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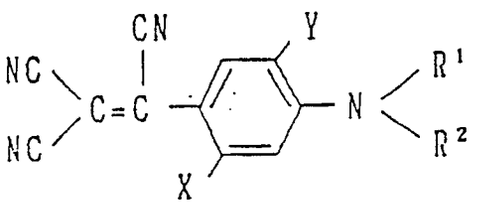
(54) Thermal transfer recording sheet and ink composition for producing the same.

(57) A thermosensitive transfer recording sheet comprising a substrate having thereon a colorant layer, the colorant layer comprising a binder and a dyestuff represented by the following general formula (I):



(I)

wherein X and Y independently represent a hydrogen atom, a lower alkyl group, or a lower alkoxyl group, provided that either of X and Y represents a lower alkoxyl group; and R^1 and R^2 independently represent a hydrogen atom, a substituted or unsubstituted alkyl group, a cycloalkyl group, an allyl group, or a substituted or unsubstituted phenyl group, provided that in the case where both of X and Y represent a lower alkoxyl group, R^1 represents a hydrogen atom. A thermosensitive transfer recording ink composition for use in forming the colorant layer on a substrate is also disclosed.

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THERMAL TRANSFER RECORDING SHEET AND INK COMPOSITION FOR PRODUCING THE SAME

The present invention relates to a thermosensitive transfer recording sheet (which has the same meaning as "thermal transfer recording sheet") for use in thermosensitive transfer recording, particularly in sublimation-type thermosensitive transfer recording, and to an ink composition for use in producing the thermosensitive transfer recording sheet.

In the field of facsimile, copying machines, or printers, studies are conventionally being made of color recording techniques based on electrophotographic printing, ink-jet printing and thermosensitive transfer printing.

Among these, the thermosensitive transfer recording technique is more advantageous than the others because the maintenance and operation of the apparatus are easy and the apparatus and its expendable supplies are inexpensive.

There are two systems in the thermosensitive transfer recording: fusion-type transfer in which a transfer recording sheet composed of a base film and formed thereon a thermally fusible ink layer is heated with a thermal head to fuse the ink and transfer the fused ink to an image-receiving surface, thereby recording an image on the receiving surface; and sublimation-type transfer in which a transfer recording sheet composed of a base film and formed thereon a colorant layer containing a sublimable dyestuff is heated with a thermal head to sublimate and/or heat-diffuse the dyestuff and transfer the dyestuff from the transfer recording sheet to an image-receiving surface, thereby recording an image on the receiving surface. The sublimation-type transfer is particularly advantageous to full-color recording over the fusion-type in that gradation recording is easy since the transferred amount of the dyestuff can be controlled by changing the energy fed to the thermal head.

In the thermosensitive transfer recording of the sublimation type, sublimable dyestuffs used in transfer recording sheets and in ink compositions for producing transfer recording sheets greatly affect the speed of transfer recording and the quality and storage stability of prints. Therefore, the sublimable dyestuffs are highly important and need to satisfy the following requirements:

(1) the dyestuffs should readily sublimate and/or heat-diffuse under operation conditions for the thermorecording head;

(2) they should not undergo thermal decomposition under operation conditions for the thermorecording head;

(3) they should possess tints favorable for color reproduction;

(4) they should have high molecular absorption coefficients;

(5) they should be stable to heat, light, moisture and chemicals;

(6) they should be able to be easily synthesized;

(7) they should have good suitability for use in preparing inks; and

(8) they should have no health and safety problems.

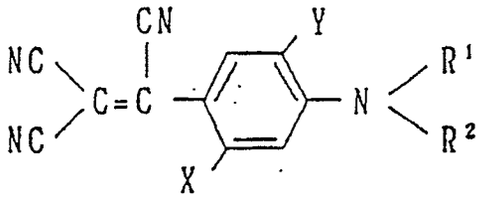
However, a dyestuff which meets all the above requirements has not been found so far. Magenta dyestuffs, in particular, have various defects and satisfactory one has not yet been developed.

Conventionally known magenta dyestuffs having suitability to thermosensitive transfer recording of the sublimation type are disclosed, for example, in JP-A-60- 31563, JP-A-59-78896, and JP-A-63-203393. (The term "JP-A" as used herein means an "unexamined published Japanese patent application".) These magenta dyestuffs are tricyanovinyl dyestuffs having the same basic structure as that of the dyestuff employed in the present invention. However, even the dyestuffs whose structural formulae are specified in those references have had still insufficient performances, particularly in light resistance.

