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(54) **COLOR-DEVELOPING SHEET FOR PRESSURE-SENSITIVE RECORDING.**

(57) A color-developing sheet for pressure-sensitive recording, which contains in a color-developing layer (i) semi-synthetic solid acid prepared by acid-treating a clay mineral having a laminar structure composed of regular tetrahedrons of silica so that the SiO_2 content based on dry weight (drying for 3 hr at 105°C) is 82 to 96.5 wt %, bringing the resulting clay mineral in an aqueous medium into contact with a magnesium and·or aluminum compound at least partly soluble in the medium and, when the soluble compound is other than a hydroxide, neutralizing with alkali or acid to thereby introduce a magnesium and/or aluminum ingredient and, if necessary, drying the clay mineral, (ii) a phenol compound, and (iii) a zinc compound.

EP 0 111 564 A1

COLOR-DEVELOPING SHEET FOR PRESSURE-SENSITIVE RECORDING

TECHNICAL FIELD

This invention relates to a color-developing sheet having a novel constitution for pressure-sensitive recording.

BACKGROUND ART

The pressure-sensitive recording material comprises usually a color-forming sheet having an electron-donative leuco dye on the surface and a color-developing sheet having a color developer, which is electron attractive, on the surface. In this recording material, a color-forming reaction based on electron transfer is utilized for recording by bringing both the surfaces into contact with each other and applying printing pressure thereto.

Accordingly, the color developer is one of the principal components of this recording material and various color developers have hitherto been proposed. For example, there have been proposed activated clay, which is obtained by treating a natural clay mineral with acid to a slight or medium extent, phenol compounds, phenolic resins of novolak type, and metal salts of aromatic carboxylic acids.

Activated clay first mentioned, which is the oldest of the above color developers, is insufficient in an essential property, i.e. the color developing ability.

Hence, there are cases where activated clay has been replaced with some of the above-mentioned organic color developers.

On the other hand, a novel color developer has been proposed recently which is prepared by a semi-synthetic process (Japanese Patent Application Kokai No. 15996/82).

It is a color developer for use in pressure-sensitive recording materials which is prepared in the following way: A clay mineral having a layer structure build up of regular tetrahedrons of silica is treated with an acid so as to give a silica content of 82 - 96.5% by weight on a dry basis (dried at 105°C for 3 hours); a magnesium component and/or aluminum component is introduced into the acid-treated clay mineral by bringing it, in an aqueous medium, into contact with a magnesium compound and/or aluminum compound soluble at least partially in the medium and if this soluble compound is other than the hydroxide, by neutralizing it with alkali or acid to form the hydroxide; and if desired, the resulting clay mineral is dried (hereinafter this color developer is referred to as "semi-synthetic solid acid"). This technique has brought about an improvement in the color-developing ability for electron-donative leuco dyes, long lasting of the color-developing effect under high humidity conditions, and less decay with time of the formed color density. Thus, the semi-synthetic solid acid can be regarded as a new type of color developer capable of offsetting sufficiently drawbacks of conventional activated clays and expected to be comparable or superior in the color developing ability to organic color developers.

The present inventors evaluated by various tests the aptitude of the semi-synthetic solid acid, which is a new type of inorganic color developer prepared in the above process, for use in the color-developing layer for pressure-sensitive recording. As a result, a marked improvement in the color developing ability and a good retention of the colored image density under high humidity conditions were surely recognized and hence distinct differences were observed between this semi-synthetic solid acid and the clay mineral group color developer so far known and used. On the other hand, it was found as a drawback of the semi-synthetic solid acid that some fastness, for example, light fastness, of the color image formed in the color-developing layer employing the semi-synthetic solid acid is rather deteriorated.

DISCLOSURE OF THE INVENTION

In view of the above, the present inventors made extensive studies in the search for a means of improving the fastness of the color image formed in such a color-developing layer. As a result, this invention has been accomplished through new finding that the addition of any of various known antioxydants such as aromatic amines and hindered phenols and any of ultraviolet absorbers such as benzotriazole derivatives is little effective, but the addition of necessary amounts of a phenol compound and a zinc compound markedly improves the light fastness of the color image formed; in particular the use of a selected phenol compound together with a zinc compound gives a semi-synthetic solid acid-containing color-developing layer really excellent in practical use which does not cause any objectionable side reaction such as the yellowing of the blank areas (image-less areas on the color-developing layer).

BEST MODE FOR CARRYING OUT THE INVENTION

The phenol compound used jointly with the semi-synthetic solid acid in this invention may be either a low molecular weight phenol compound or a phenolic resin. Especially suitable phenol compounds which do not cause such a side reaction as the discoloration or coloration of the blank areas or the degradation are, for example, alkyl, aralkyl, or aryl p-hydroxybenzoates, p-hydroxybenzonitrile, p-hydroxybenzenesulfonamide, 4-hydroxybenzophenone, 2,4-dihydroxybenzophenone, dialkyl, diaralkyl, or diaryl 4-hydroxyphthalic acid esters, and various hindered phenols. Suitable amounts thereof used are 1-100 parts per 100 parts of the semi-synthetic solid acid.

