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(54) COLOR DEVELOPER FOR PRESSURE-SENSITIVE RECORDING MEDIUM, AQUEOUS DISPERSION OF COLOR DEVELOPER, AND PROCESS FOR ITS PREPARATION.

(57) A color developer for pressure-sensitive recording medium containing a polyvalent metal salt of a salicylic acid and a polyvalent metal salt of rosin-modified phenol resin and an aqueous dispersion of color developer containing said color developer are disclosed. The color developer shows excellent initial color-forming properties and waterproofness and, since inexpensive resin-modifed phenol resin is used as a starting material, serves to markedly decrease production cost.

COLOR DEVELOPER FOR PRESSURE-SENSITIVE RECORDING MEDIUM, AQUEOUS DISPERSION OF COLOR DEVELOPER AND PROCESS FOR PREPARING THE SAME

TECHNICAL FIELD

The present invention relates to a color developer for pressure-sensitive recording medium, an aqueous dispersion of a color developer and a process for preparing the same.

BACKGROUND ART

Pressure-sensitive recording mediums represented by a pressure-sensitive copying paper which is generally known as a no carbon copying paper develop color when the pressure-sensitive recording mediums are mechanically pressured by means of hand-writing, a typewriter and the like, and are the mediums which can provide plural copied papers at a time. Accordingly, in accordance with the recent high growth of information in the industrial environment, the used amount has been rapidly increased.

It is said that the coloring principle of the pressure-sensitive recording mediums is based upon the generation of a color reaction caused by the contact of a color developer with a pressure-sensitive colorless dye solution flowed from a microcapsule destroyed by printing pressure of a typewriter and the like between the coated surface of an upper paper coated with a microcapsule of a non-volatile type solvent containing an electron donative organic compound (so-called pressure-sensitive colorless dye) and the coated surface of a lower paper coated with an aqueous coating composition containing an electron acceptive color developer.

As the above-mentioned electron acceptive color developer, inorganic solid acid such as activated clay or attapulgite, various phenolic resins, aliphatic or aromatic carboxylic acids and metallic salts thereof have been conventionally used (Japanese Unexamined Patent Publication No. 32011/1973). However, the inorganic solid acid has defects that the inorganic solid acid type color developer is influenced by light, gas, moisture and the like and the printed mark generated from the developer easily disappears or fades, and the viscosity index is wrong when the inorganic solid acid is used in a paint. The phenolic resin has defects that color fastness to light at printing is low and the color developer layer is yellowed by light and gas. Therefore, in recent years, aromatic carboxylic acid polyvalent metallic salts have been used because the metallic salts is excellent in color fastness to light at printing and shows little yellowing of a color developer layer caused by light or gas. Among them, polyvalent metallic salts of salicylic acids have been widely used.

However, nevertheless the polyvalent metallic salts of salicylic acids have the above-mentioned various excellent properties, the polyvalent metallic salts have a serious defect of poor waterproofness at printing. Recently, it has been known that salicylic acids wherein various oil soluble groups are introduced into the aromatic ring remove the above-mentioned defects to a certain degree. However, it cannot be said that the salicylic acids are sufficiently practical matters, and in particular there is a room for improving initial color-forming properties and waterproofness.

As a method for coating a substrate for a recording medium with a color developer, a method for coating a support such as paper with an aqueous dispersion of a color developer is well known.

As a method for preparing the above-mentioned aqueous dispersion, for instance, a method for using a water soluble polymer such as polyvinyl alcohol, sodium polyacrylate or sodium polystyrenesulfonate as a dispersing agent, and wet grinding the dispersing agent, water and a color developer by means of Kady mill, sand mill, ball mill or the like, has been generally employed. However, according to the method, the particle size of the color developer in the obtained aqueous dispersion is usually at least 1 μm. Therefore, the storage stability of the dispersion deteriorate and the surface area of the color developer comes to be small. Accordingly, there is a defect that desired color developing properties are not exhibited.

As a method for preparing an aqueous solution of a color developer other than the above-mentioned, there is a method for emulsifying and dispersing a color developer in the presence of a dispersing agent and a solvent by a mechanical pressure with a homogenizer or the like. However, there is a defect that the color developer is not sufficiently emulsified and dispersed with a conventional dispersing agent.

