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(54) Paper-processing composition and use thereof

(57) A composition for processing paper comprising a carboxyl group containing polyvinyl alcohol resin and a hydrophilic group and fluorine containing compound, a heat-sensitive recording material and a release paper comprising a layer formed by said composition and a base material. This composition is capable of imparting superior barrier property, paper strength and coating property; a heat-sensitive recording material comprising this composition is superior in printing property, resistance to plasticizer, oil resistance, solvent resistance, water resistance and the like; and the release paper can prevent permeation of a releasing agent and is superior in releasing property and recyclability.

EP 0 867 562 A1

Description

FIELD OF THE INVENTION

5 The present invention relates to a composition for processing paper. More particularly, the present invention relates to a paper-processing composition capable of imparting superior barrier property, superior coating property and sufficient strength to paper, particularly a composition capable of imparting excellent barrier property such that a paper coated therewith can prevent permeation of air and oils.

10 Also, the present invention relates to a laminate such as a heat-sensitive recording material and a release paper, to which the above-mentioned composition has been applied, and more particularly, the invention relates to a heat-sensitive recording material wherein a heat-sensitive coloring agent layer comprising the composition as mentioned above, a coloring substance and a color developer is formed on a substrate such as paper and plastic film, and to a release paper comprising a glassine paper as a base paper, which has superior releasing property, recycling property and resistance to solvent in the releasing agent to be coated.

BACKGROUND OF THE INVENTION

Conventionally, vinyl ester resins, particularly polyvinyl alcohol resins, have been widely used as coating agents (processing agents) for paper surfaces to achieve improved paper surface properties inclusive of strength, smoothness, gloss and tackiness.

20 The present applicant has also proposed a paper coating composition comprising, as the main component, a modified polyvinyl alcohol having lactone ring in a molecule (Japanese Examined Patent Publication No. 39442/1977).

On the other hand, there have been proposed a composition for preventing tackiness (Japanese Unexamined Patent Publication No. 40579/1982) comprising a copolymer of a polymerizable compound containing perfluoroalkyl having 3 to 12 carbon atoms and a compound capable of copolymerization thereof, and a shellac (secreted from Taccardia Lacca), and a composition for preventing tackiness (Japanese Unexamined Patent Publication No. 57688/1994) comprising an organic fluoro compound as an active ingredient, which is to be used for printing newspaper by offset printing, both aiming at improving tackiness of the paper surfaces.

30 According to the technique disclosed in Japanese Examined Patent Publication No. 39442/1977, however, while barrier property of paper as requested those days was ensured, its level is far from satisfactory when recent requirements are to be fulfilled. The technique disclosed in Japanese Unexamined Patent Publication No. 40579/1982) and Japanese Unexamined Patent Publication No. 57688/1994 has succeeded in improving tackiness, but an improved barrier property of paper to air and ink is unlikely to be attained by this technique. Thus, a need exists for a paper processing agent noticeably superior in imparting barrier property, paper strength, coating property required by high speed processing of paper painting, particularly, a composition capable of imparting markedly superior barrier property which prevents permeation of air or oil through paper after coating.

In the meantime, a heat-sensitive recording method utilizing heat has been spreading, since it does not, unlike conventional printing methods, require steps of development and fixing or supply of materials, but permits easy recording.

40 In particular, a method comprising heating a color developing substance such as Crystal violet lactone and a color developer such as phenol compounds to allow reaction for color development, stands high in evaluation and has been put to practical use.

This method involves use of a water soluble compound such as polyvinyl alcohol (PVA) as a binder of both the aforementioned color developing substance and color developer. However, an extended heating and recording is associated with problems in that leaf of PVA attaches to a thermal head due to the abrasion, the thermal head and heat-sensitive recording paper stick to each other during high temperature treatment (sticking), the printed matter disappears upon contact of the recorded paper with water or plasticizer, and the recording paper becomes sticky.

45 To solve these problems, the use of an itaconic acid modified PVA as a binder (Japanese Patent Unexamined Publication No. 189889/1982), the use of an ethylene-carboxyl group modified PVA as an overcoating agent (Japanese Patent Unexamined Publication No. 156424/1996), the use of a carboxyl group modified PVA as a dispersing agent of heat-sensitive dye (Japanese Patent Unexamined Publication No. 48076/1996) and the use of a protecting layer (overcoating layer) comprising a modified PVA and zinc stearate (Japanese Patent Unexamined Publication No. 164763/1997) have been proposed. The present applicant has also proposed a heat-sensitive recording paper using an ethylenic unsaturated dicarboxylic monoamide modified PVA (Japanese Patent Unexamined Publication No. 252977/1996).

55 When the technique disclosed in the above-mentioned Japanese Patent Unexamined Publication No. 189889/1982 is used, color sensitivity becomes poor on recent high speed recording machines (e.g., recorder and printer); when the techniques disclosed in Japanese Patent Unexamined Publication Nos. 156424/1996 and 48076/1996 are used, bubbling and cissing occur during high speed printing; when the technique disclosed in Japanese Patent Unexamined Publication No. 164763/1997 is used, water resistance becomes insufficient; and when the technique disclosed in

Japanese Patent Unexamined Publication No. 252977/1996 by the present applicant is used, the production thereof becomes very difficult due to the technique required for the use of a specific modified PVA. Thus, there is left a room for an improvement, and a heat-sensitive recording paper superior in printing performance, oil resistance, solvent resistance and water resistance is awaited.

In the meantime, a release paper has been used in wide applications as a base material of pressure sensitive adhesive label, pressure sensitive adhesive tape, pressure sensitive adhesive sheet and the like.

Such release paper generally comprises a base paper and a layer of a release agent formed thereon. For the purpose of forming the layer of a release agent on the surface of the base paper without allowing permeation thereof into paper, a polyolefin resin layer of polyethylene or a barrier layer of polyvinyl alcohol resin, carboxymethyl cellulose, casein, polyvinyl acetate emulsion and the like is formed in the interface thereof.

When a polyolefin resin layer is formed, a barrier effect may be sufficient. However, its resin waste poses a big problem when the paper is recycled. In the case of a conventional layer of polyvinyl alcohol, the recycling problem can be overcome, whereas barrier property is not sufficient. Thus, a release paper having a barrier layer simultaneously satisfying recyclability and barrier property, which has superior releasability, is desired.

