following Examples, the properties of each ink jet recording sheet were measured by the following methods.

(1) Cloudiness

Measured using a color-difference meter (Σ80, a product of Nippon Denshoku Kogyo Co., Ltd.), according to JIS K 6714.

(2) Ink absorption speed

Blue solid printing was conducted on the recording layer of an ink jet recording sheet by the use of an ink jet color printer (MJ-700V2C, a product of SEIKO EPSON CORP.). The printed image formed on the recording layer was touched by fingers at given time intervals to measure a time up to the moment when the printed image dried and showed no adhesion to the fingers.

(3) Water resistance

Waterdrops were let fall on the recording layer of an ink jet recording sheet, after which the recording layer was rubbed by fingers to examine the peelability of the layer. The water resistance of the recording sheet was evaluated based on the following yardstick.

○ : No peeling of the recording layer
Δ : Slight peeling of the recording layer
X : Peeling of the recording layer

(4) Tackiness

An ink jet recording sheet was allowed to stand in a room of a relative humidity of 80% for 24 hours, after which the recording layer of the sheet was touched by fingers to examine the degree of the tackiness of the layer. The tackiness of the recording sheet was evaluated based on the following yardstick.

○ : The recording layer has no tackiness.
X : The recording layer has tackiness.

(5) Nonuniformity in image density

A red color, a green color and a blue color were solid-printed in this order on the recording layer of an ink jet recording sheet. The resulting recording layer was examined for the degree of nonuniformity in image density. The nonuniformity in image density, of the recording sheet was evaluated based on the following yardstick.

○: The recording layer has no nonuniformity in image density.
Δ: The recording layer has slight nonuniformity in image density.
X : The recording layer has nonuniformity in image density.

(6) Blurring of printed image

A red color, a green color and a blue color were solid-printed in this order on the recording layer of an ink jet recording sheet. The resulting recording layer was visually examined for the degree of blurring and the distinctness of printed image contour. The blurring of printed image, of the recording sheet was evaluated based on the following yardstick.

○: The printed image shows no excessive blurring and its contour is distinct.
Δ: The printed image shows slight blurring and its contour is slightly indistinct.
X : The printed image shows severe blurring and its contour is indistinct.

(7) Condition between dots

A red color, a green color and a blue color were solid-printed in this order on the recording layer of an ink jet recording sheet. The resulting recording layer was visually examined for the degree of gap between dots and the distinctness of printed image. The condition between dots of the recording sheet was evaluated based on the following yardstick.

◎ There is no gap between dots and the printed image is distinct and strong.
○: There are places showing very small gaps between dots but the printed image is strong.
Δ : There are small gaps between dots and the printed image is slightly indistinct.
X : There are gaps between dots and the printed image is indistinct and weak.

(8) Tranferability

An ink jet recording sheet was set in an ink jet printer (MJ-700V2C, a product of SEIKO EPSON CORP.) and it was examined whether or not the sheet could be smoothly transferred in the printer so that normal printing could be made. The transferability of the recording sheet was evaluated based on the following yardstick.

○ : Printing is possible with no manual correction.
Δ : Printing is possible with slight manual correction.
X : Printing is possible with considerable manual correction.

Example 1

In 45.3 parts by weight of water were dissolved 0.08 part by weight of sodium laurylsulfonate and 1.4 parts by weight of a polyvinyl alcohol (GOHSENOL GH-17, a product of The Nippon Synthetic Chemical Industry Co., Ltd.). The resulting aqueous solution was heated to 70°C. Thereto were added 22.8 parts by weight of pentaerythritol triacrylate and 0.9 part by weight of a photopolymerization initiator (DAROCUR-1173, a product of MERCK JAPAN K.K.). The mixture was stirred to obtain an aqueous dispersion of pentaerythritol triacrylate.