The present invention aims at providing an excellent color developer and an excellent aqueous dispersion thereof improved in initial color-forming properties and waterproofness which are the defects of the above-mentioned polyvalent metallic salts of salicylic acids while maintaining color-forming properties, NO_x gas yellowing resistance and the like, and remarkably improved in storage stability which is a defect of a method for preparing an aqueous dispersion thereof.

In consideration of the problems of the above-mentioned prior art, the present inventors have been eagerly studied concerning a compound which can be used together with polyvalent metallic salts of salicylic acids. As a result, when a specific polyvalent metallic salt of a rosin-modified phenolic resin is used, it has been for the first time found that the initial color-forming properties and waterproofness which are the defects of a salicylic acid color developer are remarkably improved while maintaining the merits of the salicylic acid color developer. The present invention has been accomplished based upon the novel finding.

DISCLOSURE OF THE INVENTION

The present invention relates to (1) a color developer for pressure-sensitive recording medium characterized in that a polyvalent metallic salt of a salicylic acid and a polyvalent metallic salt of a rosin-modified phenolic resin are contained, (2) an aqueous dispersion of a color developer containing the color developer, and (3) a method for preparing an aqueous dispersion of a color developer characterized in that an amorphous oligomer and polyvinyl alcohol are used as a dispersing agent when a color developer is mechanically emulsified and dispersed in the presence of a dispersing agent and a solvent.

BEST MODE FOR CARRYING OUT THE INVENTION

In the instant specification, salicylic acids mean salicylic acid and various known salicylic acid derivatives, and various salicylic acid derivatives can be effectively used. In consideration of resistances such as waterproofness and lightfastness, salicylic acid derivatives having an alkyl group of at least 8 carbon atoms, desirably 12 to 20 carbon atoms can be particularly preferably used. Examples of the salicylic acid derivatives are, for instance, 3-methyl salicylic acid, 5-methyl salicylic acid, 3-ethyl salicylic acid, 5-ethyl salicylic acid, 3-t-butyl salicylic acid, 5-t-butyl salicylic acid, 3-phenyl salicylic acid, 5-phenyl salicylic acid, 3,5-di-t-butyl salicylic acid, 3-methyl-5-phenyl salicylic acid, 3-t-butyl-5-(p-t-butylbenzyl) salicylic acid, 3-cyclohexyl-5-(α,α-dimethylbenzyl) salicylic acid, 3-phenyl-5-(α,α-methylbenzyl) salicylic acid, 3-phenyl-5-(α,α -dimethylbenzyl) salicylic acid, 3,5-di(α-dimethylbenzyl) salicylic acid, 3,5-di(α,α-dimethylbenzyl) salicylic acid, and the like. Known various condensates of salicylic acids such as salicylic acid-formaldehyde condensate are also included in the above-mentioned salicylic acids. When the salycyclic acid-formaldehyde condensate is used solely or together with other salicylic acids, the plasticizer resistance of an image is particularly remarkably improved.

In the instant specification, rosin-modified phenolic resin is defined to as follows.

One of (A) a product prepared by the addition reaction of rosins and phenols in the presence of an inorganic acid such as sulfunic acid or an organic acid such as methanesulfonic acid; (B) a polymerized product of the above-mentioned (A); (C) a product prepared by a addition-reacting rosins and phenols in the presence of the above-mentioned acid catalyst and then condensation-reacting the adduction product with formalin; and (D) a product prepared by the addition-condensation reaction of a resol primary condensate, which is prepared by the reaction of phenols and formadehyde in the presence of an alkaline catalyst, and rosins in the presence or absence of the above-mentioned acid catalyst can be exemplified as the rosin-modified phenolic resin. As the phenols, various known phenols, for instance, carbolic acid, cresol, p-t-butylphenol, octylphenol, nonylphenol, phenylphenol and the like can be exemplified.

As the rosins which are starting materials of a rosin-modified phenolic resin, for instance, natural rosins such as gum rosin, wood rosin and tall oil rosin, and modified rosins such as disproportionated rosins, hydrogenated rosin, polymerized rosin, rosin modified with maleic acid, rosin modified with fumalic acid and formaldehyde-modified resin can be effectively used. In consideration of stability of priting and the like, among them it is preferable to use hydrogenated rosin and disproportionated rosin.

