

# United States Patent [19]

Hayashi et al.

[11] 3,874,895

[45] Apr. 1, 1975

[54] RECORDING SHEET

3,427,180	2/1969	Phillips .....	117/36.8 X
3,664,858	5/1972	Huffman .....	117/36.8
3,689,302	9/1972	Kubo et al. ....	117/36.8
3,746,563	7/1973	Farber et al. ....	117/36.2

[75] Inventors: **Takao Hayashi; Hajime Kato**, both of Shizuoka, Japan

[73] Assignee: **Fuji Photo Film Co., Ltd.**, Kanagawa, Japan

[22] Filed: **Oct. 30, 1972**

[21] Appl. No.: **301,931**

*Primary Examiner*—Thomas J. Herbert, Jr.

*Attorney, Agent, or Firm*—Sughrue, Rothwell, Mion, Zinn & Macpeak

## [30] Foreign Application Priority Data

Nov. 1, 1971 Japan..... 46-86950

[52] U.S. Cl..... 117/36.8, 117/36.9

[51] Int. Cl. .... B41M 5/00

[58] Field of Search..... 117/36.8, 36.2, 36.9

## [56] References Cited

### UNITED STATES PATENTS

3,418,250 12/1968 Vassiliades..... 117/36.2

## [57] ABSTRACT

A recording sheet comprising a support having thereon a color developer layer capable of reacting with a color former to form a color image, which color developer layer comprises (1) an acidic polymer and (2) an organic carboxylic acid or a metal salt thereof.

14 Claims, No Drawings

## RECORDING SHEET

## FIELD OF THE INVENTION

The present invention relates to a recording sheet. More particularly, it relates to a recording sheet wherein an improved color developer is used.

## DESCRIPTION OF THE PRIOR ART

Recording sheets are well known wherein a coloring reaction between two types of compounds are described below is used to yield a colored product, i.e., reaction between: (1) a nearly colorless organic compound (hereinafter referred to as a color former), e.g., Malachite Green lactone, benzoylleucomethylene blue, Crystal Violet lactone, Rhodamine B lactam, 3-dialkylamino-7-dialkylaminofluoran and 3-methyl-2,2'-spiro-bi(benzof[f]chromene), and (2) an adsorptive or reactive compound (hereinafter referred to as a color developer) capable of developing color when contacted with the color former.

As recording sheets utilizing this phenomenon, there are pressure sensitive copying papers (for example, see U.S. Pat. Nos. 2,505,470; 2,505,489; 2,550,471; 2,548,366; 2,712,507; 2,730,456; 2,730,457; 3,418,250; etc.), heat sensitive recording papers (for example, see Japanese Pat. Publication No. 4160/68, U.S. Pat. No. 2,939,009, etc.), and the like. In addition, there is known a printing method wherein an ink containing a color former is supplied to a color developer-coating sheet through a stencil or like medium to thereby obtain colored images (see German Patent OLS No. 1,939,624, etc.).

In many cases, the above-described color reaction requires pressure with a pen or typewriter, heat or like physical conditions.

A pressure sensitive copying paper is the most representative embodiment of a recording sheet. A pressure sensitive copying paper can be prepared by dissolving a color former in chlorinated paraffin, chlorinated diphenyl or like solvents, dispersing the solution in a binder or encapsulating it in microcapsules, and then applying it to a support such as paper, plastic, resin-coated paper, etc.

A heat sensitive recording paper can be prepared by applying a color former to a support together with an acetanilide or like heat-meltable material. In this case, the heat-meltable material is one that will be melted by heat to dissolve the color former.

A color developer is usually dissolved or dispersed in water or an organic solvent together with a binder and coated on or impregnated in a support. The color developer may also be coated or impregnated immediately before recording in a manner similar to an ink.

In general, the color former and color developer may be applied to the same or opposite surfaces of a support, or to different supports.

As examples of such color developers, there are generally used clays such as acid clays, active clays, attapulgite, zeolite, bentonite, etc.; organic acids such as succinic acid, tannic acid, phenol compounds, etc.; phenol resins or like acidic polymers; etc. Phenol resins are rather recent color developers, (Japanese Patent Publication No. 20144/67) though many improvements thereof have been suggested (U.S. Pat. Nos. 3,516,845; 3,540,911; British Pat. No. 1,065,587).

A phenol resin is excellent in that when it is reacted with a color former there are formed colored images

stable against water. However, phenol resins do not have a sufficient color-developing ability, and the light resistance of the developed color images is weak. For example, the colored images obtained from a phenol resin and Crystal Violet lactone easily fade when left in a room or exposed to sunlight and, further, the surface of phenol resin which has not participated in the color formation turns yellow.