An object of the present invention is to provide a thermosensitive transfer recording sheet employing a magenta dyestuff which satisfies all of the above-listed requirements.

Another object of the present invention is to provide an ink composition for use in manufacturing the thermosensitive transfer recording sheet.

In one aspect of the present invention, a thermosensitive transfer recording sheet is provided which comprises a substrate having thereon a colorant layer, the colorant layer comprising a binder and a dyestuff represented by the following general formula (I):

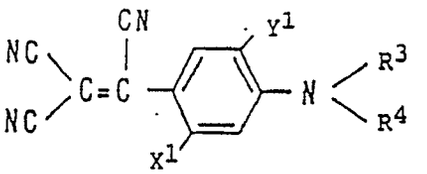


(I)

wherein X and Y independently represent a hydrogen atom, a lower alkyl group, or a lower alkoxyl group, provided that either of X and Y represents a lower alkoxyl group; and R^1 and R^2 independently represent a hydrogen atom, a substituted or unsubstituted alkyl group, a cycloalkyl group, an allyl group, or a substituted or unsubstituted phenyl group, provided that in the case where both of X and Y represent a lower alkoxyl group, R^1 represents a hydrogen atom.

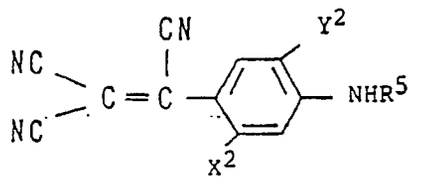
In another aspect of the present invention, an ink composition for use in manufacturing the above thermosensitive transfer recording sheet is provided which ink composition comprises the tricyanovinyl dyestuff represented by general formula (I), a binder resin, and a medium.

The dyestuff employed in the present invention is represented by general formula (I) given above, and includes dyestuffs represented by general formula (II) given below and dyestuffs represented by general formula (III) given next.



(II)

(In general formula (II), R^3 and R^4 independently represent a hydrogen atom, a substituted or unsubstituted alkyl group, a cycloalkyl group, allyl group, or a substituted or unsubstituted phenyl group; and X^1 and Y^1 independently represent a hydrogen atom, a lower alkyl group, or a lower alkoxyl group, provided that either of X^1 and Y^1 represents a lower alkoxyl group and the remaining one represents another group.)



(III)

(In general formula (III), R^5 represents a substituted or unsubstituted alkyl group, a cycloalkyl group, allyl group, or a substituted or unsubstituted phenyl group, and X^2 and Y^2 independently represent a lower alkoxyl group.)

Specific examples of the substituted or unsubstituted alkyl group, cycloalkyl group, allyl group, or substituted or unsubstituted phenyl group represented by R^1, R^2, R^3, R^4, and R^5 in general formulae (I), (II), and (III) given above are as follows.

Examples of the unsubstituted alkyl group include straight-chain or branched alkyl groups having 1 to 8 carbon atoms. Examples of the substituted alkyl group include hydroxy-substituted alkyl groups such as 2-hydroxyethyl group, 3-hydroxypropyl group, 4-hydroxybutyl group, and 2-hydroxypropyl group; carboxy-substituted alkyl groups such as carboxymethyl group, 2-carboxyethyl group, and 3-carboxypropyl group; cyano-substituted alkyl groups such as 2-cyanoethyl group and cyanomethyl group; amino-substituted alkyl groups such as 2-aminoethyl group; halogen-substituted alkyl groups such as 2-chloroethyl group, 3-chloropropyl group, 2-chloropropyl group, and 2,2,2-trifluoroethyl group; alkyl groups substituted with phenyl group which may further be substituted, such as benzyl group, p-chlorobenzyl group, and 2-phenylethyl group; alkoxy-substituted alkyl groups such as 2-methoxyethyl group, 2-ethoxyethyl group, 2-n-propoxyethyl group, 2-isopropoxyethyl group, 2-n-butoxyethyl group, 2-isobutoxyethyl group, 2-(2-ethylhexyloxy)ethyl group, 3-methoxypropyl group, 4-methoxybutyl group, and 2-methoxypropyl group; alkoxyalkoxy-substituted