Especially effective zinc compounds used in this invention are, for example, zinc oxide, zinc hydroxide, zinc carbonate, basic zinc carbonate, zinc sulfide, zinc phosphate, and zinc salts of various organic acids. Suitable amounts thereof used are 1-100 parts per 100 parts of the semi-synthetic solid acid.

The semi-synthetic solid acid used in this invention is derived from a clay mineral having a layer structure build up of regular tetrahedrons of silica, and this color developer for pressure-sensitive copying paper is featured by

(A) indicating an electron diffraction pattern based on the crystals of the above layer structure built up of regular tetrahedrons of silica,

(B) indicating no X-ray diffraction pattern based on the above layer structure, and

(C) containing at least silicon and magnesium and/or aluminum as elements besides oxygen.

Preferred examples of the above color developer for pressure-sensitive copying paper used in this invention satisfy the above conditions (A), (B), and (C) and additionally the condition that

(D) the atomic ratio of [silicon]/[the sum of magnesium and/or aluminum] therein is 12/1.5 - 12/12, particularly 12/3 - 12/10. Herein, when only one of magnesium and aluminum is contained, the sum of magnesium and/or aluminum in the above atomic ratio means the amount of the contained one.

As stated above, it has been found in this invention that the combined use of the semi-synthetic solid acid, phenol compound, and zinc compound gives a color-developing sheet for pressure-sensitive recording materials which is far more improved in the fastness of the color image than does the use of the semi-synthetic solid acid alone. Moreover, as will be shown later in Examples, the simultaneous addition of the phenol compound and zinc compound has excellent effects particularly in improving the fastness of the color image formed as compared with the separate addition of the compounds. That is, a synergistic effect is observed in the former case.

In this invention, the color-developing layer for pressure-sensitive recording is formed by; mixing the semi-synthetic solid acid, one or more of the zinc compounds, one or more of the phenol compounds, a binder, a dispersant, some other additive, and if desired, a pigment such as clay, kaolin, satin white, calcium carbonate, titanium white, magnesium oxide, talc, alumina, aluminum hydroxide, urea resin pigment, or plastic pigment; applying the resulting coating liquid on a sheet-like support such as paper, plastic film, plastic-coated paper, or the like by using an air knife coater, blade coater, roll coater, flexo coater, gravure coater, rubber doctor coater, curtain coater, or some other coating means; and drying the coat.

As described above, the color developing layer in this invention is formed by using the semi-synthetic solid acid as color developer and using cojointly the zinc compound and the phenol compound. In this way, this invention has been successful in providing a pressure-sensitive recording system unprecedentedly markedly improved in all the color forming rate, formed color density, fastness of the formed color image (to light, water, humidity, plasticizer, oxidizing gas, etc.), and stability (retention of color developing ability, resistance to yellowing) of the image-less areas (blank areas). In particular, it is noteworthy that the formed color density, the retention thereof under high humidity conditions, and the fastness of the formed color image to NOx are improved, the fading with light is reduced, and the blank areas do not undergo the yellowing.

Referring now to a typical example, preferred embodiments of this invention are illustrated in more detail. In the following example, "parts" are all by weight.

Example

The following mixture was ball-milled for two days.

Mixture:

Benzyl p-hydroxybenzoate	100 parts
Hydroxyethylcellulose	5 parts
Water	145 parts
	Total 250 parts

Then, 100 parts of a semi-synthetic solid acid (tradename: Silton SS-1, mfd. by Mizusawa Chem. Ind. Co., Ltd.), 10 parts of zinc oxide, and 50 parts of the above dispersion of benzyl p-hydroxybenzoate prepared by the wet grinding were dispersed in 200 parts of water dissolving 1 part of sodium pyrophosphate. To the resulting dispersion were added 50 parts of a 10% aqueous solution of oxidized starch and 50 parts of a 48% SBR latex to prepare a coating liquid. It was coated on 40-g/m^2 base paper to give a dry coating weight of 4.5 g/m^2. Thus, color-developing sheets (CF) were prepared (sample D).

For the purpose of comparative tests, samples were prepared without adding either benzyl p-hydroxybenzoate or zinc oxide (sample A), without adding benzyl p-hydroxybenzoate but with adding the same amount of zinc oxide (sample C), and without adding zinc oxide but with adding the same amount of benzyl p-hydroxybenzoate (sample B) were prepared in the same manner as the above.