Other acidic polymers, for example, maleic acid-rosin resins or partly or completely hydrolyzed styrene-maleic anhydride copolymers and the like are also essentially too low in color-developing ability to be used practically.

## SUMMARY OF THE INVENTION

A primary object of the invention is to improve the color-developing ability of acidic polymers.

Another object of the invention is to prevent the yellowing of acidic polymer which has not participated in the color forming reaction.

A further object of the invention is to provide an acidic polymer capable of forming colored images of excellent light resistance.

Still a further object of the invention is to provide a color developer having the above-described advantages.

Yet another object of the invention is to provide a recording sheet having the above-described advantages.

The above-stated objects of the present invention are attained by using a color developer containing, as necessary constituents, an acidic polymer and an organic carboxylic acid or a metal salt thereof.

## DETAILED DESCRIPTION OF THE INVENTION

The recording sheet of the present invention can comprise a support and a layer coated thereon containing an acidic polymer and an organic carboxylic acid or a metal salt thereof. Therefore, any form of recording sheet structure known in the art can be employed. For instance, the color developer and color former can be provided on the same or opposite sides of a support, or on the surfaces of different supports. In addition, it is also possible to store the developer in a form of ink and, when needed, coat or print it on a support.

The organic carboxylic acids used in the invention include organic compounds having at least one carboxyl group, and include aliphatic carboxylic acids and aromatic carboxylic acids. Most preferred of such acids are those having a maximum of three carboxyl groups and from about 5 to about 20 carbon atoms.

The inventors have found, as a result of the investigating of organic carboxylic acids in combination with acidic polymers that all of the compounds within the above class are excellent in color-developing ability, fading-resistance, yellowing-resistance, and the like.

However, aromatic carboxylic acids are especially preferred as they provide excellent effects and, in particular, aromatic carboxylic acids having at least one hydroxy group are preferred with those having from one to three hydroxyl groups being most preferred. Of course, any organic carboxylic acid exhibits an improved effect as compared to the use of an acidic polymer alone, and aliphatic carboxylic acids or metal salts thereof, in particular, the monobasic acids and dibasic acids thereof are excellent from the viewpoint of film quality. Monobasic acids are most preferred, however. The aromatic carboxylic acid is preferably from the

benzene series, especially salicylic acid derivatives, which preferably have at least one alkyl group having more than 3 carbon atoms, or at least one aryl group, or a cyclohexyl group, or is substituted with a combination of such groups.

The same basic preference as described above applies to the metal salts of organic carboxylic acids, i.e., the metal salts of aromatic carboxylic acids are especially preferred from the viewpoint of color-developing ability, light resistance of the developed color images and resistance to yellowing.

As the specific examples of organic carboxylic acids used in the present invention, there are formic acid, acetic acid, caproic acid, heptanoic acid, caprylic acid, pelargonic acid, capric acid, n-undecylenic acid, lauric acid, n-dodecylenic acid, myristylenic acid, n-pentadecylenic acid, margaric acid, stearic acid, n-nonadecylenic acid, arachidic acid, heneicosanoic acid, behenic acid, n-tricosanoic acid, lignoceric acid, n-pentacosanoic acid, cerotic acid, n-heptacosanoic acid, montanic acid, n-nonacosanoic acid, melissic acid, n-hentriaccontanoic acid, n-dotriaccontanoic acid, n-tetraaccontanoic acid, ceroplastic acid, n-hexatetraaccontanoic acid, n-octatriaccontanoic acid, n-hexatetraaccontanoic acid, oleic acid, linolenic acid, linoleic acid, stearolic acid, alpha-chlorolauric acid, alpha-chlorostearic acid, alpha-bromomyristic acid, 1,8-octanedicarboxylic acid, 1,12-dodecanedicarboxylic acid, 2,4-decanedienoic acid, 2-hydroxy-2,4-dimethylpentanoic acid, o-toluic acid, m-toluic acid, p-toluic acid, benzoic acid, o-chlorobenzoic acid, m-chlorobenzoic acid, p-chlorobenzoic acid, o-bromobenzoic acid, p-nitrobenzoic acid, salicylic acid, o-chlorosalicylic acid, m-hydroxysalicylic acid, p-hydroxysalicylic acid, anisic acid, gallic acid, phthalic acid, trimellitic acid, diphenic acid, phenylacetic acid, alpha-phenyl-n-valerianic acid, p-isopropylbenzoic acid, 2,4-cresotinic acid, 5-methylsalicylic acid, 5-tert-butylsalicylic acid, 3,5-di-sec-butylsalicylic acid, 3,5-di-sec-butylsalicylic acid, 3-methyl-5-tert-butylsalicylic acid, 3,5-di-tert-butylsalicylic acid, 5-isoamylsalicylic acid, 3-phenylsalicylic acid, 5-cyclohexylsalicylic acid, and the like.