alkyl groups such as 2-(2-methoxyethoxy)ethyl group, 2-(2-ethoxyethoxy)ethyl group, 2-(2-n-propoxyethoxy)ethyl group, 2-(2-isopropoxyethoxy)ethyl group, 2-(2-n-butoxyethoxy)ethyl group, 2-(2-isobutoxyethoxy)ethyl group, and 2-(2-(2-ethylhexyloxy)ethoxy)ethyl group; allyloxyethyl group; aryloxyalkyl groups such as 2-phenoxyethyl group; aralkyloxyalkyl groups such as 2-benzyloxyethyl group; acyloxy-substituted alkyl groups such as 2-acetyloxyethyl group, 2-propionyloxyethyl group, 2-n-butyryloxyethyl group, 2-isobutyryloxyethyl group, and 2-trifluoroacetyloxyethyl group; alkyl groups substituted with a substituted or unsubstituted alkoxycarbonyl group, such as methoxycarbonylmethyl group, ethoxycarbonylmethyl group, n-propoxycarbonylmethyl group, isopropoxycarbonylmethyl group, n-butoxycarbonylmethyl group, isobutoxycarbonylmethyl group, 2-ethylhexyloxycarbonylmethyl group, benzyloxycarbonylmethyl group, furfuryloxycarbonylmethyl group, tetrahydrofurfuryloxycarbonylmethyl group, 2-methoxycarbonylethyl group, 2-ethoxycarbonylethyl group, 2-n-propoxycarbonylethyl group, 2-isopropoxycarbonylethyl group, 2-n-butoxycarbonylethyl group, 2-isobutoxycarbonylethyl group, 2-(2-ethylhexyloxycarbonyl)ethyl group, 2-benzyloxycarbonylethyl group, and 2-furfurylcarbonylethyl group; alkyl groups substituted with a substituted or unsubstituted alkoxycarbonyloxy group, such as 2-methoxycarbonyloxyethyl group, 2-ethoxycarbonyloxyethyl group, 2-n-propoxycarbonyloxyethyl group, 2-isopropoxycarbonyloxyethyl group, 2-n-butoxycarbonyloxyethyl group, 2-isobutoxycarbonyloxyethyl group, 2-(2-ethylhexyloxycarbonyloxy)ethyl group, 2-benzyloxycarbonyloxyethyl group, and 2-furfuryloxycarbonyloxyethyl group; and heterocyclic ring-substituted alkyl groups such as furfuryl group and tetrahydrofurfuryl group.

Examples of the cycloalkyl group include the cyclopentyl and cyclohexyl group.

Examples of the substituted phenyl group include phenyl group substituted with a straight-chain or branched alkyl group having 1 to 8 carbon atoms; phenyl group substituted with a straight-chain or branched alkoxyl group having 1 to 4 carbon atoms; phenyl group substituted with a halogen atom such as fluorine atom, chlorine atom, or bromine atom; and phenyl group substituted with nitro group, cyano group, trifluoromethyl group.

Particularly preferred examples of the groups of R^1, R^2, R^3, R^4, and R^5 include hydrogen atom, straight-chain or branched alkyl groups having 1 to 8 carbon atoms, and alkoxyalkyl groups having 3 to 8 carbon atoms, provided that R^5 preferably represents groups other than a hydrogen atom.

Among the dyestuffs represented by the above-described general formula (I), those represented by the general formula (I) in which either of R^1 and R^2 is hydrogen atom are particularly preferred from the standpoints of the tints of dyestuffs and the light resistance of prints obtained therefrom, etc.

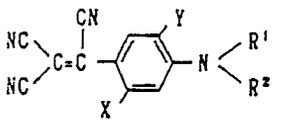
Examples of the lower alkyl group represented by X, Y, X^1, and Y^1 include straight-chain or branched alkyl groups having 1 to 4 carbon atoms. Examples of the lower alkoxyl group represented by X, Y, X^1, Y^1, X^2, and Y^2 include straight-chain and branched alkoxyl groups, having 1 to 4 carbon atoms.

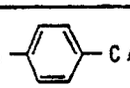
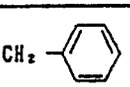
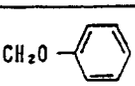
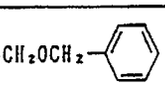
In the above general formulae (I) and (II), either of X and Y and either of X^1 and Y^1 represent a lower alkoxyl group, and the remaining ones preferably represent a lower alkyl group or a lower alkoxyl group. More preferably, both X and Y and both X^1 and Y^1 are a lower alkoxyl group.