SUMMARY OF THE INVENTION

According to the present invention, a composition for processing paper is provided, which comprises a carboxyl group containing polyvinyl alcohol resin, and a hydrophilic group and fluorine containing compound. This composition affords superior barrier property, paper strength, coating property, particularly superior barrier property to prohibit permeation of air or oil through paper after coating. A composition comprising, as the hydrophilic group and fluorine containing compound, a compound of the following formula (1) noticeably shows the above-mentioned action and effect:



wherein X is $-SO_2NR-$ in which R is a hydrogen, an alkyl or a carbonyl, n is an integer of 1 to 40, m is an integer of 1 to 100 and k is 0 or 1.

In another aspect of the present invention, a laminate comprising a layer made from the above-mentioned composition, which is laminated on a base material, particularly, a heat-sensitive recording material and a release paper, are provided.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention, any carboxyl group containing polyvinyl alcohol resin may be used and the production method thereof is not particularly limited. For example, the production method may be one comprising producing a copolymer of an unsaturated monomer having a carboxyl group and a vinyl ester compound and hydrolyzing the copolymer, or one comprising reacting a polyvinyl alcohol resin and a polyfunctional carboxylic acid having two or more carboxyl groups or a compound having, in a molecule, a functional group reactive with OH group in polyvinyl alcohol and carboxyl group. The former method is practical in terms of production steps and property of the resin.

This method is explained in detail in the following.

Examples of the unsaturated monomer having carboxyl group include ethylenically unsaturated monocarboxylic acid (e.g., acrylic acid, methacrylic acid and crotonic acid), ethylenically unsaturated dicarboxylic acid (e.g., maleic acid, fumaric acid and itaconic acid), ethylenically unsaturated dicarboxylic monoester (e.g., monoalkyl maleate, monoalkyl fumarate and monoalkyl itaconate), ethylenically unsaturated dicarboxylic diester (e.g., dialkyl maleate, dialkyl fumarate and dialkyl itaconate, note that a part of the ester moiety of the diester must be converted to carboxyl by hydrolysis upon preparation of polyvinyl alcohol), ethylenically unsaturated carboxylic anhydride (e.g., maleic anhydride and fumaric anhydride) and salts thereof, with preference given to ethylenically unsaturated dicarboxylic monoester and salt thereof.

Examples of vinyl ester compounds include vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate, vinyl caprylate, vinyl laurate, vinyl versate, vinyl palmitate, vinyl stearate and the like, which may be used alone or in combination. Preferred from the practical viewpoint is vinyl acetate.

In the present invention, polymerization may be carried out in the presence of, in addition to the above-mentioned monomer having carboxyl group and vinyl ester compound, a monomer copolymerizable with vinyl ester, such as allyl ester of saturated carboxylic acid (e.g., allyl stearate, allyl laurate, allyl ester of coconut oil fatty acid, allyl octylate and allyl butyrate), α -olefin (e.g., ethylene, propylene, α -hexene, α -octene, α -decene, α -dodecene, α -hexadecene and α -octadecene), alkyl vinyl ether (e.g., propyl vinyl ether, butyl vinyl ether, hexyl vinyl ether, octyl vinyl ether, decyl vinyl ether, dodecyl vinyl ether, tetradecyl vinyl ether, hexadecyl vinyl ether and octadecyl vinyl ether), alkyl allyl ether (e.g., propyl allyl ether, butyl allyl ether, hexyl allyl ether, octyl allyl ether, decyl allyl ether, dodecyl allyl ether, tetradecyl allyl ether, hexadecyl allyl ether and octadecyl allyl ether), (meth)acrylamide, (meth)acrylonitrile, (meth)allylsulfonate, ethyl-

enically unsaturated sulfonate, styrene, vinyl chloride and the like, in a proportion of not more than 50 mol%.

The copolymerization is subject to no particular limitation, and a known polymerization method is used. It is typically a solution polymerization using alcohol (e.g., methanol or ethanol) as a solvent.

According to this method, monomers are charged as in the following. First, the entire amount of vinyl ester compound and a part of the above-mentioned carboxyl group containing unsaturated monomer are charged to initiate polymerization, and the remaining unsaturated monomer is successively or portionwise added during the polymerization period, or the total amount of the two monomers is charged at once to initiate polymerization. The copolymerization reaction is carried out using a known radical polymerization catalyst such as azobisisobutyronitrile, acetyl peroxide, benzoyl peroxide, lauroyl peroxide and the like. The reaction temperature is selected from the range of from 50°C to boiling point.

The copolymer thus obtained is then hydrolyzed to give a carboxyl group containing unsaturated monomer.

For hydrolysis, the copolymer is dissolved in alcohol, acetic acid ester or a mixed solvent thereof and the reaction is carried out in the presence of an alkaline catalyst. As the alcohol, used is methanol, ethanol, butanol and the like, and the acetic acid ester is exemplified by methyl acetate, ethyl acetate and the like.

The concentration of the copolymer in alcohol is 20-50 wt%. As the hydrolysis catalyst, it is required to use a hydroxide of alkali metal, such as sodium hydroxide, potassium hydroxide, sodium methylate, sodium ethylate and potassium methylate, and an alkali catalyst such as alcoholate. The catalyst is added in an amount of 1-100 mmol equivalent of the vinyl ester compound.

The hydrolysis temperature is not particularly limited. It is generally 10-70°C and particularly 30-40°C. The reaction generally proceeds for 2-3 hours. The preferable degree of hydrolysis is 10-100 mol%, more preferably 50-100 mol%, most preferably 70-100 mol%.

When a vinyl alcohol component is added, the method is not limited to the one mentioned above. For example, alkylene oxide is reacted with polyvinyl alcohol (e.g., partially hydrolyzed compound and completely hydrolyzed compound).

In this way, a carboxyl group containing polyvinyl alcohol resin is obtained. The carboxyl content is preferably 0.1-10 mol%, more preferably 0.5-5 mol%, of resin. When the carboxyl content is less than 0.1 mol%, the use thereof for a heat-sensitive recording material results in degraded oil resistance and solvent resistance, and the use thereof for a release paper results in degraded solvent resistance of the release paper. When the content exceeds 10 mol%, the solubility of the processing agent (e.g., coating liquid) becomes undesirably low.

In the present invention, an average degree of polymerization of the carboxyl group containing polyvinyl alcohol resin is preferably 100-10000, more preferably 300-3000. When the average degree of polymerization is less than 100, the strength of paper reduces to the point that printing property becomes defective. When it is used for a heat-sensitive recording material, the color development of the recorded matter becomes poor. In addition, the thermal head is more stained, and when it is applied to a release paper, the barrier property of the paper reduces, thus increasing the amount of releasing agent permeated into paper. When the average degree of polymerization exceeds 10000, the coating property thereof when prepared into a processing agent undesirably becomes poor.