Both of salicylic acids and rosin-modified phenolic resin can be easily obtained as polyvalent metallic salts thereof by reacting with a polvalent metallic compound described later with heating in the presence of a catalyst and a solvent described later. As the above-mentioned polyvalent metallic compound, for instance, compounds of polyvalent metallic compounds such as magnesium, aluminium, calcium or zinc can be used without any limitation. Concretely, oxides, hydroxides, oxides, hydroxides, chlorides, carbonates and sulfates of the polyvalent metal, and the like can be exemplified. More concretely, for instance, zinc oxide, zinc hydroxide, zinc chloride, zinc sulfate, magnesium oxide, aluminium oxide, calcium oxide, titan oxide, manganese oxide, magneisum hydroxide, aluminium hydroxide, calcium hydroxide, and the like can be exemplified. Among them, it is preferable to use zinc oxide.

As a catalyst used when preparing a polyvalent metallic salt of salicylic acids and a polyvalent metallic salt of rosin-modified phenolic resin which are used in the above-mentioned color developers, for instance, inorganic ammonium salts such as ammonium carbonate and ammonium bicarbonate, alkali hydroxides such as sodium hydroxide, potassium hydroxide, and the like are exemplified. The used amount of the catalyst cannot be absolutely determined, but is usually 0.05 to 1.0 equivalent, preferably 0.1 to 0.4 equivalent per one equivalent of a metal in the polyvalent metallic compound. When the used amount of the catalyst is so smaller than 0.05 equivalent, it takes a long time for the reaction, and when the used amount is so greater than 0.1 equivalent, there is no meaning and it comes to be merely economically disadvantageous.

As a solvent used in the above-mentioned reaction, for instance, eters, ketones, acetic acid esters and the like can be exemplified. The reaction temperature is usually 40° to 100° C, preferably 60° to 80° C. The reaction time is 1 to 6 hours. After the completion of the reaction, a polyvalent metallic salt of salicylic acid and a polyvalent metallic salt of a rosin-modified phenolic resin which are color developing components in the present invention are prepared by filtration and distillation of a resulting product to remove unreacted inorganic compounds and a solvent from the product.

The color developer of the present invention is a mixture of a polyvalent metallic salt of salicylic acids and a polyvalent metallic salt of a rosin-modified phenolic resin as mentioned above. The ratio of them is not particularly limited. The amount of the latter, i.e. the polyvalent metallic salt of a rosin-modified phenolic resin is usually adjusted to 0.1 to 100 parts by weight or so, preferably 0.1 to 50 parts by weight, more preferably 0.1 to 10 parts weight based upon 100 parts by weight of the former, i.e. the polyvalent metallic salt of salicylic acids. When the amount of the latter is less than 0.1 parts by weight, effects such as waterproofness and initial color-forming properties of the present invention are not sufficiently exhibited, and when the amount exceeds 100 parts by weight, there is a tendency that the color-forming properties deteriorate. In the present invention, it is sufficient if the both are contained in a color developer. Accordingly, as to a method for mixing the both, there is no limitation, and a method for heating and melting the both can be usually employed.

There is no limitation as to a method for coating the obtained color developer onto a substrate for a recording medium, and known methods can be adopted as they are. That is, for instance, various known methods such as a method for coating an aqueous paint, in which aqueous dispersion of the color developer is used, onto a substrate such as paper; a method for applying the color developer during paper sheet formation; a method for coating a solution or dispersion, which is prepared by mixing the color developer with an organic solvent, onto the surface of a substrate and drying it can be adopted.

Hereinafter a method for using the color developer of the present invention in a state of aqueous paint is explained.

As a method for preparing an aqueous dispersion of the present invention, for instance, a wet grinding method comprising using a water soluble polymer such as polyvinyl alcohol, sodium polyacrylate or sodium polystyrenesulfonate as a dispersing agent, adding the color developer of the present invention into the aqueous solution of the dispersing agent and wet grinding them by means of Kady mill, sand mill, ball mill or the like to give a dispersion, a method comprising dissolving the color developer in a suitable solvent, adding a protective colloid of polyvinyl alcohol carboxymethyl cellulose, ethylene-maleic anhydride copolymer or the like, water and if necessary, a suitable emulsifier, mechanically emulsifying them by means of a homogenizer and distilling an organic solvent from them under reduced pressure as occasion demands to give a dispersion, and the like can be adopted, and thereby improvement of waterproofness of printing which is the purpose of the present invention can be achieved.