Color-forming sheets (CB) herein used were prepared as follows: A solution of electron-donative leuco dyes in a high boiling solvent having the composition:

Crystal violet lactone	4 parts
Benzoyl leucomethylene blue	1 part
3-Diethylamino-6-methyl-7-anilinofluoran	0.5 part
Diisopropylnaphthalene (tradename KMC, mfd. and sold by Kureha Chem. Ind. Co., Ltd.)	100 parts

was micro-capsuled with a melamine resin according to the method of U.S. Patent No. 4,233,178. To 100 parts (dry basis) of the micro-capsules were added 25 parts of wheat starch and 150 parts of a 10% aqueous solution of oxidized starch. The resulting mixture was coated on 40-g/m^2 base paper to give a dry coating weight of 5 g/m^2.

A specimen of each of the thus obtained CF sheets (4 types) and a specimen of the CB sheets were superposed so as to oppose the coating surfaces and were super-calendered. After one or more days, tests of exposure to sunlight and room scattered light and other fastness tests were conducted on the thus colored specimens of the color-developing sheets (Table 1).

Table 1 Results of color image fastness tests

Sample	Presence of components in color-developing layer			Formed color density after super-calendering
	Semi-synthetic solid acid	Phenol compd.	Zinc compd.	
A	Yes	No	No	0.74
B	Yes	Yes	No	0.76
C	Yes	No	Yes	0.73
D	Yes	Yes	Yes	0.74

- cont'd -

Table 1 (cont'd)

Fastness of color image (color density and its retention, after exposure)					Note
(1) Exposure to sunlight	(2) Exposure to NOx	(3) Exposure to room scattered light	(4) Exposure to plasticizer	(5) Exposure to moisture	
0.39 (53%)	0.50 (68%)	0.32 (43%)	0.56 (76%)	0.76	Comparative example
0.49 (64%)	0.62 (82%)	0.50 (66%)	0.60 (79%)	0.76	"
0.40 (55%)	0.51 (70%)	0.34 (47%)	0.56 (77%)	0.74	"
0.56 (76%)	0.76 (91%)	0.56 (76%)	0.63 (85%)	0.74	Example of this invention

Remarks: (1) One hour exposure to direct sunlight.

(2) 30-minute exposure to 900 ppm Nox.

(3) 20-day exposure on a room inside wall (at about 1000 lux).

(4) Superposed on a plasticized PVC sheet at 45°C for 48 hours.

(5) 4-day exposure to 90% R.H. at 40°C.

From Table 1, a synergy is observed in the effect of this invention. In other words, when (the retentions of the samples B, C, and D) (%) - (the retention of the sample A) (%) are designated as ΔB, ΔC, and ΔD(%) in the sunlight exposure tests, $\Delta B = 11$(%), $\Delta C = 2$(%), and $\Delta D = 23$(%) and therefore $\Delta D > \Delta B + \Delta C$.

The same relations are found in the NOx exposure, room scattered light exposure, and plasticizer exposure test results.

Thus, according to this invention, much greater improvements in the fastness of the color image have been attained by combined use of the phenol compound and the zinc compound than by separate use of these compounds.

CLAIM

A color-developing sheet for pressure-sensitive recording, characterized in that the color-developing layer of the sheet contains (a) a semi-synthetic solid acid prepared by (1) treating a clay mineral which has a layer structure built up of regular tetrahedrons of silica, with an acid so as to give a silica content of 82 - 96.5% by weight on a dry basis (drying at 105°C for 3 hours), (2) bringing the resulting clay mineral, in an aqueous medium, into contact with a magnesium compound and/or aluminum compound soluble at least partially in the medium and if this soluble compound is other than the hydroxide, neutralizing it with alkali or acid to form the hydroxide, thus introducing a magnesium component and/or aluminum component into the acid-treated clay mineral, and (3) if desired, drying the resulting clay mineral, (B) a phenol compound, and (C) a zinc compound.

INTERNATIONAL SEARCH REPORT

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International Application No. PCT/[illegible]

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[3]

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

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II. FIELDS SEARCHED

Minimum Documentation Searched[4]

Classification System	Classification Symbols
I P C	B41M 5/12 - 5/22

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[5]

Jitsuyo Shinan Koho	1960 - 1982
Kokai Jitsuyo Shinan Koho	1971 - 1982

III. DOCUMENTS CONSIDERED TO BE RELEVANT[14]

Category*	Citation of Document,[16] with indication, where appropriate, of the relevant passages[17]	Relevant to Claim No.[18]
A	JP,A, 57-15996 (Mizusawa Kagaku Kogyo Kabushiki Kaisha) 27. January. 1982 (27.01.82)	1

* Special categories of cited documents:[15]

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

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"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[2]	Date of Mailing of this International Search Report[2]
July 20, 1983 (20.07.83)	August 1, 1983 (01.08.83)
International Searching Authority[1]	**Signature of Authorized Officer**[20]
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