Examples of the hydrophilic group and fluorine containing compound to be added with the above-mentioned carboxyl group containing polyvinyl alcohol resin include a compound containing perfluoroalkyl group (C_nF_{2n+1} - in which n is an integer of 1-40) and a hydrophilic group such as alkylene oxide and sulfonic acid group, inclusive of alkyl oligomer and urethane oligomer. A compound of the following formula (1) containing perfluoroalkyl group (C_nF_{2n+1} - in which n is an integer of 1-40) and alkylene oxide is preferable:



wherein X is $-SO_2NR-$ in which R is a hydrogen, an alkyl preferably having 1 to 20 carbon atoms or a carbonyl, n is an integer of 1 to 40, m is an integer of 1 to 100 and k is 0 or 1.

In this formula (1), n is preferably 3-20, more preferably 5-10, and m is preferably 3-30, more preferably 5-20.

This compound is commercially available as "MEGAFAC F-142D" and "MEGAFAC F-144D" manufactured by DAINIPPON INK AND CHEMICALS, INC.

The inventive composition for paper processing comprises a carboxyl group containing polyvinyl alcohol resin and a hydrophilic group and fluorine containing compound. The proportion of the hydrophilic group and fluorine containing compound is preferably 0.01-5.0 parts by weight per 100 parts by weight of the carboxyl group containing polyvinyl alcohol resin. When the content is less than 0.01 part by weight, the addition produces no effect, whereas when it exceeds 5.0 parts by weight, the paper strength decreases to ultimately produce cissing during painting, thus failing to accomplish the object of the present invention. When this composition is used for a heat-sensitive recording material, ink is repelled to show poor printing property, whereas when it is used for release paper, the barrier property of paper reduces to allow an increased amount of releasing agent to be permeated through paper and poor adhesion to the releasing agent to be coated thereon. The more preferable content is 0.05-3.0 parts by weight, and particularly preferably 0.1-2.0

parts by weight.

The thus-obtained composition for paper processing of the present invention is generally used upon dissolution in water. An organic solvent may be also used. The kind of solvent may be appropriately determined according to the property of the carboxyl group containing polyvinyl alcohol resin, and the contents of the carboxyl group containing polyvinyl alcohol resin and the hydrophilic group and fluorine containing compound. For example, a composition having a relatively low hydrolysis degree is obtained in a paste. Thus, the solvent used for polymerization or hydrolysis may be used as it is, or the solvent may be changed. Specific examples of the solvent are methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, methyl acetate, ethyl acetate, ethylene glycol, propylene glycol, butanediol and the like.

The composition for paper processing of the present invention is used as a coating liquid. The coating liquid may be prepared by any method as long as the above-mentioned carboxyl group containing polyvinyl alcohol resin and hydrophilic group and fluorine containing compound are mixed with water or a solvent. The concentration thereof is appropriately adjusted according to the object. A particularly preferable concentration of the mixture of carboxyl group containing polyvinyl alcohol resin and hydrophilic group and fluorine containing compound is generally 0.1-40% by weight, more preferably 1-20% by weight, in view of the workability. When a release paper is to be produced, the concentration is generally about 0.1-20% by weight, more preferably 0.1-10% by weight.

The composition for paper processing of the present invention contains, as mentioned above, a carboxyl group containing polyvinyl alcohol resin and a hydrophilic group and fluorine containing compound. Where necessary, known additives such as water resistance imparting agents (e.g., glyoxal, poly(amide amine), polyethyleneimine, isocyanate, glutaraldehyde methylolled melamine, zirconium salt such as ammonium zirconium carbonate, titanate such as tetra-n-butyl titanate, epichlorohydrin and urea resins), defoaming agents, releasing agents, surfactants (exclusive of hydrophilic group and fluorine containing compounds mentioned above), preservatives, insecticides, rust preventing agents, tackifiers and the like. As long as the characteristic features of the present invention are not impaired, polyvinyl alcohol, starch, carboxymethyl cellulose, poly(vinylpyrrolidone), acrylic latex, SBR latex, pigment such as kaolin, calcium carbonate, clay, titanium oxide and the like may be also added.

The paper on which the paper processing composition (coating liquid) of the present invention is to be applied is not subject to any particular limitation, and is exemplified by heat-sensitive recording paper, release paper, ink-jet paper, carbonic paper, noncarbonic paper, stencil for paper cup, oil proofing paper, cardboard such as manila board, white board and liner, paper of generally fine quality, paper of middle quality, printing paper such as paper for gravure printing, high, middle or lower class paper, paper for newspaper and the like.

For coating a paper processing composition, a known method such as size press coating method, roll coater method, air doctor method, blade coater method, gate roll coater method, spray coater method and the like may be used.

Thus, the composition for paper processing is coated in an amount of carboxyl group containing polyvinyl alcohol resin of 0.1-20 g/m² (converted to solid), preferably 0.1-10 g/m² (converted to solid), more preferably 0.5-10 g/m² (converted to solid), and most preferably 0.5-5 g/m² (converted to solid). The coating method is not limited to the above-mentioned method, but may be an internal sizing method wherein the inventive composition for paper processing is dissolved in a pulp dispersion and paper is made therefrom, or a method including mixing the inventive composition for paper processing in the form of powder or fiber in paper or other method, whereby the inventive composition for paper processing can be applied to paper.

The inventive composition for paper processing is generally used as a clear coating agent as mentioned above. It can be also used as a binder for a pigment, wherein the pigment may be a conventional one (e.g., clay, calcium carbonate, kaoline, diatom earth, titanium oxide, iron oxide, satin white and the like). When it is used as a binder, a clay shock, which has been the problem in conventional pigment coating (a phenomenon of pigment agglutination upon addition of binder to pigment dispersion), does not occur, thus exhibiting very superior effect in terms of dispersibility of pigment.

The inventive heat-sensitive recording material comprises a base material and a layer formed from the paper processing composition as mentioned above, hereinafter composition (a), comprising the carboxyl group containing polyvinyl alcohol resin and the hydrophilic group and fluorine containing compound which are laminated directly or via a different layer on said base material. The composition (a) can be added to (i) heat-sensitive color developing layer, (ii) protecting layer or (iii) undercoat layer. It is also possible to concurrently use composition (a) in two of the layers (i) to (iii) or three of the layers (i) to (iii). These layers are explained in detail in the following.