Metals forming a metal salt with the organic carboxylic acids include sodium, lithium, potassium, magnesium, calcium, zinc, cadmium, aluminum, tin, lead, chromium, manganese, cobalt, nickel, and the like. There is no overly critical aspect to the selection of the exact metal used, i.e., substantially all metal salts are useful.

It should be specifically noted that, if desired, mixtures of various organic carboxylic acids, metal salts thereof and acidic polymers may be used in the present invention. For instance for certain applications one might wish to utilize two or more organic carboxylic acids with two or more types of metal salts to obtain a certain effect. On the other hand, one might wish to use a blend of different types of acidic polymers. All such embodiments are included within the present invention.

The process of producing the recording sheet of the invention is not particularly limited so long as the acidic polymer and the layer containing organic carboxylic acid or the metal salt thereof are present on a support or on a layer provided on a support (hereinafter, both are referred to as "support") as described hereinbefore.

The term acidic polymer in this invention includes all polymers having an acid property, i.e., a polymer which can denate, or emit, an H proton, with preferred polymers being reactive acidic polymers such as phenolic polymers.

Typical examples of such phenolic polymers are phenolaldehyde polymers and phenol-acetylene polymers. In the present invention, phenolic polymers and salicylic acid-formaldehyde polymers are most preferred, both polymers preferably having a polymerization degree of from 2 to about 15. Examples of other acidic polymers especially useful in the present invention are malic acid-rosin resins, partially or completely hydrolyzed styrene-maleic anhydride copolymers, partially or completely hydrolyzed ethylenemalic anhydride copolymers, and partially or completely hydrolyzed vinylmethylether-maleic anhydride copolymers. These polymers are inferior to phenol polymers and salicylic acid formaldehyde polymers, however.

Both solid and liquid acidic polymers may of course, be used in the present invention.

Some embodiments of processes for the production of such a sheet are illustrated below:

1. A binder is dissolved in water and, after adding thereto an acidic polymer and at least one organic carboxylic acid or a metal salt thereof, the mixture is subjected to ball milling. If necessary, further binder is added thereto. The resulting coating solution is applied to support.

2. The acidic polymer, a binder and the organic carboxylic acid or metal salt thereof are dispersed or dissolved in an organic solvent such as ethanol, methanol, acetone, methyl ethyl ketone, benzene, etc. When the acid polymer, the binder and organic carboxylic acid or the metal salt thereof are not dissolved but are dispersed, it is preferred to subject the dispersion to ball milling, or to previously pulverize solid components to less than 10 microns in size. The coating solution thus obtained is applied to a support such as paper, a paper substitute, a film, etc.

3. A binder is dissolved in water, and acidic polymer is added thereto, whereafter the grain size is adjusted to the desired value by ball milling and the coating solution applied to a support. At least one or more organic carboxylic acids and/or metal salts thereof are dissolved in an organic solvent such as methanol, ethanol, acetone, benzene, etc., and applied to the above-described coated layer.

50 The amount of components such as the acidic polymer and binder used in the production of the recording sheet of the invention are in accordance with the standard amounts as are used in the prior art and can be determined with ease by those skilled in the art. The amount of the organic carboxylic acid or the metal salt thereof is more than about 0.05 parts by weight, preferably, about 0.1 to about 2 parts by weight per 1 part by weight of acidic polymer. Since the upper limit thereof is decided only by economic factors, the effects of the present invention are obviously not lost outside the range defined above.

55 The binder used is not particularly limited so long as it is usable in a recording sheet. Specific examples are synthetic materials such as styrene-butadiene latex, polyvinyl alcohol, maleic anhydride-styrene copolymer, etc., and natural materials such as casein, gum arabic, gelatin, etc. The amount thereof used is usually

more than about 0.05 parts by weight, preferably about 0.1 to about 0.2 parts by weight, per 1 part by weight of the acid polymer. The kind of the binder and the amount thereof added have no special influence on the effects of the invention.

Furthermore, in the above-described coated layer there can be incorporated a standard color-developer such as an acid clay (produced in Japan and having properties similar to attapulgite) an active clay, etc. in order to increase the color-developing ability, and/or inorganic pigments in order to increase the adsorptive property of the layer. The clay or inorganic pigment is added to increase the adsorptive property of the color-developer layer. As the amount of such a substance is increased, the adsorptive property is increased.

