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(54) **VAPORIZABLE DYE COMPOSITION AND SHEET CONTAINING SAME.**

(57) A vaporizable dye composition for preparing heat-sensitive recording sheet forming images with excellent resolution on photographic paper, and a sheet containing it. The composition comprises a vaporizable dye, a binder, and a solvent, with part or the whole of the binder being a crosslinking resin.

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DESCRIPTION

TITLE OF THE INVENTION

VAPORIZABLE DYE COMPOSITION AND SHEET CONTAINING THE SAME

TECHNICAL FIELD

The present invention relates to a vaporizable dye composition used to manufacture a dye carrier sheet material which is used to form on a printing paper a clear picture image of excellent resolution and a sheet containing the same.

BACKGROUND ART

In the prior art, such a system has been developed that a picture picked up by a video camera or a still picture and the like from a television receiver, a VTR, a video disc and a computer is directly reproduced with full color on a printing paper. A coupler used for such system is a dye which is vaporizable and dyed on the printing paper by heating. Generally, this coupler is formed on the surface of a sheet base material such as paper or the like with a synthetic resin binder. The above sheet material is superposed on the printing paper and then heated by a thermal print head in response to the picture signal. Thus, the dye is vaporized and then transferred to the printing paper. Although such sheet material coated with vaporizable dye is well known in the

field of the heat transfer printing technique, such well-known sheet material can not be used as the dye carrier sheet material for the above system. The reasons are as follows. While in the conventional heat transfer printing system, the sheet material is superposed on the textile and then heated for a relatively long time, the above new system admits quite short time of heating, with a relatively high temperature. Also, the material to which the dye is transferred is not the textile material but the sheet material (the printing paper) with the smooth surface, so that the dye carrier sheet material is melted on the printing paper, alternatively, the dye as well as the binder itself is transferred to the printing paper. Thus, the resolution is lowered, the clearness of the picture is lost and it is difficult to present the gradation thereof.

DISCLOSURE OF INVENTION

After various vigorous researches for removing the above defects, the present inventors succeeded in obtaining a vaporizable dye composition which can obviate the above defects inherent in the prior art technique and which can make a dye carrier sheet.

The present invention relates to a vaporizable dye composition consisting of vaporizable dye, binder and solvent in which a part or whole of the binder is made of curable resin.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will be described in detail. A vaporizable dye used in the present invention is an organic dye of a relatively small molecular weight (for example, about 200 to 400) which is contained much in a well-known sublimation dye and a dispersing dye. And, this vaporizable dye is vaporized from solid or liquid state at temperature ranging from approximately 100 to 200°C (under atmospheric pressure), which can be dyed on a hydrophobic synthetic resin material such as polyester, polypropyrene, acetate and the like. In view of the chemical structure, it is made of mainly dye such as azo-series, anthraquinone-series, styryl-series, quinophthalol-series, nitrodiphenyl amine-series and so on.

One example of the binder used in the present invention is made of natural or synthetic resin material containing a reactive functional group and a curing agent. As the reactive functional group, there are hydroxyl group, carboxyl group, amino group, isocianate group, epoxy group or the like which are main ones. As the resin material containing hydroxyl group, there are cellulose derivative, gum arabic, tragacanth gum, starch derivative, alginic acid derivative, polyvinyl alcohol, polyvinyl alcohol derivative, acrylpolyol, alkyd resin and the like. As the resin material containing carboxyl group, there are alkyd resin, cellulose derivative, polymer or copolymer of unsaturated carboxylic acid. As the resin material containing amino

group, there are melamine resin, urea resin or the like. As the resin material containing isocianate group, there are polyisocianate compounds of various kinds, isocianate terminated prepolymer and the like. As the resin material containing epoxy group, there are various epoxy resins.

As the curing agent which is used together with the resins as described above, the above resin having the functional group which can be reacted with the functional group of the resin selected from the above resin materials can be used as the curing agent as it is. In addition, there can be used well-known curing agents formed of various kinds of silane coupling agent, titanate coupling agent, zirconium chelate agent, aluminium chelate agent, metal compound such as Mg, Ca, Zn, Pb or the like, organic acid, inorganic acid, various kinds of inorganic and organic salts, metal soap, various kinds of polyamine and the like.

As an example of other curable resin which can be used in the present invention, there is a resin which is hardened or cross-linked by irradiation of radiation energy such as ultraviolet rays, electron beam and the like. Such resin is made of monomer, prepolymer or polymer or a mixture of them which contain in its structure at least one polymerizable unsaturated double bonds. If necessary, such resin contains photo-polymerization initiator. These curable resins themselves are well known.