(i) heat-sensitive color developing layer

Using the composition (a) as a binder, a mixture comprising the binder, a color developing substance and a color developer is applied to a base material. A homogeneous coating dispersion for forming said heat-sensitive color developing layer is obtained by preparing an aqueous dispersion containing the color developing substance and an aqueous dispersion containing the color developer separately, thoroughly stirring same, finely dividing same and mixing the both dispersions by stirring. The composition (a) as a binder is added to the aqueous dispersion containing the color devel-

oping substance and/or the aqueous dispersion containing the color developer in a proportion of 10-200 wt% of the total amount of the color developing substance and the color developer. The solid content of said coating dispersion is 10-40 wt% in view of the workability.

Examples of the color developing substance include leuco compound of triphenylmethane dye such as 3,3-bis(p-dimethylaminophenyl)-phthalide, 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide [Crystal violet lactone], 3,3-bis(p-dimethylaminophenyl)-6-diethylamino-phthalide, 3,3-bis(p-dimethylaminophenyl)-6-chlorophthalide, 3-dimethyl-amino-6-methoxyfluorane, 7-acetamido-3-diethylaminofluorane, 3-diethylamino-5,7-dimethylfluorane, 3-diethyl-amino-5,7-dimethylfluorane, 3,6-bis- β -methoxyethoxyfluorane, 3,6-bis- β -cyanoethoxyfluorane and the like.

The color developer may be any as long as it develops color upon reaction during heating with the above-mentioned color developing substance, and liquidized or gasified at not less than normal temperature, preferably at not less than 70°C. Examples thereof include phenol, p-methylphenol, p-tert-butylphenol, p-phenylphenol, α -naphthol, β -naphthol, 4,4'-isopropylidenediphenol (bisphenol A), 4,4'-sec-butylidenediphenol, 4,4'-cyclohexylidenediphenol, 4,4'-isopropylidenebis(2-tert-butylphenol), 4,4'-(1-methyl-n-hexylidene)diphenol, 4,4'-isopropylidenedicatechol, 4,4'-pendilidenediphenol, 4,4-isopropylidenebis(2-chlorophenol), phenyl-4-hydroxybenzoate, salicylic acid, 3-phenylsalicylic acid, 5-methylsalicylic acid, 3,5-di-tert-butylsalicylic acid, 1-oxy-2-naphthoenoic acid, m-oxybenzoic acid, 4-oxyphthalic acid, gallic acid and the like. The color developing substance and color developer are not limited to those exemplified.

The base material to be coated with said coating dispersion is not particularly limited, and may be paper (e.g., cardboard such as manila board, white board and liner, general fine quality paper, paper of middle quality, printing paper such as paper for gravure printing, high, middle or lower class paper, paper for newspaper, release paper, carbonic paper, noncarbonic paper, glassine paper and the like), plastic film (e.g., polyester film, nylon film, polyolefin film, polyvinyl chloride film and laminates thereof) and the like. For coating, a known method may be used, such as roll coater method, air doctor method, blade coater method, bar coater method and the like. The amount to be coated is 1-20 g/m², particularly 3-10 g/m², by dry weight.

(ii) protecting layer

The protecting layer is applied to a heat-sensitive color developing layer comprising a color developing substance, a color developer and a binder which may be composition (a) or a composition comprising undenatured PVA, modified PVA (e.g., carboxyl group containing PVA), methylcellulose, carboxymethylcellulose, starch, latex, etc. The composition (a) is contained in the protecting layer. The coating liquid for the protecting layer is suitably an aqueous solution containing the composition (a) in a proportion of 1-10 wt%. The amount to be coated is about 0.5-5 g/m² by the dry weight of the composition (a). After coating, the layer is air dried or lightly heated to give an objective protecting layer.

For the coating, roll coater method, air doctor method, blade coater method, bar coater method, rod coater method and the like may be used.

The protecting layer may contain various known auxiliaries or such auxiliaries may be applied before or after application of the coating liquid or otherwise. Examples of auxiliaries include glyoxal, methylolled melamine, epihalohydrinic resins such as polyamide epichlorohydrin, epibromohydrin and the like, potassium persulfate, ammonium persulfate, persulfuric carbonate, metal salts such as ferric chloride, magnesium chloride and the like, polyfunctional isocyanates such as diisocyanate, and compounds known as water resistance imparting agent such as ammonium chloride, formalin, glycine, glycidyl ester, glycidyl ether, dimethylol urea, ketene dimer, boric acid and sodium tetraborate, and the like.

In addition, known additives such as a thermoplastic material (e.g., higher fatty amide), a filler (e.g., calcium carbonate and titanium dioxide), a dispersing agent and the like may be added.

(iii) undercoat layer

An undercoat layer is disposed as necessary between a base material and a heat-sensitive color developing layer, and comprises the composition (a). The base material on which the undercoat layer is to be formed is not particularly limited and may be paper, plastic film and the like. The coating method may be a known one such as roll coater method, air doctor method, blade coater, bar coater method, size press method, gate roll method and the like. The coating liquid used for this end is suitably an aqueous solution having a concentration of the composition (a) of 0.5-20 wt%. The amount to be coated is about 0.5-5 g/m² by the dry weight of the composition (a). After coating, the layer is air dried or lightly heated to give an objective undercoat layer.

The undercoat layer may contain various known additives as does the protecting layer.

The inventive heat-sensitive recording material can be obtained by forming a heat-sensitive color developing layer, or heat-sensitive color developing layer and a protecting layer on the undercoat layer thus formed.

In the heat-sensitive recording material of the present invention having a layer structure of base material/undercoat layer/heat-sensitive color developing layer/protecting layer, base material/ undercoat layer/heat-sensitive color develop-

ing layer, base material/heat-sensitive color developing layer/protecting layer, or base material/heat-sensitive color developing layer need only comprise any of the above-mentioned layers (i) to (iii) using the composition (a) and is subject to no other limitation. Other layers may be formed by a method conventionally known. It is possible to combine two or more kinds of layers from the above-mentioned layers (i) to (iii).

When the composition (a) is applied to a release paper to be formed, the base paper is not particularly limited. Examples thereof include glassine paper, semiglassine paper, graft paper, Japanese paper, woodfree paper, nonwoven fabric and the like, with preference given to glassine paper and semiglassine paper.