Other additives such as a wetting agents or a deforming agents standard in this art may also be added in a manner known to the art.

The amount of the above-described color developer coated is more than about 0.1 g, preferably about 0.3 to about 3 g per 1 m<sup>2</sup> of coated areas. This amount is the total solid content of acidic polymer in the coating composition. Of course, the effects thereof are not lost when coated in a greater amount. In the above production process 3, where the organic carboxylic acid or the metal salt thereof is coated, an amount of solution greater than 0.1 g/m<sup>2</sup>,\* preferably about 0.3 to about 1 g/m<sup>2</sup> is preferred.

\* based on acid present

The acidic polymer used as one component of the color developer of the invention can be any such polymer described in the aforesaid literature, such as phenol-aldehyde polymers, phenol-acetylene polymers, maleic acid-rosin polymers, partly or wholly hydrolyzed styrene-maleic anhydride polymers, ethylene-maleic anhydride copolymers, etc.

As will be clear from the following Examples, the recording sheet of the invention has a number of merits. These are enumerated below.

#### 1. Improvement in color-developing ability

The color-developing ability of the recording sheet of the invention is so improved that the amount of the color developer or the amount of the color former on a color former sheet can be reduced and still provide the same developed color density. That is, a reduction in the production cost of the recording sheet is achieved.

#### 2. Improvement in the light resistance of the developed color image

The degree of the fading of the developed color image is extremely small when irradiated with sunlight or left in a room. Therefore, even when used in combination with an usual color former comprising a mixture of Crystal Violet lactone and benzoylleucomethylene blue, the color changes quite little since Crystal Violet lactone is markedly difficult to fade, so that the commercial value of the sheet is remarkably improved.

#### 3. Improvement in resistance to yellowing

The greatest defect of the phenol resin, that it is easily yellowed when irradiated with sunlight or left in a room, is largely obviated.

#### 4. Improvement in film surface strength and film quality

By using an organic carboxylic acid or a metal salt thereof the amount of a binder necessary to obtain the same film surface strength can be reduced and, in addition, the film quality is higher, i.e., it is smooth and re-

sistance to abrasion and printability etc., are markedly improved. As a result, the commercial value thereof is further improved.

In the present invention, various conditions other than the aforesaid ones, i.e., additives to the color developer, kind of color former, kind of solvent, and the like can be selected with ease in accordance with the skill of the art.

The recording sheet of the invention will now be described in detail by reference to several Examples; the effects in the Examples were confirmed using the combination of an upper paper and a lower paper, the upper paper being prepared by producing microcapsules containing a color former as described below and applying them to the support, and the lower paper being prepared by applying the color developer in accordance with the invention to a support. Hereinafter, "parts" are all by weight.

Microcapsules containing color former can be prepared in a variety of known processes, but herein the microcapsules were prepared according to the specification of U.S. Pat. No. 2,800,457:

10 parts of acid-processed pigskin gelatin and 10 parts of gum arabic are dissolved in 400 parts of 40°C water, 0.2 part of Turkey red oil is added thereto as an emulsifier, and 40 parts of a color former oil is emulsified and dispersed therein, said color former oil being prepared by dissolving 2% by weight of Crystal Violet lactone or 3-N,N-diethylamino-6,8-dimethyl-fluoran in an oil comprising 4 parts of chlorinated diphenyl and 1 part of lamp oil.

When the oil droplets reach an average size of 5 microns the emulsification is discontinued. To this system is added 40°C water to make the total 900 parts, and stirring is continued. Subsequently, the pH of the solution is adjusted to 4.0 – 4.2 by the addition of 10% acetic acid to cause coacervation. Continuing the stirring for a further 20 minutes, the solution is then cooled with ice water to cause gelation of the coacervate film deposited around the oil droplets. When the temperature of the solution reaches 20°C, 7 parts of 37% formaldehyde is added, and, at 10°C, 15% sodium hydroxide is added thereto. Subsequently, the solution is heated for 20 minutes with stirring to raise the temperature of the solution to 50°C.

After adjusting the temperature to 30°C, the microcapsules thus obtained are applied to a 40 g/m<sup>2</sup> paper in an amount of 6 g/m<sup>2</sup> (solid components) and dried.

Microcapsule-coated sheet containing other color formers can be also prepared in the same manner as described above.