The aqueous dispersion was mixed with 2,820 parts by weight of an aqueous solution containing 10% by weight of a polyvinyl alcohol (GOHSENOL KH-17, a product of The Nippon Synthetic Chemical Industry Co., Ltd.) to prepare a polymerizable composition. The polymerizable composition was coated, by the use of a bar coater, on a polyethylene terephthalate film (O-300E, a product of Diafoil Hoechst Co., Ltd.) having a thickness of 100 μm, so as to give a coating film thickness of 7 μm as dried. The coated composition was dried with hot air of 60°C and then irradiated once with a UV irradiator (a high-pressure mercury lamp, made by Toshiba Corp., 80 W/cm x 2 lamps, conveyor speed: 3 m/min) to give rise to its polymerization.

The resulting ink jet recording sheet was subjected to printing with the above-mentioned ink jet printer, and the properties of the recording layer of the sheet after printing were evaluated. The results are shown in Table 1.

Example 2

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 1 except that the amount of the aqueous solution containing 10% by weight of a polyvinyl alcohol was changed to 4,700 parts by weight. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 1. The results are shown in Table 1.

Example 3

The preparation of a polymeri zable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 1 except that the amount of the aqueous solution containing 10% by weight of a polyvinyl alcohol was changed to 1,950 parts by weight. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 1. The results are shown in Table 1.

Example 4

The preparation of a polymeri zable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 1 except that the total amount of the aqueous solution containing 10% by weight of a polyvinyl alcohol was changed to 3,525 parts by weight of an aqueous solution containing 8% by weight of hydroxypropyl methyl cellulose (METOLOSE 65SH50, a product of Shin-Etsu Chemical Co., Ltd.). The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 1. The results are shown in Table 1.

Example 5

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 1 except that the total amount of pentaerythritol triacrylate was changed to dipentaerythritol hexaacrylate. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 1. The results are shown in Table 1.

Example 6

The preparation of a polymeri zable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 1 except that the total amount of pentaerythritol triacrylate was changed to 11.4 parts by weight of di pentaerythri tol hexaacrylate and 11.4 parts by weight of pentaerythritol triacrylate hexamethylene diisocyanate. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 1. The results are shown in Table 1.

Example 7

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 1 except that the amount of the aqueous solution containing 10% by weight of a polyvinyl alcohol was changed to 28,200 parts by weight. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 1. The results are shown in Table 1.

Example 8

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 1 except that the amount of the aqueous solution containing 10% by weight of a polyvinyl alcohol was changed to 587 parts by weight. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 1. The results are shown in Table 1.

Example 9

The preparation of a polymeri zable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 1 except that the total amount of pentaerythritol triacrylate was changed to diethylene glycol dimethacrylate. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 1. The results are shown in Table 1.

Table 1

	Amount of polymer of sparingly-soluble-in-water monomer (parts by weight)*	Cloudiness (%)	Ink absorption speed (sec)	Water resistance	Tackiness	Nonuniformity in image density
Example 1	8.1	8.8	10 or less	○	○	○
Example 2	4.9	6.3	10 or less	○	○	○
Example 3	11.7	10.9	10 or less	○	○	○
Example 4	8.1	11.2	50	○	○	○
Example 5	8.1	8.3	10 or less	○	○	○
Example 6	8.1	7.8	20	○	○	○
Example 7	0.81	4.4	30	X	X	○
Example 8	38.8	35.8	120	○	○	△
Example 9	8.1	5.8	70	△	X	○

* Parts by weight per 100 parts by weight of water-soluble polymer

Example 10

In 45.3 parts by weight of water were dissolved 0.08 part by weight of sodium laurylsulfonate and 1.4 parts by weight of a polyvinyl alcohol (GOHSENOL GH-17, a product of The Nippon Synthetic Chemical Industry Co., Ltd.). The resulting aqueous solution was heated to 70°C. Thereto were added 22.8 parts by weight of pentaerythritol triacrylate and 0.9 part by weight of a photopolymerization initiator (DAROCUR-1173, a product of MERCK JAPAN K.K.). The mixture was stirred to obtain an aqueous dispersion of pentaerythritol triacrylate.