A release paper can be obtained by forming a layer of a releasing agent on the layer of the composition (a) formed on a base paper. The releasing agent is not particularly limited and is exemplified by silicone resin, fluororesin and the like.

The present invention is explained in detail by way of Examples, wherein "part" and "%" mean "part by weight" and "wt%" unless otherwise specified.

Example 1

【Preparation of carboxyl group containing polyvinyl alcohol resin】

Vinyl acetate (500 parts), maleic acid (3.4 parts) and methanol (85 parts) were charged in a polymerization vessel. The system was heated in a nitrogen stream while stirring and refluxed at 60°C for 30 min. Azobisisobutyronitrile was added in a proportion of 0.08 mol% of the vinyl acetate. The polymerization was carried out for 6 hr, during which time a solution of maleic acid in methanol was dropwise added to make the degeneration degree 1.0 mol%. After the completion of the reaction, methanol vapor was blown in to remove unreacted monomers to give a solution of copolymer in methanol.

The thus-obtained methanol solution was diluted to 40% with methanol. Sodium hydroxide was added in a proportion of 40 mmol% of the vinyl acetate in the copolymer for hydrolysis. The hydrolyzed product thus obtained was filtrated and dried at 70°C to give a carboxyl group containing polyvinyl alcohol resin (degree of hydrolysis 94.0 mol%, average degree of polymerization 1700).

【preparation of coating material】

The above-mentioned carboxyl group containing polyvinyl alcohol resin (6 parts) was dissolved in water (94 parts), and a hydrophilic group and fluorine containing compound of the formula : $C_8F_{17}-(CH_2-CH_2-O)_{10}-H$ (0.048 part, 0.8 part per 100 parts of polyvinyl alcohol resin) was added to give a coating composition, which was applied in a proportion of 2.0 g/m² to an acid paper (basic weight 60 g/m²) by size press coating (rate; 90 m/min, linear load; 11 kg/cm), which was followed by drying with a cylindrical rotary dryer at 105°C for 2 min and finishing of both sides by super calendar (temperature; 80°C, linear load; 40 kg/cm) to give a coating material.

The barrier properties (air permeation and oil absorption), paper surface strength and coating property of the obtained paper were evaluated by the following methods.

barrier properties

• air permeation

According to JIS P 8117, a test strip was fixed on an Okenshiki gas permeation tester (manufactured by ASAHI SEIKO CO., LTD.) and the time (sec) necessary for 100 ml of air to pass the paper was measured.

• oil absorption

According to JIS P 8130, the time (sec) necessary for oil to be absorbed by paper from the surface thereof to the inside thereof was measured by an oil absorption tester (manufactured by KUMAGAI RIKI KOGYO CO., LTD.).

paper surface strength

Using IGT print tester (manufactured by KUMAGAI RIKI KOGYO CO., LTD.) and FINE INK TV-20 (manufactured by DAINIPPON INK AND CHEMICALS, INC.), IGT pick strength (cm/sec) was measured.

coating property

The gloss and cissing of the coating layer were visually observed and evaluated as follows.

- 5 ○ : fine gloss, no cissing
 △ : fine gloss, occurrence of cissing
 X : less gloss, occurrence of cissing

Examples 2-17, Comparative Examples 1-3

10 In the same manner as in Example 1, carboxyl group containing polyvinyl alcohol resins and hydrophilic group and fluorine containing compound as shown in Table 1 were used to give heat-sensitive recording materials which were subjected to evaluation.

15 In Examples 5 and 6, itaconic acid was used instead of maleic acid. The evaluation results are shown in Table 2.

Table 1

	polyvinyl alcohol resin		hydrophilic group and fluorine containing compound	
	carboxyl content (mol%)	amount (parts)	kind*	amount (parts)
Ex. 1	1.0**	100	F-1	0.8
Ex. 2	2.0**	100	F-2	0.8
Ex. 3	1.5**	100	F-3	0.5
Ex. 4	1.0**	100	F-4	1.5
Ex. 5	1.0***	100	F-1	1.0
Ex. 6	1.5***	100	F-2	1.2
Ex. 7	3.0**	100	F-5	3.0
Com.Ex.1	1.0**	100		0 (not added)
Com.Ex.2	1.0**	100	F-0	0.8
Com.Ex.3	0****	100	F-1	0.8

Note

* F-1; $C_8F_{17}-(CH_2-CH_2-O)_{10}-H$

F-2; MEGAFAC F-142D, manufactured by DAINIPPON INK AND CHEMICALS, INC.

F-3; $C_8F_{17}-(CH_2-CH_2-O)_{20}-H$

F-4; MEGAFAC F-144D, manufactured by DAINIPPON INK AND
CHEMICALS, INC.

$$\text{F-5; } \text{C}_8\text{F}_{17}\text{SO}_2\text{N}-(\text{CH}_2-\text{CH}_2-\text{O})_{10}-\text{H}$$

$$\quad \quad \quad |$$

$$\quad \quad \quad \text{CH}_3$$

F-0; perfluoroalkyltrimethyl ammonium bromide MEGAFAC F-150BR,
manufactured by DAINIPPON INK AND CHEMICALS, INC.

** modified with maleic acid

*** modified with itaconic acid

**** not modified

Table 2

	barrier property		paper surface strength (cm/sec)	coating property
	air permeation (sec)	oil absorption (sec)		
Ex. 1	30	25	200	○
Ex. 2	35	30	195	○
Ex. 3	25	25	175	○
Ex. 4	35	35	190	○
Ex. 5	30	30	180	○
Ex. 6	35	30	190	○
Ex. 7	40	35	200	○
Com.Ex.1	15	10	175	△
Com.Ex.2	18	12	180	△
Com.Ex.3	10	8	150	X

The composition for paper processing of the present invention is capable of imparting superior barrier property, paper strength and coating property, particularly superior barrier property prohibiting permeation of air or oil after coating, as a result of the addition of a carboxyl group containing polyvinyl alcohol resin and a hydrophilic group and fluorine containing compound. The composition can be appropriately used for heat-sensitive recording paper, separating paper, release paper, ink jet paper, carbonic paper, noncarbonic paper, base paper for paper cup, oil resistant paper, paper board such as manila board, white board and liner, general fine quality paper, paper of middle quality, (light weight) coat paper, wrapping paper, printing paper such as paper for gravure printing, high, middle or lower class paper, paper for newspaper and the like.