#### EXAMPLE 1

55 170 Parts of p-phenylphenol, 70 parts of an aqueous 37% formaldehyde solution, 10 ml of concentrated (37%) hydrochloric acid and 50 parts of water were charged in a reactor for the production of resin, and reaction was effected at 140°C for 10 hours. Upon cooling, there was obtained phenol resin powder of phenol resins having a polymerization degree of 2~6.

50 Parts of the phenol resin obtained by the above-described process, 10 parts of the sodium salt of styrene-maleic anhydride copolymer, 500 ml of water and 20 parts of an organic carboxylic acid a metal salt thereof as shown in Table I were charged into a ball mill and subjected to ball milling for 10 hours to prepare a coating solution. The resulting coating solution

was applied to a 50 g/m<sup>2</sup> paper in an amount of 3 g/m<sup>2</sup> (solid components) and dried to prepare a recording sheet (lower paper) of the invention.

For comparison, 70 parts of the above-described phenol resin, 10 parts of the sodium salt of the styrene-maleic anhydride copolymer and 500 ml of water were subjected to ball milling for 10 hours to prepare a coating solution, which was then applied to a 50 g/m<sup>2</sup> paper in an amount of 3 g/m<sup>2</sup> (solid components) and then dried to prepare a comparative recording sheet.

With respect to the resulting two recording sheets,

density. The spectral absorption curve of the developed color images was measured after irradiating the sheets with sunlight for 2 hours, and the density at the absorption maximum (at a wavelength of 525 m $\mu$ ) was determined.

3. After leaving each of the recording sheets (these were not contacted with the capsule sheet) for 1 month in a room, the whiteness of the surface thereof was measured by means of a Hunter whiteness meter. A higher value shows that yellowing of the sheet is more difficult. The results obtained are shown in Table 1.

Table 1

No.	Kind	Organic carboxylic acid or the metal salt thereof	Crystal Violet lactone		3-N,N-diethyl-amino-6,8-dimethyl-fluororan		Yellowing property
			Color-developing ability*	Light resistance (%)	Color-developing ability	Light resistance (%)	
1.	Comparison	—	0.820	48.3	0.661	48.6	44.5
2.	Present invention	Caprylic acid	0.853	54.4	0.702	55.0	48.4
3.	"	Sodium oleate	0.856	55.6	0.707	56.2	49.8
4.	"	Zinc stearate	0.860	58.3	0.736	59.3	51.6
5.	"	Zinc salicylate	0.910	66.7	0.803	67.5	55.3
6.	"	Tin salicylate	0.912	60.5	0.805	60.9	49.2
7.	"	Aluminum salicylate	0.894	61.4	0.710	61.8	52.4
8.	"	5-Methyl-salicylic acid	0.871	60.1	0.784	60.7	50.7

\*ability to convert color former into a color dye

the following comparison tests (1), (2) and (3) were carried out.

1. A microcapsule-coated paper containing Crystal Violet lactone was superposed on each of the recording sheets, and a load of 600 kg/cm<sup>2</sup> was applied thereto to develop color. After placing the developed sheets for 1 hour in the dark, the spectral absorption curve of the images was measured between the wavelengths of 400 to 700 m $\mu$ . The density at the absorption maximum (at a wavelength of 610 m $\mu$ ) was regarded as the fresh density.

The spectral absorption curve of the developed color image was then measured after irradiating the sheets with sunlight for 2 hours, and the density at the absorption maximum (at a wavelength of 610 m $\mu$ ) was determined. The light resistance value was determined according to the following formula:

$$\text{Light resistance value} (\%) = \frac{\text{Density at absorption maximum after irradiation with light}}{\text{Fresh density at absorption maximum}} \times 100$$

The spectral absorption curve was measured by means of a DB-type Beckman spectrophotometer made by Tokyo Shibaura Electric Co., Ltd.

2. A microcapsule-coated paper containing 3-N,N-diethylamino-6,8-dimethylfluororan prepared as heretofore described was superposed on each of the recording sheets, and a load of 600 kg/cm<sup>2</sup> was applied thereto to develop color. After storing the developed sheets for 1 hour in the dark, the spectral absorption curve of the images was measured between the wavelengths of 400 to 700 m $\mu$ . The density at the absorption maximum (at a wavelength of 525 m $\mu$ ) was regarded as the fresh

35

## EXAMPLE 2

194 Parts of p-tert-butylphenol, 65 parts of an aqueous 37% formaldehyde solution, 10 ml of concentrated (37%) hydrochloric acid, 1 part of oxalic acid and 50 parts of water were charged in a reactor for the production of resin, and polymerization was conducted at 160°C for 12 hours. After cooling, there was obtained a phenol resin powder.