The aqueous dispersion was mixed with 2,820 parts by weight of an aqueous solution containing 10% by weight of a polyvinyl alcohol (GOHSENOL KH-17, a product of The Nippon Synthetic Chemical Industry Co., Ltd.) and 11.28 parts by weight of Fluorad-170C to prepare a polymerizable composition. The polymerizable composition was coated, by the use of a bar coater, on a polyethylene terephthalate film (O-300E, a product of Diafoil Hoechst Co., Ltd.) having a thickness of 100 μm, so as to give a coating film thickness of 7 μm as dried. The coated composition was dried with hot air of 60°C and then irradiated once with a UV irradiator (a high-pressure mercury lamp, made by Toshiba Corp., 80 W/cm x 2 lamps, conveyor speed: 3 m/min) to give rise to its polymerization.

The resulting ink jet recording sheet was subjected to printing with the above-mentioned ink jet printer, and the properties of the recording layer of the sheet after printing were evaluated. The results are shown in Table 3. Also, in Table 2 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the fluorine-containing surfactant both used per 100 parts by weight of the water-soluble polymer.

Example 11

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 10 except that the amount of Fluorad-170C was changed to 2.82 parts by weight. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 10. The results are shown in Table 3. Also, in Table 2 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the fluorine-containing surfactant both used per 100 parts by weight of the water-soluble polymer.

Example 12

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 10 except that the amount of Fluorad-170C was changed to 22.56 parts by weight. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 10. The results are shown in Table 3. Also, in Table 2 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the fluorine-containing surfactant both used per 100 parts by weight of the water-soluble polymer.

Example 13

The preparation of a polymeri zable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 10 except that the total amount of Fluorad-170C was changed to Fluorad-129. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 10. The results are shown in Table 3. Also, in Table 2 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the fluorine-containing surfactant both used per 100 parts by weight of the water-soluble polymer.

Example 14

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 10 except that the amount of the aqueous solution containing 10% by weight of a polyvinyl alcohol was changed to 7,600 parts by weight and the amount of Fluorad-170C was changed to 30.4 parts by weight. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 10. The results are shown in Table 3. Also, in Table 2 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the fluorine-containing surfactant both used per 100 parts by weight of the water-soluble polymer.

Example 15

The preparation of a polymeri zable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 10 except that the amount of the aqueous solution containing 10% by weight of a polyvinyl alcohol was changed to 2,072 parts by weight and the amount of Fluorad-170C was changed to 8.29 parts

by weight. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 10. The results are shown in Table 3. Also, in Table 2 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the fluorine-containing surfactant both used per 100 parts by weight of the water-soluble polymer.

Example 16

The preparation of a polymeri zable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 10 except that the total amount of pentaerythri tol triacrylate was changed to diethylene glycol dimethacrylate. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 10. The results are shown in Table 3. Also, in Table 2 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the fluorine-containing surfactant both used per 100 parts by weight of the water-soluble polymer.

Example 17

The preparation of a polymeri zable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 10 except that the total amount of the aqueous solution containing 10% by weight of a polyvinyl alcohol was changed to 3,525 parts by weight of an aqueous solution containing 8% by weight of hydroxypropyl methyl cellulose (METOLOSE 65SH50, a product of Shin-Etsu Chemical Co., Ltd.). The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 10. The results are shown in Table 3. Also, in Table 2 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the fluorine-containing surfactant both used per 100 parts by weight of the water-soluble polymer.

Example 18

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 10 except that no Fluorad-170C was used. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 10. The results are shown in Table 3. Also, in Table 2 are shown the amount of the polymer of sparingly-solubl e-in-water monomer and the amount of the fluorine-containing surfactant both used per 100 parts by weight of the water-soluble polymer.