Therefore, the most preferred of the dyestuffs of general formula (I) which can be used in the present invention are dyestuffs represented by general formula (III) given hereinabove, from the standpoints of the tints of dyestuffs, and the light resistance of prints obtained therefrom.

Specific examples of the dyestuff represented by general formula (I) described above are listed in the following Tables 1 and 2.

TABLE 1



No.	R^1	R^2	X	Y
1	$-CH_3$	$-CH_3$	$-OC_4H_9(n)$	- H
2	$-C_4H_9(n)$	- H	- H	$-OCH_3$
3	$-C_2H_5$	- H	$-OCH_3$	- H
4	$-C_4H_9(iso)$	$-C_4H_9(iso)$	〃	〃
5	$-C_8H_{17}(n)$	- H	$-CH_3$	$-OCH_3$
6	$-CH_2-CH=CH_2$	$-C_4H_9(iso)$	$-OCH_3$	- H
7	$-CH_2CH_2OH$	$-C_4H_9(n)$	〃	〃
8	$-CH_2CH_2COOH$	$-C_8H_{17}(n)$	$-OC_4H_9(iso)$	〃
9	$-CH_2CH_2CN$	$-C_4H_9(iso)$	$-OCH_3$	〃
10	$-CH_2CH_2NH_2$	$-C_4H_9(n)$	〃	〃
11	$-CH_2CH_2C\ell$	$-C_4H_9(iso)$	〃	〃
12	$-CH_2CF_3$	$-C_4H_9(n)$	$-C_4H_9(n)$	$-OC_4H_9(n)$
13		〃	$-OCH_3$	- H
14		〃	〃	$-CH_3$
15		〃	〃	- H
16	$-CH_2CH_2OCH_3$	$-CH_2CH_2OCH_3$	〃	〃
17	$-CH_2CH_2OC_4H_9(n)$	$-CH_2CH_2OC_4H_9(n)$	〃	〃
18	$-CH_2CH_2OCH_2-CH=CH_2$	$-CH_2CH_2OCH_2-CH=CH_2$	〃	〃
19		$-C_2H_5$	〃	〃
20		- H	〃	$-C_4H_9(iso)$
21	$-(CH_2CH_2O)_2C_4H_9(n)$	〃	〃	〃
22	$-CH_2CH_2OCOCH_3$	$-CH_2CH_2OCOCH_3$	〃	- H

(continued)

TABLE 1 (continued)

No.	R^1	R^2	X	Y
23	$-CH_2CH_2OCO-C_6H_5$	$-C_2H_5$	- H	$-OCH_3$
24	$-CH_2CH_2OCOCF_3$	〃	$-OCH_3$	- H
25	$-CH_2CH_2COOCH_3$	〃	〃	〃
26	$-CH_2CH_2COOC_4H_9(n)$	〃	〃	〃
27	$-CH_2CH_2COOC_8H_{17}(n)$	〃	〃	〃
28	$-CH_2CH_2COOCH_2-C_6H_5$	〃	〃	〃
29	$-CH_2CH_2COO-CH_2-$ 	〃	〃	〃
30	$-CH_2CH_2COOCH_2-$ 	〃	〃	〃
31	$-CH_2CH_2OCOOCH_3$	〃	〃	〃
32	$-CH_2CH_2OCOOC_4H_9(n)$	〃	〃	〃
33	$-CH_2CH_2OCOOC_8H_{17}(n)$	〃	〃	〃
34	$-CH_2CH_2OCOO-C_6H_5$	〃	〃	〃
35	$-CH_2CH_2OCOOCH_2-C_6H_5$	〃	〃	〃
36	$-CH_2-$ 	〃	〃	〃
37	$-CH_2-$ 	〃	〃	〃
38		$-C_4H_9(n)$	〃	〃
39		〃	〃	〃
40		〃	〃	〃
41		- H	〃	$-CH_3$

(continued)

TABLE 1 (continued)

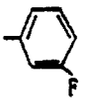
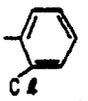
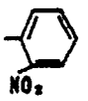
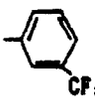
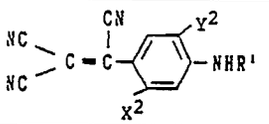
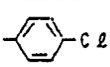
No.	R^1	R^2	X	Y
42		-C_4H_9(n)	-OCH_3	- H
43		〃	〃	〃
44		〃	〃	〃
45		〃	〃	〃
46		〃	〃	〃