50 Parts of the phenol resin described above, 20 parts of gum arabic, 500 ml of water and 30 parts of the organic carboxylic acid or a metal salt thereof, as shown in Table 2, were charged into a ball mill and subjected to ball milling for 15 hours to prepare a coating solution. The resulting coating solution was applied to a 50 g/m<sup>2</sup> paper in an amount of 3 g/m<sup>2</sup> (solid components)

50

and then dried to prepare a recording sheet of the present invention.

For comparison, 70 parts of the above-described phenol resin, 20 parts of gum arabic and 500 ml of water were subjected to ball milling for 15 hours to prepare a coating solution, which was then applied to a 50 g/m<sup>2</sup> paper in an amount of 3 g/m<sup>2</sup> (solid components) and then dried to prepare a comparative recording sheet.

65 Each of the resulting sheets were compared with each other in the same manner as in Example 1. The results obtained are given in Table 2.

Table 2

No.	Kind	Organic carboxylic acid or the metal salt thereof	Crystal Violet lactone		3-N,N-diethyl-amino-6,8-dimethyl-fluoran		Yellowing property
			Color-developing ability	Light resistance (%)	Color-developing ability	Light resistance (%)	
9.	Comparison	—	0.714	30.5	0.570	31.3	63.3
10.	Present invention	Lauric acid	0.741	36.4	0.616	38.1	67.1
11.	"	Dodecane-1,12-di-carboxylic acid	0.732	37.6	0.603	38.8	66.6
12.	"	o-Chloro-salicylic acid	0.825	59.7	0.700	60.3	67.0
13.	"	Zinc o-chloro-salicylate	0.846	61.1	0.713	62.5	68.8
14.	"	Zinc stearate	0.753	39.9	0.614	40.4	67.5
15.	"	Benzoic acid	0.774	40.2	0.622	41.2	65.2
16.	"	p-Chloro-benzoic acid	0.797	41.3	0.635	42.4	65.0

## EXAMPLE 3

170 Parts of p-phenylphenol, 70 parts of an aqueous 37% formaldehyde solution, 10 ml of concentrated (37%) hydrochloric acid and 50 parts of water were charged in a reactor for the production of resin, and polymerization was conducted at 160°C for 10 hours. Upon cooling, there was obtained a phenol resin powder.

50 Parts of the above-described phenol resin, 10 parts of polyvinyl alcohol 205 (made by Kurashiki

60 of coating solution A and 80 parts of coating solution B were admixed and applied to a 50 g/m<sup>2</sup> paper in an amount of 2 g/m<sup>2</sup> (solid components) and then dried to prepare a recording sheet II of the invention.

On the other hand, for purposes of comparison, coating solution A was applied to a 50 g/m<sup>2</sup> paper in an amount of 2 g/m<sup>2</sup> (solid components) and then dried to prepare a comparative recording sheet.

Each of the resulting recording sheets was compared with each other in the same manner as in Example 1. The results obtained are given in Table 3.

Table 3

No.	Kind	Organic carboxylic acid or the metal salt thereof	Crystal Violet lactone		3-N,N-diethyl-amino-6,8-dimethyl-		Yellowing property
			Color-developing property	Light resistance (%)	Color-developing ability	Light resistance (%)	
17.	Comparison	—	0.811	47.9	0.657	47.5	44.5
18.	Present invention I	3,5-Di-tert-butyl-salicylic acid zinc salt	0.925	65.5	0.816	66.7	54.2
19.	Present invention II	"	0.942	73.7	0.823	71.3	58.7

Rayon Co., Ltd.) and 500 parts of water were charged into a ball mill and subjected to a ball milling for 10 hours to thereby obtain coating solution A.

4 Parts of sodium hydroxide was dissolved in 200 parts of water, and 25 parts of 3,5-di-tert-butylsalicylic acid was added thereto while stirring. Further continuing the stirring, a solution prepared by dissolving 7 parts of zinc chloride in 100 parts of water was gradually added thereto. To this was added 50 parts of 10% polyvinyl alcohol 205 (made by Kurashiki Rayon Co., Ltd.), and the resulting solution was subjected to ball milling for 10 hours to thereby obtain coating solution B.

60 Parts of coating solution A and 40 parts of coating solution B were admixed and applied to a 50 g/m<sup>2</sup> paper in an amount of 2 g/m<sup>2</sup> (solid components) and then dried to obtain a recording sheet I of the invention.

55 128.5 Parts of p-chlorophenol, 70 parts of an aqueous 37% formaldehyde solution, 5 ml of concentrated (37%) hydrochloric acid, 2 parts of oxalic anhydride and 50 parts of water were charged in a reactor for the production of resin, and polymerization was conducted at 140°C for 10 hours. Upon cooling, there was obtained a phenol resin powder.