Example 19

The preparation of a polymeri zable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 10 except that the amount of Fluorad-170C was changed to 0.14 part by weight. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 10. The results are shown in Table 3. Also, in Table 2 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the fluorine-containing surfactant both used per 100 parts by weight of the water-soluble polymer.

Example 20

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 10 except that the amount of Fluorad-170C was changed to 56.4 parts by weight. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 10. The results are shown in Table 3. Also, in Table 2 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the fluorine-containing surfactant both used per 100 parts by weight of the water-soluble polymer.

Example 21

The preparation of a polymeri zable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 10 except that no aqueous dispersion of pentaerythritol triacrylate was added. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 10. The results are shown in Table 3. Also, in Table 2 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the fluorine-containing surfactant both used per 100 parts by weight of the water-soluble polymer.

Example 22

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 10 except that the total amount of Fluorad-170C was changed to EMULGEN 920 (a polyoxyethylene nonylphenyl ether, a product of Kao Corp.). The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 10. The results are shown in Table 3. Also, in Table 2 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the fluorine-containing surfactant both used per 100 parts by weight of the water-soluble polymer.

Table 2

	Amount of polymer of sparingly-soluble-in-water monomer (parts by weight)*	Amount of surfactant (parts by weight)*
Example 10	8.1	4.0
Example 11	8.1	1.0
Example 12	8.1	8.0
Example 13	8.1	4.0
Example 14	3.0	4.0
Example 15	11.0	4.0
Example 16	8.1	4.0
Example 17	8.1	4.0
Example 18	8.1	-
Example 19	8.1	0.05
Example 20	8.1	20.0
Example 21	-	4.0
Example 22	8.1	-

* Parts by weight per 100 parts by weight of water-soluble polymer

Table 3

	Cloudiness (%)	Ink absorption speed (sec)	Water resistance	Blurring of printed image	Condition between dots
Example 10	7.8	10 or less	○	○	◎
Example 11	7.2	10 or less	○	○	◎
Example 12	9.8	10 or less	○	○	◎
Example 13	8.0	10 or less	○	○	○
Example 14	5.4	10 or less	○	○	◎
Example 15	11.1	10 or less	○	○	◎
Example 16	6.2	60	△	○	◎
Example 17	11.5	60	○	○	◎
Example 18	8.8	10 or less	○	○	×
Example 19	6.5	10 or less	○	○	×
Example 20	21	10 or less	×	○	◎
Example 21	6.7	90	×	○	△
Example 22	6.7	10 or less	○	○	×

Example 23

In 45.3 parts by weight of water were dissolved 0.08 part by weight of sodium laurylsulfonate and 1.4 parts by weight of a polyvinyl alcohol (GOHSENOL GH-17, a product of The Nippon Synthetic Chemical Industry Co., Ltd.). The resulting aqueous solution was heated to 70°C. Thereto were added 22.8 parts by weight of pentaerythritol tria-

crylate and 0.9 part by weight of a photopolymerization initiator (DAROCUR-1173, a product of MERCK JAPAN K.K.). The mixture was stirred to obtain an aqueous dispersion of pentaerythritol triacryl ate.

The aqueous dispersion was mixed with 2,820 parts by weight of an aqueous solution containing 10% by weight of a polyvinyl alcohol (GOHSENOL KH-17, a product of The Nippon Synthetic Chemical Industry Co., Ltd.) and 11.28 parts by weight of a water-soluble polyether-modified silicone oil [KF 615(A), a product of Shin-Etsu Chemical Co., Ltd.] to prepare a polymerizable composition. The polymerizable composition was coated, by the use of a bar coater, on a polyethylene terephthalate film (O-300E, a product of Diafoil Hoechst Co., Ltd.) having a thickness of 100 μm, so as to give a coating film thickness of 7 μm as dried. The coated composition was dried with hot air of 60°C and then irradiated once with a UV irradiator (a high-pressure mercury lamp, made by Toshiba Corp., 80 W/cm x 2 lamps, conveyor speed: 3 m/min) to give rise to its polymerization.