The binder in the present invention may be the

above curable resin only. However, when such binder is the above curable resin only, if the curing is advanced too much thereafter, frequently the dye contained therein is not vaporized smoothly. Therefore, it is desired to vaporize the dye smoothly by properly adjusting the using amount of the curing agent or by adding the conventional thermo-plastic resin or proper plasticizers of various kinds to the above curable resin. As such well-known thermo-plastic resin, there may be non-reactive cellulose derivative, vinyl polymer, polyester, polyamide and the like. Moreover, a well-known plasticizer may be used. When such thermo-plastic resin and plasticizer are used, its amount must be selected so as to share less than approximately 30 weight % of the whole amount of the binder. If it exceeds the above amount, the object of the present invention can not be attained sufficiently.

As the solvent used in the present invention, there can be used, in addition to water, solvents of various kinds such as alcohol-series, ester-series, ketone-series, aromatic-series, aliphatic-series, naphthene-series, isoparafin-series and the like solely or as a mixture thereof.

The fundamental component of the composition according to the present invention is the same as described above, and if necessary, various kinds of well-known additives and filler can be used.

The composition of the present invention is

produced by mixing the above components at a suitable ratio and carrying out the ordinary dispersing treatment therefor. The ratio of each component used in the composition is preferably selected such that the dye is approximately 1 to 20 weight %, the binder is approximately 2 to 40 weight % and the solvent is approximately 40 to 97 weight % for the total amount of 100 weight %.

The dye composition of the present invention thus obtained is a liquid-phase composition and is then coated on desirably a sheet-like base material such as a thin paper with an amount ranging from approximately 0.1 to 2 g/m^2 (as the amount of dye) by well-known coating means such as blade coater, air knife coater, roll coater, curtain coater, bar coater, gravure coater and the like. Then, it is cured by heating and drying or irradiating the radiant energy, which is further heated, if necessary, to thereby produce the dye carrier sheet material. As described above, the binder contained in the composition is cross-linked and the resin is formed of three dimensional network structure. In consequence, even when this dye carrier sheet is superposed on the printing paper and the vaporizable dye is transferred to the printing paper by the thermal print head driven in accordance with a video signal to provide a picture image, the binder in the dye layer can be prevented from being softened excessively and being adhesive by the heating of the thermal print head. And, the dye carrier sheet and the printing paper can be prevented from being

bonded to each other excessively and also the binder itself can be prevented from being transferred to the printing paper thus a clear picture image being made.

According to the detailed researches done by the present inventors, it was found out that an example of the most preferable curing binder which does not prevent the vaporization of the dye and is not bonded to the printing paper excessively was a mixture of cellulose-series derivative and melamine series resin.

Particularly when a radiation curable resin is used as the binder, the heating is not required upon curing thereof and the curing thereof are completed in several seconds to several minutes so that the fugacity of the vaporizable dye does not occur at all. This binder is also preferable for the aspect of productivity.

Now, the present invention will be described more specifically with reference to examples. In the description below, the reference of "part" or "%" is weight.

Example 1

5 parts of KAYASET YELLOW AG (manufactured by NIPPON KAYAKU CO., LTD.), 3 parts of carboxymethyl cellulose, 4 parts of polyvinyl alcohol, 0.1 parts of antifoaming agent and 88 parts of water are mixed, dispersed in a ball mill and added with 1 part of methylol melamine (curing agent) and 0.1 part of ammonium chloride to provide the vaporizable dye composition of the present invention.

Example 2

10 parts of KAYASET RED B (manufactured by NIPPON KAYAKU CO., LTD.), 15 parts of cellulose acetate propyonate, 2 parts of silica, 73 parts of toluene and 3 parts of xylylene diisocianate are used to produce the vaporizable dye composition of the present invention.

Example 3

Instead of the xylylene diisocianate in the example 2, 1 part of tetrabenzyltitanate is used. As the solvent, 50 parts of toluene and 23 parts of isopropyl alcohol are used and other components are selected to be the same as those in the example 2, thus the vaporizable dye composition of the present invention being made.

Example 4

10 parts of PTB-67 (which is the dye for blue color and manufactured by MITSUBISHI CHEMICAL INDUSTRIES CO., LTD.,) 15 parts of ethyl cellulose, 1 part of silica and 74 parts of toluene are mixed together, dispersed by a centrifugal mill and added with 2 parts of methylol melamine and 0.5 parts of paratoluene sulfonic acid, thus the vaporizable dye composition of the present invention being made.