That is, when the above-mentioned known wet grinding method is applied to the color developer of the present invention, using a homogenizer as a means for mechanically emulsifying and dispersing can remarkably improve storage stability of an aqueous dispersion, coloring speed of a color developer and coloring density in comparison with using a ball mill as a means for wet grinding. However, it cannot be said that the physical properties of an obtained dispersion such as storage stability are sufficient in this case. There is also a disadvantage that the storage stability of a dispersion is not sufficient even if the above-mentioned known method for dispersing in an organic solvent is applied.

Thus, the method for preparing the aqueous dispersion of the present invention has been developed in order to improve storage stability of the aqueous dispersion. The storage stability is remarkably improved by mechanically emulsifying the color developer of the present invention in the coexistence of a specific dispersing agent, i.e. amorphous oligomer and polyvinyl alcohol.

As the above-mentioned amorphous oligomer, for instance, rosin ester, terpene resin, terpenephenolic resin, aromatically modified terpene resin, petroleum resin, hydrogenated petroleum resin, hydrogenated terpene resin, and the like are exemplified, and the amorphous oligomer is selected from one or more of them and used. Among them, it is preferable to use rosin ester and hydrogenated petroleum resin. It is preferable that the polyvinyl alcohol has an average polymerization degree of 100 to 2400 and a saponification value of 80 to 90 % by mole.

The used amount of the amorphous oligomer is 10 to 100 % by weight, preferably 20 to 50 % by weight of a polyvalent metallic salt compound. The used amount of the polyvinyl alcohol is 1 to 30 % by weight, preferably 1 to 10 % by weight of solid components of the color developer and the amorphous oligomer to be emulsified. At emulsifying, known emulsifier and the like can be added thereto within a range that physical properties of the aqueous solution of the color developer are not impared.

The detailed explanation of a method for preparing an aqueous dispersion of the color developer of the present invention is as follows.

The method comprises the steps of dissolving the above-mentioned color developer in a suitable solvent such as ketones such as methyl ethyl ketone and methyl isobutyl ketone, acetic acid esters such as ethyl acetate and butyl acetate, and aromatic hydrocarbon solvents such as toluene and xylene; adding polyvinyl alcohol and water thereto and pre-emulsifying them sufficiently while keeping the temperature constantly to a range of 30° to 80° C; emulsifying and dispersing them with a homogenizer; and removing a solvent from them by distillation under reduced pressure to give a purposed aqueous dispersion of the color developer.

A paint having a suitable viscosity and coating properties is prepared by properly mixing the aqueous dispersion prepared by the above-mentioned method with kaoline, calcium carbonate, starch, synthetic or natural latex, and the like. The content of the color developer in the paint is 5 to 60 % by weight, preferably 5 to 20 % by weight of the total amounts of solid components. When the content is less than 5 % by weight, color-forming properties are not sufficiently exhibited, and when the content exceeds 60 % by weight, there is a tendency that characteristics of paper of a color developing paper deteriorate.

The amount of the color developer coated on a substrate such as paper is adjusted to 0.1 to 3.0 g/m^2, preferably 0.2 to 0.7 g/m^2 n a dry state.

A lower paper can be prepared by applying the color developer of the present invention in accordance with the above-mentioned method.

On the other hand, when an upper paper is prepared, conventionally known technics can be employed. For instance, kinds of a colorless dye, which develops color when the colorless dye reacts with a color developer, are not particularly limited.

A capsule can be produced by dissolving various known color couplers such as triallylmethane compounds, diphenylmethane compounds, xanthene compounds, thiazine compounds, spiropyran compounds in a solvent such as an aliphatic hydrocarbon such as alkylnaphthalene, alkylated diphenylalkane, alkylated triphenyldimethane or alkylated diphenyl, kerosene, chlorinated diphenyl, chlorinated paraffin, cotton seed oil, linseed oil or soya bean oil in a known method for producing a capsule. As the method for producing a capsule, for instance, a method for producing a capsule in which coacervation is used, disclosed in USP 2,800,457 and U.S. Patent No. 2,800,458; a method for producing a capsule in which interfacial polymerization method is used, disclosed in U.K. Patent No. 990,443 and U.S. Patent No. 3,287,154; a method for producing a capsule in which precipitate of polymer is used, disclosed in U.S. Patent No. 3,418,250, U.S. Patent No. 3,660,304 and the like; a method for producing a capsule in which polymerization method of a reactant from the inner part of a drop of oil, disclosed in U.S. Patent No. 3,726,804 and U.S. Patent No. 3,796,669; and the like are exemplified.