Example 8

【Preparation of carboxyl group containing polyvinyl alcohol resin】

In the same manner as in Example 1, a carboxyl group containing polyvinyl alcohol resin (degree of hydrolysis 94.0 mol%, average degree of polymerization 1700) was obtained.

The above-mentioned carboxyl group containing polyvinyl alcohol resin (6 parts) and a hydrophilic group and fluorine containing compound of the formula : $C_8F_{17}-(CH_2-CH_2-O)_{10}-H$ (0.048 part, 0.8 part per 100 parts of polyvinyl alcohol resin) were dissolved in 100 parts of tetrahydrofuran.

hol resin) were dissolved in water (94 parts) to give a coating composition (A).

Using the coating composition (A), a heat-sensitive recording material was prepared as in the following.

A liquid	
Crystal violet lactone	10 parts
coating composition (A)	10 parts
water	15 parts

B liquid	
bisphenol A	50 parts
5% aqueous solution containing same carboxyl group containing polyvinyl alcohol resin as in A liquid	50 parts
water	75 parts

The above-mentioned A liquid and B liquid were separately divided to an average particle size of about 2 μm in a sand grinder, and A liquid, B liquid, calcium carbonate (50 parts) and a 15% aqueous solution of the same carboxyl group containing polyvinyl alcohol resin as in A liquid were mixed to give a coating liquid.

The obtained coating liquid was applied to a fine quality paper (base material, basic weight 50 g/m^2), so that the coated amount after drying became 5.0 g/m^2 , dried and a heat-sensitive color developing layer of (i) was formed, whereby a heat-sensitive recording material was prepared.

The color density of the printed letters, resistance to plasticizer, oil resistance, organic solvent resistance, water resistance and staining of thermal head were evaluated by the following methods.

The evaluation results are shown in Table 4.

color density of the printed letters

The printed letters were allowed to develop color under the conditions of 120°C, 2 kg/cm^2 , 5 sec using a Heat Gradient tester (manufactured by TOYOSEIKI SEISAKUSHO CO., LTD.) and the color density was determined by Macbeth densitometer (RD-100R type, manufactured by Macbeth, using an Umber filter).

resistance to plasticizer

A recording paper after color development was sandwiched between soft vinyl chloride sheets. A load of 20 g/cm^2 was applied and left standing at 40°C for 168 hr. The color density (x) of the letters was determined by Macbeth densitometer and the difference from the color density (y) of the letters before standing was calculated from the following formula and taken as color remaining percentage (%).

$$\text{color remaining percentage (\%)} = [1 - (y - x)/y] \times 100$$

oil resistance

Several drops of edible soybean oil were dropped on the color developed letters, and allowed to stand at room temperature for 24 hr. The soybean oil was wiped off and color remaining percentage (%) from the color density thereof before dropping oil was calculated in the same manner as in resistance to plasticizer.

organic solvent resistance

Several drops of ethyl acetate were dropped on the heat-sensitive recording material and left standing at room tem-

perature for one hour. Ethyl acetate was wiped off and color density was calculated by Macbeth densitometer, wherein smaller values mean better resistance to organic solvent.

water resistance

Several drops of water were dropped on the part where color had been developed, and left standing at room temperature for one hour. Water was wiped off and color remaining percentage (%) from the color density thereof before dropping was calculated in the same manner as in resistance to plasticizer.

staining of thermal head

A lattice pattern was printed by facsimile for consecutive 100 m, and occurrence of sticking and leaf remaining on the thermal head was visually observed. Evaluation was done in four levels of ◎-X.

- ◎ : Excellent
○ : Good
△ : Normal
X : Bad

Examples 9-16, Comparative Examples 4-6

In the same manner as in Example 8, carboxyl group containing polyvinyl alcohol resins and hydrophilic group and fluorine containing compound as shown in Table 3 were used to give heat-sensitive recording materials which were subjected to evaluation as heat-sensitive color developing layer (binder).

The evaluation results are shown in Table 4.

Table 3

	polyvinyl alcohol resin		hydrophilic group and fluorine containing compound	
	carboxyl content (mol%)	amount (parts)	kind	amount (parts)
Exs. 8, 17, 26	1.0**	100	F-1	0.8
Exs. 9, 18, 27	2.0**	100	F-1	0.8
Exs. 10, 19, 28	1.0**	100	F-2	1.8
Exs. 11, 20, 29	3.0***	100	F-1	0.8
Exs. 12, 21, 30	1.5**	100	F-3	0.5
Exs. 13, 22, 31	1.0**	100	F-4	1.5
Exs. 14, 23, 32	1.0***	100	F-1	1.0
Exs. 15, 24, 33	1.5***	100	F-2	1.2
Exs. 16, 25, 34	3.0**	100	F-5	3.0
Com.Exs. 4, 7, 10	1.0**	100	not added	
Com.Exs. 5, 8, 11	1.0**	100	F-0	0.8
Com.Exs. 6, 9, 12	0****	100	F-1	0.8

Note

** modified with maleic acid

*** modified with itaconic acid

**** not modified

Table 4

	color density of print	resistance to plasticizer (%)	resistance to oil (%)	resistance to organic solvent	water resistance(%)	staining of thermal head
Ex. 8	1.51	96	90	0.25	85	◎
Ex. 9	1.46	93	85	0.25	83	○
Ex. 10	1.48	95	88	0.20	90	◎
Ex. 11	1.52	95	89	0.19	92	○
Ex. 12	1.40	96	93	0.18	90	◎
Ex. 13	1.42	93	90	0.18	89	○
Ex. 14	1.50	94	91	0.20	90	◎
Ex. 15	1.50	92	92	0.20	88	◎
Ex. 16	1.53	95	88	0.23	90	◎
Com.Ex.4	1.32	88	75	0.43	89	○
Com.Ex.5	1.30	86	73	0.45	88	△
Com.Ex.6	1.03	48	60	0.75	46	X

Example 17

A heat-sensitive recording material was prepared in the following manner.

A liquid	
Crystal violet lactone	10 parts
unmodified PVA 5% aqueous solution (degree of hydrolysis 99.0 mol%, 4% aqueous solution viscosity 14 cps/20°C)	10 parts
water	15 parts

B liquid	
bisphenol A	50 parts
5% aqueous solution containing same unmodified PVA as in A liquid	50 parts
water	75 parts

The above-mentioned A liquid and B liquid were separately divided to an average particle size of about 2 μm in a sand grinder, and 15% aqueous solution of the same unmodified PVA (500 parts) used in A and B solutions was added to give a coating liquid.