The resulting ink jet recording sheet was subjected to printing with the above-mentioned ink jet printer, and the properties of the recording layer of the sheet after printing were evaluated. The results are shown in Table 5. Also, in Table 4 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the silicone oil both used per 100 parts by weight of the water-soluble polymer.

Example 24

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 23 except that the amount of KF 615(A) was changed to 2.82 arts by weight. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 23. The results are shown in Table 5. Also, in Table 4 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the silicone oil both used per 100 parts by weight of the water-soluble polymer.

Example 25

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 23 except that the amount of KF 615(A) was changed to 45.12 parts by weight. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 23. The results are shown in Table 5. Also, in Table 4 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the silicone oil both used per 100 parts by weight of the water-soluble polymer.

Example 26

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 23 except that the total amount of KF 615(A) was changed to a dispersion of a polydimethylsiloxane in water (SH-7028, a product of Dow Corning Toray Silicone Co., Ltd., effective component: 30% by weight). The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 23. The results are shown in Table 5. Also, in Table 4 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the silicone oil both used per 100 parts by weight of the water-soluble polymer.

Example 27

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 23 except that the amount of the aqueous solution containing 10% by weight of a polyvinyl alcohol was changed to 7,600 parts by weight and the amount of KF 615(A) was changed to 30.4 parts by weight. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 23. The results are shown in Table 5. Also, in Table 4 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the silicone oil both used per 100 parts by weight of the water-soluble polymer.

Example 28

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 23 except that the amount of the aqueous solution containing 10% by weight of a polyvinyl alcohol was changed to 2,072 parts by weight and the amount of KF 615(A) was changed to 8.29 parts by weight. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 23. The results are shown in Table 5. Also, in Table 4 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the silicone oil both used per 100 parts by weight of the water-soluble polymer.

Example 29

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 23 except that the total amount of pentaerythritol triacrylate was changed to diethylene glycol dimethacrylate. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 23. The results are shown in Table 5. Also, in Table 4 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the silicone oil both used per 100 parts by weight of the water-soluble polymer.

Example 30

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 23 except that the total amount of the aqueous solution containing 10% by weight of a polyvinyl alcohol was changed to 3,525 parts by weight of an aqueous solution containing 8% by weight of hydroxypropyl methyl cellulose (METOLOSE 65SH50, a product of Shin-Etsu Chemical Co., Ltd.). The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 23. The results are shown in Table 5. Also, in Table 4 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the silicone oil both used per 100 parts by weight of the water-soluble polymer.

Example 31

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 23 except that no KF 615(A) was used. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 23. The results are shown in Table 5. Also, in Table 4 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the silicone oil both used per 100 parts by weight of the water-soluble polymer.

Example 32

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 23 except that the amount of KF 615(A) was changed to 0.56 part by weight. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 23. The results are shown in Table 5. Also, in Table 4 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the silicone oil both used per 100 parts by weight of the water-soluble polymer.

Example 33

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 23 except that the amount of KF 615(A) was changed to 67.68 parts by weight. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 23. The results are shown in Table 5. Also, in Table 4 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the silicone oil both used per 100 parts by weight of the water-soluble polymer.

Example 34

The preparation of a polymerizable composition and the production of an ink jet recording sheet were conducted in the same manner as in Example 23 except that no aqueous dispersion of pentaerythritol triacrylate was used. The evaluation of the recording layer of the sheet was conducted in the same manner as in Example 23. The results are shown in Table 5. Also, in Table 4 are shown the amount of the polymer of sparingly-soluble-in-water monomer and the amount of the silicone oil both used per 100 parts by weight of the water-soluble polymer.