60 50 Parts of the above-described phenol resin, 10 parts of polyvinyl alcohol 205 (made by Kurashiki Rayon Co., Ltd.) and 500 parts of water were charged into a ball mill and subjected to ball milling for 10 hours to obtain coating solution C.

4 Parts of sodium hydroxide was dissolved in 200 parts of water and, with stirring, 21.8 parts of

## EXAMPLE 4

3-cyclohexylsalicylic acid was dissolved therein. Further continuing the stirring, a solution prepared by dissolving 7 parts of zinc chloride in 100 parts of water was gradually added thereto. To this was added 50 parts of 10% polyvinyl alcohol 205 (made by Kurashiki Rayon Co., Ltd.), and the resulting solution was subjected to ball milling for 10 hours to obtain coating solution D.

60 Parts of coating solution O and 40 parts of coating solution D were admixed and applied to a 50 g/m<sup>2</sup> paper in an amount of 2 g/m<sup>2</sup> (solid components) and then dried to obtain recording sheet III of the invention.

60 Parts of coating solution C and 80 parts of coating solution D were admixed and applied to a 50 g/m<sup>2</sup> paper in an amount of 2 g/m<sup>2</sup> (solid components) and dried to obtain recording sheet IV of the invention.

For comparison, coating solution C was applied to a 50 g/m<sup>2</sup> paper in an amount of 2 g/m<sup>2</sup> (solid components) to prepare a comparative recording sheet.

Each of the resulting sheets was compared with each other in the same manner as in Example 1. The results obtained are given in Table 4.

Table 4

No.	Kind	Organic carboxylic acid or the metal salt thereof	Crystal Violet lactone		3-N,N-diethyl-amino-6,8-dimethyl-fluoran		Yellowing property
			Color-developing ability	Light resistance (%)	Color-developing ability	Light resistance (%)	
20.	Comparison	—	0.811	47.9	0.657	47.5	44.5
21.	Present invention	Zinc 3-cyclohexylsalicylate	0.925	65.6	0.816	66.7	54.2
22.	IV	"	0.942	73.7	0.823	71.3	58.7

Table 5

No.	Kind	Organic carboxylic acid or the metal salt thereof	Crystal Violet lactone		3-N,N-diethyl-amino-6,8-dimethyl-fluoran		Yellowing property
			Color-developing ability	Light resistance (%)	Color-developing ability	Light resistance (%)	
24.	Comparison	—	0.410	32.3	0.337	27.2	75.3
25.	Present invention	5-Tert-butylsalicylic acid	0.750	61.6	0.665	58.1	75.9
26.	VI	"	0.826	67.5	0.724	63.3	76.1

## EXAMPLE 5

4 Parts of sodium hydroxide was dissolved in 200 parts of water, and 19.4 parts of 5-tert-butylsalicylic acid was added thereto while stirring. Continuing the stirring, a solution prepared by dissolving 7 parts of zinc chloride in 100 parts of water was gradually added thereto. The white precipitate formed was filtrated out and washed several times with water. After drying, there was obtained a white powder of zinc 5-tert-butylsalicylate.

20 Parts of partly hydrolyzed ethylene-maleic anhydride copolymer, 5 parts of ethyl cellulose and 5 parts of the abovedescribed white powder were added to 300

55 As is apparent from Tables 1 – 5, the color developer and the recording sheet of the present invention are excellent in color-developing ability, light resistance of the developed color images and the resistance to yellowing.

60 While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

65 What is claimed is:

1. A recording sheet comprising a support having thereon a color developer layer capable of reacting with a color former to form a color image, which color

ml of ethyl alcohol and subjected to ball milling for 15 hours. The resulting coating solution was applied to a 50 g/m<sup>2</sup> paper in an amount of 2 g/m<sup>2</sup> (solid components) and then dried to prepare recording sheet V of the invention.

20 Parts of partly hydrolyzed ethylene-maleic anhydride copolymer, 6 parts of ethyl cellulose and 10 parts of the abovedescribed white powder were added to 360 ml of ethyl alcohol and subjected to ball milling for 15 hours. The resulting coating solution was applied to a 50 g/m<sup>2</sup> paper in an amount of 2 g/m<sup>2</sup> (solid components) and then dried to prepare recording sheet VI of the invention.