The present invention is specifically explained by means of the following Preparation Examples, Examples and Comparative Examples. However, it should be understood that the present invention is not limited to these examples. In examples, "parts" and "%" are by weight unless otherwise noted.

Preparation Example 1

A flask equipped with an agitator, a Liebig-Graham condenser and a temperature gauge was charged with 1000 part of gum rosin, 1000 parts of carbolic acid and 0.7 part of paratoluenesulfonic acid as a catalyst, and the temperature was raised to 150° to 170° C. The reaction was carried out at the same temperature for 5 hours, and further the temperature was raised to 250° to 260° C while the carbolic acid was distilled off to give about 1250 parts of rosin-phenol addition reaction product. The product had an acid value of 107 and a softening point of 110° C.

Then, a flask was charged with 1000 parts of the rosin phenol addition reaction product, 45 parts of paraformaldehyde, 1.5 parts of paratoluenesulfonic acid and 15 parts of xylene, and the temperature was raised to 100° to 110° C. After the reaction was carried out at the same temperature for 4 hours to form a novolak type structure, the temperature was decreased to 80° C, 77 parts of ammonium bicarbonate and 155 parts of zinc oxide were added thereto and addition reaction of zinc salt was carried out for 2 hours. After that, the reaction mixture was filtrated and xylene was distilled off to give about 1070 parts of zinc salt of rosin-modified phenolic resin.

Preparation Example 2

A reactor which is the same as that used in Preparation Example 1 was charged with 1000 parts of gun rosin, 1000 parts of carbolic acid and 0.6 part of paratoluenesulfonic acid as a catalyst, and the temperature was raised to 150° to 170° C. The reaction was carried out at the same temperature for 7 hours. After that, the temperature was decreased to about 100° C, and 2.7 parts of 5 % aqueous solution of lithium hydroxide was added thereto to carry out the neutralization of paratoluenesulfonic acid. The temperature was rasied to 290° to 300° C while unreacted carbolic acid was distilled off, and the polymerization reaction was carried out at the same temperature for 5 hours to give about 920 parts of rosin-phenol addition reaction product. The product had an acid value of 55 and a softening point of 150° C.

Then, a flask was charged with 1000 parts of the rosin-phenol addition reaction product, 150 parts of xylene, 40 parts of ammonium bicarbonate and 80 parts of zinc oxide, the temperature was raised to 80° C, and addition reaction of zinc salt was carried out at the same temperature for 2 hours. After that, the reaction mixture was filtrated and xylene was distilled off to give about 1060 parts of zinc salt of rosin-modified phenolic resin.

Example 1

A flask equipped with an agitator, a Liebig-Graham condenser and a temperature gauge was charged with 1000 parts of zinc 3,5-di-(α-methylbenzyl)salicylate and 50 parts of zinc salt of rosin-modified phenolic resin obtained in Preparation Example 1, and they were melted and mixed together at 180° C with stirring to give about 1050 parts of a color developer.

Example 2

The same procedure of Example 1 was repeated except that 50 parts of zinc salt of rosin-modified phenolic resin obtained in Preparation Example 2 was used instead of 50 parts of the zinc salt of rosin-modified phenolic resin obtained in Preparation Example 1 to give about 1050 parts of a color developer.

Example 3

The same procedure of Example 1 was repeated except that 1000 parts of zinc 3,5-di-tertiallybutylsalicylate was used instead of 1000 parts of zinc 3,5-di-(α-methylbenzyl)salicylate to give about 1050 parts of a color developer.

Example 4

The same procedure of Example 1 was repeated except that the used amount of the zinc salt of rosin-modified phenolic resin was changed to 500 parts to give about 1500 parts of a color developer.