TABLE 2



No.	R^1	X^2	Y^2
1	$-CH_3$	$-OC_4H_9(n)$	$-OC_4H_9(n)$
2	$-C_2H_5$	$-OCH_3$	$-OCH_3$
3	$-C_4H_9(n)$	〃	〃
4	$-C_4H_9(iso)$	〃	〃
5	$-C_8H_{17}(n)$	〃	〃
6	$-CH_2-CH=CH_2$	$-OC_2H_5$	$-OC_2H_5$
7	$-CH_2CH_2OH$	$-OC_3H_7(n)$	$-OC_3H_7(n)$
8	$-CH_2CH_2COOH$	$-OC_4H_9(n)$	$-OC_4H_9(n)$
9	$-CH_2CH_2CN$	〃	〃
10	$-CH_2CH_2NH_2$	〃	〃
11	$-CH_2CH_2C\ell$	$-OCH_3$	$-OCH_3$
12	$-CH_2CF_3$	〃	〃
13	$-CH_2-$ 	〃	〃
14	$-CH_2-$  $C\ell$	〃	〃
15	$-CH_2CH_2-$ 	〃	〃

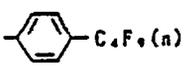
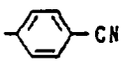
(continued)

TABLE 2 (continued)

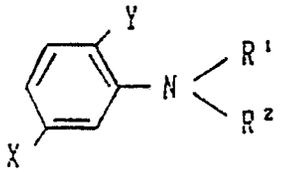
No.	R^1	X^2	Y^2
16	$-CH_2CH_2OCH_3$	$-OCH_3$	$-OCH_3$
17	$-CH_2CH_2OC_4H_9(n)$	〃	〃
18	$-(CH_2CH_2O)_2C_4H_9(n)$	〃	〃
19	$-CH_2CH_2OCH_2CH=CH_2$	〃	〃
20	$-CH_2CH_2O-$ 	〃	〃
21	$-CH_2CH_2OCH_2-$ 	〃	〃
22	$-CH_2CH_2OCOCH_3$	〃	〃
23	$-CH_2CH_2OCO-$ 	〃	〃
24	$-CH_2CH_2OCOCF_3$	〃	〃
25	$-CH_2CH_2COOCH_3$	〃	〃
26	$-CH_2CH_2COOC_4H_9(n)$	〃	〃
27	$-CH_2CH_2COOC_8H_{17}(n)$	〃	〃
28	$-CH_2CH_2COOCH_2-$ 	〃	〃
29	$-CH_2CH_2COO-CH_2-$ 	〃	〃
30	$-CH_2CH_2COO-CH_2-$ 	〃	〃
31	$-CH_2CH_2OCOOCH_3$	〃	〃

(continued)

TABLE 2 (continued)

No.	R^1	X^2	Y^2
32	$-CH_2CH_2OCOOC_4H_9(n)$	$-OCH_3$	$-OCH_3$
33	$-CH_2CH_2OCOOC_8H_{17}(n)$	〃	〃
34	$-CH_2CH_2OCOO-$ 	〃	〃
35	$-CH_2CH_2OCOOCH_2-$ 	〃	〃
36	$-CH_2-$ 	〃	〃
37	$-CH_2-$ 	〃	〃
38		$-OC_4H_9(n)$	$-OC_4H_9(n)$
39		$-OCH_3$	$-OCH_3$
40		〃	〃
41		〃	〃
42		〃	〃
43		〃	〃
44		$-OC_4H_9(iso)$	$-OC_4H_9(iso)$
45		〃	〃
46		〃	〃

The tricyanovinyl dyestuff of general formula (I) to be employed in the present invention can be produced according to conventionally known methods. For example, it may be obtained by reacting tetracyanoethylene with a compound represented by the following general formula (IV):



(IV)

(wherein R^1, R^2, X and Y have the same meanings as in general formula (I) given hereinabove) in an organic solvent.

In manufacturing the thermosensitive transfer recording sheet of the present invention, methods for forming the colorant layer containing the dyestuff of general formula (I) are not particularly limited. Generally, the dyestuff is dissolved or finely dispersed, along with a binder, in a medium to prepare an ink, which is then applied on a substrate and dried, thereby forming a colorant layer on the substrate.

The binder for use in the ink preparation should have good heat resistance for the purpose of preventing the heat fusion-adhesion of the binder onto an image-receiving surface at the time of transfer recording. Especially preferred binders are those having softening points and/or heat deformation temperatures of 100 °C or more.