The obtained coating liquid was applied to a fine quality paper (base material, basic weight 50 g/m^2), so that the coated amount after drying became 5.0 g/m^2 and dried.

There to was applied a coating liquid comprising a 10% aqueous solution of the coating composition (A) used in Example 8 and calcium carbonate (5 parts) by a Dickson coater at 1.5 g/m^2 (net), air dried and a protecting layer was formed, whereby a heat-sensitive recording material was prepared.

The obtained heat-sensitive recording material was evaluated in the same manner as in Example 8.

The evaluation results are shown in Table 5.

Examples 18-25, Comparative Examples 7-9

In the same manner as in Example 17, the composition (see Table 3) used in the above-mentioned Examples 9-16, Comparative Examples 4-6 to give heat-sensitive recording materials which were subjected to evaluation for (ii) protecting layer.

The evaluation results are shown in Table 5.

Table 5

	color density of print	resistance to plasticizer (%)	resistance to oil (%)	resistance to organic solvent	water resistance (%)	staining of thermal head
Ex. 17	1.48	90	92	0.10	89	◎
Ex. 18	1.43	83	90	0.13	88	◎
Ex. 19	1.47	85	90	0.13	89	◎
Ex. 20	1.53	92	98	0.05	94	◎
Ex. 21	1.44	90	96	0.09	92	◎
Ex. 22	1.42	88	90	0.17	87	◎
Ex. 23	1.47	91	91	0.11	91	◎
Ex. 24	1.51	93	94	0.10	93	◎
Ex. 25	1.47	85	93	0.10	90	◎
Com.Ex. 7	1.38	72	78	0.33	85	○
Com.Ex. 8	1.00	74	80	0.31	80	○
Com.Ex. 9	1.03	50	59	0.80	57	△

Example 26

A heat-sensitive recording material was prepared in the following manner.

A 5% aqueous solution of coating composition (A) used in Example 8 was applied to a fine quality paper (base material, basic weight 50 g/m²) using a size pressing device for testing (manufactured by KUMAGAI RIKI KOGYO CO., LTD.) at 1.5 g/m² (net) and dried at 110°C for one min to give a coated paper having an undercoat layer.

A liquid	
Crystal violet lactone	10 parts
unmodified PVA 5% aqueous solution (degree of hydrolysis 99.0 mol%, 4% aqueous solution viscosity 14 cps/20°C)	10 parts
water	15 parts

B liquid	
bisphenol A	50 parts

(continued)

B liquid		
5	5% aqueous solution containing same unmodified PVA	50 parts
	water	75 parts

The above-mentioned A liquid and B liquid were separately divided to an average particle size of about 2 μm in a sand grinder, and 15% aqueous solution of the same unmodified PVA (500 parts) used in A and B liquids was added to give a coating liquid.

The obtained coating liquid was applied to the paper having the above-mentioned undercoat layer, so that the coated amount after drying became 5.0 g/m^2 and dried to give a heat-sensitive recording material.

The obtained heat-sensitive recording material was evaluated for color density of the printed letter and staining of thermal head as in Example 8.

The evaluation results are shown in Table 6.

Examples 27-34, Comparative Examples 10-12

In the same manner as in Example 26, the composition (see Table 3) used in the above-mentioned Examples 9-16, Comparative Examples 4-6 to give heat-sensitive recording materials which were subjected to evaluation for protecting layer.

The evaluation results are shown in Table 6.

Table 6

	color density of print	staining of thermal head
Ex. 26	1.50	◎
Ex. 27	1.45	○
Ex. 28	1.46	○
Ex. 29	1.51	◎
Ex. 30	1.40	○
Ex. 31	1.41	○
Ex. 32	1.48	○
Ex. 33	1.49	◎
Ex. 34	1.47	◎
Com.Ex.10	1.31	○
Com.Ex.11	1.25	○
Com.Ex.12	1.11	△

The heat-sensitive recording material of the present invention comprises the specific composition in at least one layer of a heat-sensitive color developing layer, a protecting layer and an undercoat layer. As a consequence, it affords superior printing property, and particularly when it is used for a heat-sensitive color developing layer or a protecting layer, it imparts superior resistance to plasticizer, oil resistance, solvent resistance and water resistance, while causing less staining of a thermal head.

Example 35

In the same manner as in Example 1, a carboxyl group containing polyvinyl alcohol resin (degree of hydrolysis 94.0 mol%, average polymerization degree 1700) was obtained.

The above-mentioned carboxyl group containing polyvinyl alcohol resin (6 parts) was dissolved in water (94 parts), and a hydrophilic group and fluorine containing compound of the formula : $\text{C}_8\text{F}_{17}-(\text{CH}_2-\text{CH}_2-\text{O})_{10}-\text{H}$ (0.048 part, 0.8 part per 100 parts of polyvinyl alcohol resin) was added to give a coating liquid, which was applied in a proportion of 0.7 g/m^2

in resin solid component to one surface of a glassine paper (basic weight 65 g/m², gas permeation 100 sec). The paper was dried using a cylindrical rotary dryer at 105°C for 2 min, passed through super calendar (temperature; 80°C, linear load; 40 kg/cm), and a solution of a releasing agent [electron beam cure type non-solvent silicone, 100 parts, X-52-131 manufactured by Shin-Etsu Chemical Co., Ltd. and platinum catalyst 30 parts) was applied to the coated/dried surface in a solid content of 1.0 g/m², which was followed by electron beam irradiation to form a releasing layer, whereby a release paper was obtained.

The obtained release paper was evaluated for barrier property (gas permeation) and releasing property in the following manner.

releasing property

An acrylic emulsion adhesive (Nicazol L-145, manufactured by Nippon Carbide Industries Co., Inc.) was applied to the surface of the releasing agent layer of a release paper so that the applied amount was 25 g/m² by reverse roll coater. After hot air drying at 130°C, a fine quality paper (basic weight 65 g/m²) was adhered. The peel strength (g/50 mm) when peeled at 0.3 m/min at normal condition was measured and evaluated as follows.

- : less than 100 g/50 mm
 △: less than 100 - 200 g/50 mm
 X: 200 g/50 mm or above

The obtained release paper was easily dissolved in water by regular recycling steps, and could be recovered as waste paper.

Examples 36-41, Comparative Examples 13-15

Using carboxyl group containing polyvinyl alcohol resins and hydrophilic group and fluorine containing compounds as shown in Table 7 were used, evaluation was performed.