Table 4

	Amount of polymer of sparingly-soluble-in-water monomer (parts by weight)*	Amount of silicone oil (parts by weight)*
Example 23	8.1	4.0

* Parts by weight per 100 parts by weight of water-soluble polymer

Table 4 (continued)

	Amount of polymer of sparingly-soluble-in-water monomer (parts by weight)*	Amount of silicone oil (parts by weight)*
Example 24	8.1	1.0
Example 25	8.1	16.0
Example 26	8.1	1.2
Example 27	3.0	4.0
Example 28	11.0	4.0
Example 29	8.1	4.0
Example 30	8.1	4.0
Example 31	8.1	-
Example 32	8.1	0.2
Example 33	8.1	24.0
Example 34	-	4.0

* Parts by weight per 100 parts by weight of water-soluble polymer

Table 5

	Cloudiness (%)	Ink absorption speed (sec)	Water resistance	Transferability
Example 23	4.9	10 or less	○	○
Example 24	4.5	10 or less	○	○
Example 25	8.5	10 or less	○	○
Example 26	9.9	10 or less	○	○
Example 27	4.3	10 or less	○	○
Example 28	10.3	10 or less	○	○
Example 29	4.8	60	△	○
Example 30	10.1	60	○	○
Example 31	4.7	10 or less	○	×
Example 32	4.8	10 or less	○	×
Example 33	31.9	10 or less	×	○
Example 34	5.0	80	×	△

Claims

1. An ink jet recording sheet comprising:

a substrate, and
a polymer composition laminated on the substrate, which polymer composition comprises:

(A) 100 parts by weight of a water-soluble polymer,
(B) from 1.0 to 30 parts by weight of a polymer of a monomer which is sparingly soluble in water and which

has at least three ethylenically unsaturated groups in the molecule, and
(C) from 0 to 20 parts by weight of a fluorine-containing surfactant or a silicone oil.

2. A sheet according to claim 1, wherein component (C) is from 0.1 to 10 parts by weight of a fluorine-containing surfactant.

3. A sheet according to claim 1, wherein component (C) is from 0.5 to 20 parts by weight of a silicone oil.

4. A sheet according to any preceding claim, wherein component (B) is a polymer of a monomer which is sparingly soluble in water and which has a molecular weight per one ethylenically unsaturated group, of 180 or less.

5. A sheet according to claim 4, wherein component (B) is a polyester of a polyol and an ethylenically unsaturated carboxylic acid.

6. A sheet according to claim 4, wherein component (B) is a polymer of a urethane (meth)acrylate monomer.

7. Use of a polymerizable composition in the preparation of an ink jet recording sheet according to any of claims 1 to 6, which composition is an aqueous dispersion or a solution of:

(a) 100 parts by weight of a water-soluble polymer,
(b) from 1.0 to 30 parts by weight of a monomer which is sparingly soluble in water and which has at least three ethylenically unsaturated groups in the molecule,
(c) from 0 to 20 parts by weight of a fluorine-containing surfactant or a silicone oil, and
(d) from 0.0005 to 5 parts by weight of a radical polymerization initiator.

8. A use according to claim 7, wherein component (c) is from 0.1 to 10 parts by weight of a fluorine-containing surfactant.

9. A use according to claim 7, wherein component (c) is from 0.5 to 20 parts by weight of a silicone oil.

10. A process for production of an ink jet recording sheet according to any of claims 1 to 6, which comprises coating a polymerizable composition on a substrate, drying the coated composition and then polymerizing the dried composition, wherein the polymerizable composition comprises an aqueous dispersion or a solution of:

(a) 100 parts by weight of a water-soluble polymer,
(b) from 1.0 to 30 parts by weight of a monomer which is sparingly soluble in water and which has at least three ethylenically unsaturated groups in the molecule,
(c) from 0 to 20 parts by weight of a fluorine-containing surfactant or a silicone oil, and
(d) from 0.0005 to 5 parts by weight of a radical polymerization initiator.

11. A process according to claim 10, wherein component (c) is from 0.1 to 10 parts by weight of a fluorine-containing surfactant.

12. A process according to claim 10, wherein component (c) is from 0.5 to 20 parts by weight of a silicone oil.