For comparison, 20 parts of partly hydrolyzed ethylenemaleic anhydride copolymer and 4 parts of ethyl cellulose were added to 240 ml of ethanol and subjected to ball milling for 15 hours. The resulting coating solution was applied to a 50 g/m<sup>2</sup> paper in an amount of 2 g/m<sup>2</sup> (solid components) to prepare a 20 comparative recording sheet.

Each of the resulting recording sheets was compared with each other in the same manner as in Example 1. The results obtained are given in Table 5.

developer layer comprises (1) an acidic polymer, (2) an organic aromatic carboxylic acid having 1 to 3 carboxylic groups and having 1 to 3 hydroxyl groups or a metal salt thereof, and (3) a binder.

2. The recording sheet of claim 1 where the acid comprises the benzene ring.

3. The recording sheet of claim 1 where the acid is substituted with one or more members from the group consisting of an alkyl group having more than three carbon atoms, an aryl group or a cyclohexyl group.

4. The recording sheet of claim 1 where the acid polymer is a phenolic polymer.

5. The recording sheet of claim 4 where the phenolic polymer is selected from the group consisting of phenol aldehyde polymers and phenol acetylene polymers.

6. The recording sheet of claim 5 where the polymers have a polymerization degree of from about 2 to about 15.

7. The recording sheet of claim 1 where the acid polymer is a salicylic acid formaldehyde polymer.

8. The recording sheet of claim 1 wherein from about 0.05 to about 2 parts by weight of the organic carboxylic acid or metal salt thereof is present per 1 part by weight of the acidic polymer.

9. The recording sheet of claim 8 where from about 0.05 to about 0.2 parts by weight of the binder is present per 1 part by weight of the acid polymer.

10. The recording sheet of claim 9 wherein the layer is coated on the support in an amount of about 0.1 g to 3 g per 1 m<sup>2</sup> of coated area, based on acidic polymer content.

11. The recording sheet of claim 1 further comprising an organic resin binder wherein the acidic polymer is a phenolic polymer or a salicylic acid-formaldehyde copolymer having a polymerization degree of from about 2 to about 15, further wherein:

the acid or metal salt thereof is present in an amount of from about 0.1 to about 2 parts by weight per part by weight of the acidic polymer;

the binder is present in an amount of from about 0.1 to about 0.2 parts by weight per part by weight of the acidic polymer; and

the layer is coated in an amount of from about 0.3 to about 3 g per m<sup>2</sup> of coated area, based on the acidic polymer.

12. In a process for forming a color image by the reaction of color former and a color developer comprising an acidic polymer, the improvement wherein the color developer and color former are reacted in the presence of an organic aromatic carboxylic acid having 1 to 3 carboxylic acid groups and having 1 to 3 hydroxyl groups or a metal salt thereof.

13. A recording sheet comprising a support having thereon a color developer layer capable of reacting with a color former to form a color image, which color developer layer comprises (1) an acidic polymer capable of donating or emitting a hydrogen proton, (2) an organic aromatic carboxylic acid having 1 to 3 carboxylic acid groups and having 1 to 3 hydroxyl groups or a metal salt thereof, and (3) a binder.

14. A recording sheet comprising a support having thereon a color developer layer capable of reacting with a color former to form a color image, which color developer layer comprises (1) an acidic polymer selected from the group consisting of phenol-aldehyde polymers, phenol-acetylene polymers, salicylic acid-formaldehyde polymers, malic acid-rosin resins, partially or completely hydrolyzed styrene-maleic anhydride copolymers, partially or completely hydrolyzed ethylenemaleic anhydride copolymers and partially or completely hydrolyzed vinylmethylether-maleic anhydride copolymers, and (2) organic aromatic carboxylic acid selected from the group consisting of salicylic acid, o-chlorosalicylic acid, m-hydroxysalicylic acid, p-hydroxysalicylic acid, gallic acid, 2,4-cresotinic acid, 5-methylsalicylic acid, 5-tert-butylsalicylic acid, 3,5-di-sec-butylsalicylic acid, 3,5-di-sec-butylsalicylic acid, 3-methyl-5-tert-butylsalicylic acid, 3,5-di-tert-butylsalicylic acid, 5-isomethylsalicylic acid, 3-phenylsalicylic acid, 5-cyclohexylsalicylic acid or a metal salt thereof and (3) a binder, the acid or metal salt being present in an amount of from about 0.1 to about 2 parts by weight per part by weight of the acidic polymer, the binder being present in an amount of from about 0.1 to about 0.2 parts by weight per part by weight of the acidic polymer, and the developer layer being coated on the support in an amount of from about 0.3 to about 3 g per m<sup>2</sup> of coated area, based on the acidic polymer.

\* \* \* \* \*