In Examples 39 and 40, itaconic acid was used instead of maleic acid.

The evaluation results are shown in Table 8.

Table 7

	polyvinyl alcohol resin		hydrophilic group and fluorine containing compound	
	carboxyl content (mol%)	amount (parts)	kind	amount (parts)
Ex. 35	1.0**	100	F-1	0.8
Ex. 36	2.0**	100	F-2	0.8
Ex. 37	1.5**	100	F-3	0.5
Ex. 38	1.0**	100	F-4	1.5
Ex. 39	1.0***	100	F-1	1.0
Ex. 40	1.5***	100	F-2	1.2
Ex. 41	3.0**	100	F-5	3.0
Com.Ex.13	1.0**	100	F-1	not added
Com.Ex.14	1.0**	100	F-0	0.8
Com.Ex.15	0****	100	F-1	0.8

Note

** modified with maleic acid

*** modified with itaconic acid

**** not modified

Table 8

	barrier property gas permeation (sec)	releasing property
Ex. 35	5100	○
Ex. 36	6800	○
Ex. 37	5000	○
Ex. 38	5200	○
Ex. 39	7800	○
Ex. 40	8000	○
Ex. 41	7500	○
Com.Ex.13	3200	△
Com.Ex.14	2500	△
Com.Ex.15	2000	X

The release paper of the present invention comprising the specific composition in the base paper shows superior barrier property. As a consequence, it can prevent permeation of a releasing agent and is superior in releasing property. In addition, the release paper can be easily dissolved in water through regular recycling steps, and can be recovered as waste paper. Thus, the inventive release paper is useful as a base material of adhesive label, heat-sensitive label, adhesive tape, adhesive sheet and the like.

Claims

1. A composition for processing paper comprising a carboxyl group containing polyvinyl alcohol resin and a hydrophilic group and fluorine containing compound.
2. The composition of claim 1, wherein the hydrophilic group and fluorine containing compound is a compound represented by the formula (1)



wherein X is -SO₂NR- wherein R is a hydrogen, an alkyl or a carbonyl, n is an integer of 1 to 40, m is an integer of 1 to 100 and k is 0 or 1.

3. The composition of claim 1, wherein the hydrophilic group and fluorine containing compound is contained in a proportion of 0.01-5.0 parts by weight per 100 parts by weight of the polyvinyl alcohol resin.
4. The composition of claim 1, wherein the carboxyl group containing polyvinyl alcohol resin comprises a carboxyl group in a proportion of 0.1-10 mol%.
5. The composition of claim 1, wherein the carboxyl group containing polyvinyl alcohol resin has an average polymerization degree of 100-10000.
6. A laminate comprising a layer made from a composition (a) for processing paper, which comprises a carboxyl group containing polyvinyl alcohol resin and a hydrophilic group and fluorine containing compound, the layer being laminated on a base material.
7. The laminate of claim 6, wherein the hydrophilic group and fluorine containing compound is a compound represented by the formula (1)



wherein X is -SO₂NR- wherein R is a hydrogen, an alkyl, or a carbonyl, n is an integer of 1 to 40, m is an integer of 1 to 100 and k is 0 or 1.

- 5 8. The laminate of claim 6, wherein the hydrophilic group and fluorine containing compound is contained in a proportion of 0.01-5.0 parts by weight per 100 parts by weight of the polyvinyl alcohol resin.
9. The laminate of claim 6, wherein the carboxyl group containing polyvinyl alcohol resin comprises a carboxyl group in a proportion of 0.1-10 mol%.
- 10 10. The laminate of claim 6, wherein the carboxyl group containing polyvinyl alcohol resin has an average polymerization degree of 100-10000.
11. The laminate of any one of claims 6 to 10, which is a heat-sensitive recording material comprising a layer prepared from the composition (a) and a base material.
- 15 12. The laminate of claim 11, wherein the composition (a) further comprises a color developing substance and a color developer to allow color development.
- 20 13. The laminate of claim 11, wherein the layer prepared from the composition (a) is a protecting layer to be formed on a heat-sensitive recording layer prepared from a composition comprising a color developing substance and a color developer to allow color development.
- 25 14. The laminate of claim 11, wherein the layer prepared from the composition (a) is an undercoat layer to be formed between a base material and a heat-sensitive recording layer prepared from a composition comprising a color developing substance and a color developer to allow color development.
15. The laminate of any one of claims 6 to 10, which is a release paper comprising a layer comprising the comprising the composition (a) and a base material.
- 30 16. The laminate of claim 15, further comprising a layer comprising a releasing agent formed on the layer prepared from the composition (a).

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EUROPEAN SEARCH REPORT

Application Number
EP 98 10 5356

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 4 898 849 A (KANG MING-HUANG J) 6 February 1990 * the whole document *	1,6,11, 13	D21H19/10 D21H19/82 B41M5/26
A	---	2-5, 7-10, 14	
A	US 5 037 871 A (JONES RAYMOND T) 6 August 1991 * the whole document *	1-3,6-8	
A	US 3 664 987 A (MOYER RONALD C ET AL) 23 May 1972 * column 1, line 51 - column 1, line 60 *	1	
D,A	DATABASE WPI Section Ch, Week 8301 Derwent Publications Ltd., London, GB; Class A14, AN 83-01427K XP002068119 & JP 57 189 889 A (RICOH KK) * abstract *		
D,A	DATABASE WPI Section Ch, Week 9634 Derwent Publications Ltd., London, GB; Class A14, AN 96-338218 XP002068120 & JP 08 156 424 A (KURARAY CO LTD) * abstract *		
D,A	DATABASE WPI Section Ch, Week 9617 Derwent Publications Ltd., London, GB; Class A14, AN 96-166776 XP002068121 & JP 08 048 076 A (KURARAY CO LTD) * abstract *		

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The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 16 June 1998	Examiner Nestby, K
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>			

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EUROPEAN SEARCH REPORT

Application Number
EP 98 10 5356

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D, A	DATABASE WPI Section Ch, Week 9649 Derwent Publications Ltd., London, GB; Class A89, AN 96-493054 XP002068122 & JP 08 252 977 A (NIPPON SYNTHETIC CHEM IND CO) * abstract *		
A	US 5 182 252 A (NAGASAWA TSUGIO ET AL) 26 January 1993		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
MUNICH		16 June 1998	Nestby, K
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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