Example 5

To 30 parts of the color developer obtained in Example 1, 15 parts of 10 % aqueous solution of sodium polyacrylate was added, and they were subjected to wet grinding by means of a ball mill for 24 hours to give a dispersion. To 5 parts of the dispersion, 22.5 parts of 50 % calcium carbonate slurry and 3.1 parts of styrenebutadiene latex (content of non-volatile components 48 %) were added, and they were kneaded for

90 minutes by means of a paint shaker to give a paint. The obtained paint was applied to a woodfree paper by means of a bar coater so that the weight of solid component was 5 g/m^2 to give a color developing sheet.

Example 6

A flask equipped with an agitator, a Liebig-Graham condenser and a temperature gauge was charged with 100 parts of the color developer obtained in Example 1, 50 parts of rosin ester (available from Arakawa Kagaku Kogyo Kabushiki Kaisha, commercial name "Super ester A-75") and 120 parts of toluene, and they were dissolved at 60°C. After 45 parts of 10 % aqueous solution of polyvinyl alcohol (available from KURARAY CO., LTD., commercial name PVA 205) and 240 parts of water were added thereto and they were pre-emulsified for 30 minutes, they were emulsified by means of a high pressure emulsifier (available from A.P.V. Gaulin Inc.). After that, toluene was removed therefrom by distillation under reduced pressure to give an aqueous dispersion. The content of non-volatile components of this aqueous dispersion was 40 %.

To 3.8 parts of this dispersion, 22.5 parts of 50 % calcium carbonate slurry and 3.1 parts of styrenebutadiene latex (content of non-volatile components 48 %) were added, and they were kneaded for 90 minutes by means of a paint shaker to give a paint. The obtained paint was applied to a woodfree paper by means of a bar coater so that the weight of solid component was 5 g/m^2 to give a color developing sheet.

Examples 7 to 9

The same procedure of Example 5 was repeated except that 30 parts of the color developer obtained in Example 2, 3 or 4 was used instead of 30 parts of the color developer obtained in Example 1 to give a color developing sheet.

Comparative Example 1

The same procedure of Example 1 was repeated except that the amount of the zinc salt of rosin-modified phenolic resin was changed from 50 parts to 1500 parts to give about 2500 parts of a color developer for comparison.

Next, the same procedure of Example 5 was repeated except that 30 parts of the above color developer for comparison was used instead of 30 parts of the color developer obtained in Example 1 to give a color developing sheet.

Comparative Example 2

The same procedure of Example 5 was repeated except that 30 parts of zinc 3,5-di-tertiallybutylsalicylate was used instead of 30 parts of the color developer obtained in Example 1 to give a color developing sheet.

Comparative Example 3

The same procedure of Example 5 was repeated except that 30 parts of zinc 3,5-di-(α-methylbenzyl)-salicylate was used instead of 30 parts of the color developer obtained in Example 1 to give a color developing sheet.

(Method for evaluating various properties)

(1) Initial color-forming percentage

An upper paper onto which microcapsule containing colorless dye was coated was superposed upon a color developing sheet, and they were pressed at a pressure of 30 Kg/cm^2 by means of a roll calender to develop color. After 1 minute passed, the reflectance was measured with a Hunter reflectometer, and coloring speed was estimated.

(Initial color-forming percentage)

$$= \frac{\text{(Reflectance before coloring)} - \text{(Reflectance after 1 minute passed)}}{\text{Reflectance before coloring}} \times 100\ (\%)$$

(2) Ultimate color forming percentage

After 24 hours passed from the coloring, reflectance was measured, and ultimate color-forming percentage was evaluated in accordance with the following equation.

(Ultimate color-forming percentage)

$$= \frac{\text{(Reflectance before coloring)} - \text{(Reflectance after 24 hours passed)}}{\text{Reflectance before coloring}} \times 100\ (\%)$$

(3) Waterproofness

(i) A color developing sheet was pressed by a roll calender to develop color. After 24 hours passed, the color developing sheet was dipped in water having a temperature of 25° C for 30 minutes and was air dried. Then, reflectance was measured with a whiteness meter, and waterproofness was evaluated in accordance with the following equation.