Examples of the binder include water soluble resins such as cellulose resins, acrylic acid-based resins, starches, polyvinyl alcohols, and polyethylene oxides, organic solvent-soluble resins such as acrylic resins, methacrylic resins, polystyrenes, polycarbonates, polysulfones, AS resins, polyethersulfones, epoxy resins, polyvinyl acetals, phenoxy resins, polyvinyl butyrals, polyesters, ethyl cellulose, and acetyl celluloses.

According to the medium to be used for the ink preparation, a binder soluble or uniformly dispersible into the medium may be suitably selected from the above resins.

The amount of such a binder resin used is generally in the range of from 1 to 40% by weight, preferably from 5 to 30% by weight, based on the total amount of the ink composition.

Besides water, examples of the medium for use in ink preparation are organic solvents which include alcohols such as methyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, and isobutyl alcohol, Cellosolves such as methyl Cellosolve, ethyl Cellosolve and butyl Cellosolve, aromatics such as toluene, xylene, and chlorobenzene, esters such as ethyl acetate and butyl acetate, ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone, chlorine-containing solvents such as methylene chloride, chloroform, and trichloroethylene, ethers such as tetrahydrofuran and dioxane, N,N-dimethylformamide, and N-methylpyrrolidone. These may be used alone or as a mixture of two or more thereof.

In addition to the ingredients described above, organic or inorganic non-sublimable fine particles, a dispersant, an anti-static agent, an anti-blocking agent, an anti-foaming agent, an antioxidant, a viscosity modifier and a release agent may be incorporated into the ink if required and necessary.

Preferred examples of the substrate on which the ink is to be applied for preparing the thermosensitive transfer recording sheet include a sheet of paper such as capacitor paper and glassine paper, and a film of heat-resistant plastics such as polyesters, polycarbonates, polyamides, polyimides and polyaramides. The thickness of such a substrate is generally in the range of from 1 to 50 μm.

Among the above substrates, polyethylene terephthalate film is particularly advantageous because of its high mechanical strength, good solvent resistance and low cost. In some cases, however, even the polyethylene terephthalate film is not always satisfactory in heat resistance, resulting in insufficient running of the thermal head. Therefore, a heat-resistant resin layer containing a surface-active agent or lubricating heat-resistant particles may be provided on the side opposite to the colorant layer, thus providing improved thermal head-running properties.

Coating of the ink on the substrate can be accomplished by use of a reverse-roll coater, a gravure coater, a rod coater, or an air-doctor coater . The coating may be performed so as to give an ink coating layer thickness in the range of from 0.1 to 5 μm on a dry basis. (Reference may be made to Yuji Harasaki, Coating Techniques, published in 1979 by Maki Shoten, Japan.)

On the other hand, the ink composition for use in producing the thermosensitive transfer recording sheet, which ink composition is provided according to another aspect of the present invention, comprises a tricyanovinyl dyestuff represented by the above-described general formula (I), a binder resin, and a medium that may be an organic solvent and/or water.

The tricyanovinyl dyestuff is as described in detail hereinabove.

The binder to be used is suitably selected from the above-mentioned resins which are soluble in water or organic solvents, according to the medium to be used.

Of the above-mentioned resins, those having heat deformation temperatures and/or softening points of

100° C or more are particularly preferred. As the organic solvent, any of the above-mentioned solvents may be used. In addition to these, non-sublimable fine particles and additives such as a dispersant, anti-static agent, anti-blocking agent, anti-foaming agent, antioxidant, viscosity modifier, and release agent may be used as mentioned hereinabove.

The amount of the dyestuff of general formula (I) contained in the ink composition of the present invention is generally from 1 to 30% by weight, preferably from 3 to 20% by weight, based on the total amount of the ink composition.

The ink composition of the present invention may be prepared as follows. In one method, a liquid mixture composed of the dyestuff, a medium, and a resin is placed in a proper vessel equipped with a stirrer and the dyestuff is dissolved in the medium, with heating if required and with addition of additives if necessary, thereby to prepare an ink composition. Alternatively, the liquid mixture may be treated with a paint conditioner, a ball mill or a sand grinding mill to uniformly disperse the dyestuff into the medium, with addition of additives if necessary, thereby to prepare an ink composition.