Example 5

10 parts of KAYASET BLUE 906 (manufactured by NIPPON KAYAKU CO., LTD.), 20 parts of epoxy resin, 30 parts of toluene, 38 parts of diacetone alcohol and 2 parts of silica are mixed, dispersed by an attrition mill and added with 5 parts of methylol melamine and 2 parts by

weight of diethylene triamine, thus the vaporizable dye composition of the present invention being made.

Example 6

10 parts of KAYASET YELLOW AG, 50 parts of polyester acrylate, 5 parts of silica and 35 parts of toluene are mixed together and dispersed by a sand mill to thereby produce the vaporizable dye composition of the present invention.

Example 7

10 parts of KAYASET RED B (manufactured by NIPPON KAYAKU CO., LTD.), 60 parts of trimethylolpropane triacrylate, 3 parts of benzophenone, 3 parts of methyldiethanol amine, 2 parts of silica and 22 parts of xylene are mixed together and dispersed by the attrition mill to thereby produce the vaporizable dye composition of the present invention.

Example 8

10 parts of PTB-67, 20 parts of polyester acrylate, 10 parts of cellulose acetate propyonate, 1 part of benzoinisobutylether, 19 parts of isopropyl alcohol and 40 parts of toluene are used to produce the vaporizable dye composition of the present invention in the same way as in the example 7.

Example of use

The compositions of the present invention according to the examples 1 to 8 are used to thereby produce the dye carrier sheet materials under the conditions tabulated on the following table 1.

T A B L E 1

Vaporizable dye composition	Sheet base material	Coating amount of the composition (g/m^2)	Curing condition	Coloring of printing paper	Adhesion to printing paper
example 1	Water proof thin paper	20	180°C x 30 seconds	Satisfactory	Hardly recognized
example 2	"	15	40°C x 3 days	"	"
example 3	"	15	120°C x 3 minutes	"	"
example 4	Polyester film	10	100°C x 3 hours	"	"
example 5	Water proof thin paper	15	100°C x 2 hours	"	"
example 6	"	15	irradiation of electronic beams	"	Not recognized at all
example 7	Polyester film	10	irradiation of ultraviolet rays	"	"
example 8	"	10	"	"	"
comparative example 1	Water proof thin paper	15	—	Unsatisfactory	Large adhesion
comparative example 2	Polyester film	10	—	"	"

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The comparative example 1 on the above table 1 is the example in which xylenediisocianate is not used in the afore-described example 2, while the comparative example 2 is the example in which methylol melamine and paratoluene sulfonic acid are not used in the afore-described example 4.

CLAIMS

1. A vaporizable dye composition comprising a vaporizable dye, a binder and a solvent in which said binder is partly or fully made of a curable resin.

2. A vaporizable dye composition according to claim 1, wherein said curable resin is made of natural or synthetic resin containing a reactive functional group and a curing agent.

3. A vaporizable dye composition according to claim 1, wherein said curable resin is a radiation curable resin.

4. A vaporizable dye composition according to claim 1, wherein the amount of said binder is selected to be 2 to 40 parts by weight relative to 1 to 20 parts by weight of vaporizable dye.

5. A dye carrier sheet comprising a base material and a dye layer formed on said base material and containing a vaporizable dye, said dye layer consisting of mainly a vaporizable dye and a binder and at least a part of said binder being made of a curable resin.

6. A dye carrier sheet according to claim 5, wherein said curable resin is made of a natural or synthetic resin containing a reactive functional group and a curing agent.

7. A dye carrier sheet according to claim 5, wherein said curable resin is a radiation curable resin.

8. A dye carrier sheet according to claim 5, wherein the amount of said binder is selected to be 2 to 40 parts by weight relative to 1 to 20 parts by weight of the vaporizable dye.

9. A vaporizable dye composition according to claim 1, wherein less than 30 weight % in the whole amount of said binder is thermoplastic resin.

10. A dye carrier sheet according to claim 5, wherein less than 30 weight % in the whole amount of said binder is thermoplastic resin.

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INTERNATIONAL SEARCH REPORT

International Application No. PCT/JP83/00168

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 5/26

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

Kokai Jitsuyo Shinan Koho 1971 - 1983

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]
X	JP,A, 55-39379 (Mitsubishi Electric Corp.), 19. March. 1980 (19.03.80)	1 - 10
X	JP,A, 55-39378 (Mitsubishi Electric Corp.), 19. March. 1980 (19. 03. 80)	1 - 10
X	JP,A, 53-43538 (Fujitsu Ltd.), 19. April. 1978 (19. 04. 78)	1 - 10
X	JP,A, 56-21895 (Fujitsu Ltd.), 28. February. 1981 (28. 02. 81)	1 - 10

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

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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]
August 2, 1983 (02.08.83)	August 15, 1983 (15.08.83)
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