(Waterproofness)

$$= \frac{\text{(Reflectance before coloring)} - \text{(Reflectance after dipping)}}{\text{(Reflectance before coloring)} - \text{(Reflectance before dipping)}} \times 100\ (\%)$$

(ii) The color developing sheet was developed by a typewriter, and the color developing sheet was allowed to stand for 24 hours. The color developing sheet was dipped in water for 24 hours, and then was air dried. The degree of descloration was evaluated by naked eyes.

○ ····· Printed marks are clearly remained.
△ ····· Printed marks are faded but the marks can be read.
× ····· Prited marks are disappeared.

(4) Stability of dispersion

After the dispersion was allowed to stand for 24 hours, generation of water separation and precipitate was observed with naked eyes.

○ ····· Precipitate is not generated.

△ ..... Precipitate is generated but is dispersed.

× ..... Precipitate is not entirely dispersed.

The above-mentioned results of evaluation are shown in Table 1.

Table 1

Ex. No.	Kind of color developer	Properties of color developing sheet				Stability of dispersion
		Inital color-forming percentage (%)	Ultimate color-forming percentage (%)	Waterproofness		
				Method (i)	Method (ii)	
5	Ex. 1	75.4	93.3	81.3	○	△
6	Ex. 1	83.4	97.5	82.0	○	○
7	Ex. 2	76.4	93.4	81.7	○	△
8	Ex. 3	73.5	92.7	79.7	○	△
9	Ex. 4	72.8	91.6	84.6	○	△
Com.						
Ex. 1	-	53.4	72.4	84.2	○	△
2	-	68.3	95.9	76.8	×	△
3	-	69.6	96.8	78.7	×	△

INDUSTRIAL APPLICABILITY

When the color developer for pressure-sensitive recording medium of the present invention is used, an aqueous dispersion of the oolor developer improved in initial color-forming properties and waterproofness, which have been the defects of conventional color developers for pressure-sensitive recording medium of polyvalent metallic salt of salicylic acids, can be prepared. Since in the color developer for pressure-sensitive reoording medium of the present invention, inexpensive rosin-modified phenolic resin is used as a starting material, production cost is markedly decreased.

Claims

1. A color developer for pressure-sensitive recording medium characterized in that a polyvalent metallic salt of salicylic acids and a polyvalent metallic salt of rosin-modified phenolic resin are contained.

2. The color developer for pressure-sensitive recording medium of Claim 1, wherein the weight ratio of the polyvalent metallic salt of salicylic acids to the rosin-modified phenolic resin is 100 : 0.1 to 100 : 100.

3. The color developer for pressure-sensitive recording medium of Claim 1 or Claim 2, wherein said polyvalent metallic salt is a zinc salt.

4. An aqueous dispersion of a color developer containing the color developer of Claim 1.

5. A method for preparing the aqueous dispersion of Claim 4, characterized in that an amorphous oligomer and polyvinyl alcohol are used as a dispersing agent when the color developer is mechanically emulsified and dispersed in the presence of a dispersing agent and a solvent.

INTERNATIONAL SEARCH REPORT

International Application No PCT/JP89/00658

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl^4 B41M5/12

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	B41M5/12

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	JP, A, 59-174384 (Mitsubishi Paper Mills Ltd.) 2 October 1984 (02. 10. 84) (Family : none)	1 - 4
Y	JP, A, 51-68307 (Mitsubishi Paper Mills Ltd.) 12 June 1976 (12. 06. 76) (Family : none)	1 - 4
Y	JP, A, 58-122891 (Takahashi Ink Kagaku Kogyosho Kabushiki Kaisha) 21 July 1983 (21. 07. 83) (Family : none)	1 - 4
A	JP, A, 50-20807 (Kanzaki Paper Mfg. Co., Ltd.) 5 March 1975 (05. 03. 75) (Family : none)	5
A	JP, A, 56-139991 (Mitsubishi Paper Mills Ltd.) 31 October 1981 (31. 10. 81) (Family : none)	5

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search September 25, 1989 (25. 09. 89)	Date of Mailing of this International Search Report October 2, 1989 (02. 10. 89)
International Searching Authority Japanese Patent Office	Signature of Authorized Officer

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	JP, A, 63-176176 (Jujo Paper Co., Ltd.) 20 July 1988 (20. 07. 88) &EP, A, 275108 & US, A, 4833119	5

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [1]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers ...., because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers ...., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim numbers ...., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [2]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.
2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:
3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:
4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.