Because the tricyanovinyl dyestuff of general formula (I) which is employed in the thermosensitive transfer recording sheet of the present invention possesses a vivid magenta color, it is suited for use in combining it with suitable cyan color dyestuffs and suitable yellow color dyestuffs to attain full-color recording with good color reproduction. Further, because the dyestuff of general formula (I) readily sublimates and/or heat-diffuses and has a high molecular absorption coefficient, recorded images having high color densities can be obtained at a high speed without a heavy load on the thermal head. The dyestuff also has good stability to heat, light, moisture and chemicals, and, hence, it never undergoes thermal decomposition during transfer recording and the permanence properties of the resulting recorded images are also good, particularly in light resistance. In addition, because the dyestuff of general formula (I) has good solubility in organic solvents and good dispersibility into water, it is easy to prepare an ink composition in which the dyestuff has been uniformly dissolved or dispersed at a high concentration, and by use of such an ink composition, a thermosensitive transfer recording sheet having a colorant coating layer in which the dyestuff is distributed uniformly at a high concentration can be obtained. Therefore, by use of such a thermosensitive transfer recording sheet, printed images having good homogeneity and color density can be obtained.

In practicing transfer recording using the thermosensitive transfer recording sheet of the present invention, infrared rays or laser light as well as a thermal head may be utilized as a heating means.

It is also possible to coat the ink composition of the present invention on a film that is heated by application of electric current and to use the resulting sheet as an electrically-heated thermosensitive sheet.

The present invention will be explained below in more detail by reference to the following examples, which should not be construed to be limiting the scope of the invention. In these examples, all parts are by weight.

EXAMPLE 1

(a) Preparation of Ink

Dyestuff No. 4 in Table 1	5 g
Polysulfone resin*	10 g
Chlorobenzene	100 g
Total	115 g

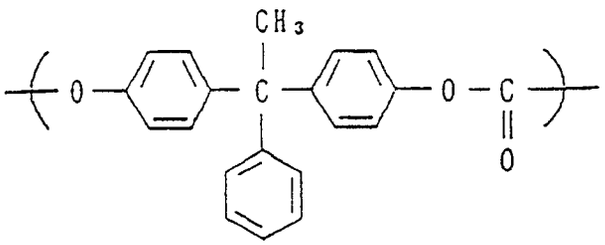
* trade name, "Udel P-1700"; manufactured by Nissan Chemical Industries, Ltd., Japan; heat-deformation temperature (ASTM D-648) 175°C.

A mixture having the above composition was treated with a paint conditioner for 10 minutes, thereby preparing an ink.

(b) Preparation of Transfer Recording Sheet

The above-obtained ink was coated with a wire bar on a polyethylene terephthalate film (6 μm thick) whose back side had undergone treatment for imparting heat resistance and lubricating properties. The coating was then dried (coating layer dry thickness, about 1 μm) to obtain a transfer recording sheet.

The above treatment for imparting heat resistance and lubricating properties to the polyethylene terephthalate film was conducted by coating the film with a composition consisting of 8 parts of a polycarbonate resin having the repeating unit of the formula



1 part of a phosphoric ester-type surfactant (trade name, "Plysurf A-208B"; manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd., Japan), and 91 parts of toluene, and drying the coating (coating layer dry thickness, about 0.5 μm).

(c) Preparation of Image-Receiving Sheet

A composition consisting of 10 parts of a saturated polyester resin (trade name, "TP-220"; manufactured by Nihon Gosei Co., Ltd., Japan), 0.5 part of an amino-modified silicone (trade name, "KF 393"; manufactured by Shin-Etsu Chemical Co., Ltd., Japan), 15 parts of methyl ethyl ketone, and 15 parts of xylene was coated on a synthetic paper (trade name, "Yupo FPG 150"; manufactured by Oji-Yuka Co., Ltd., Japan) with a wire bar, and then dried (coating layer dry thickness, about 5 μm). The coated synthetic paper was further heat-treated in an oven at 100 °C for 30 minutes to prepare an image-receiving sheet.

(d) Transfer Recording

The transfer recording sheet prepared in (b) above was superimposed on the image-receiving sheet in such a manner that the ink coating side of the transfer recording sheet was in contact with the receiving sheet, and recording was conducted by use of a thermal head under the conditions shown below. As a result, a recorded image which was of a vivid magenta color and had a uniform color density as shown in Table 3 could be obtained.

Recording Conditions

Lineal density for main scanning and sub-scanning:	8 dots/mm
Recording power:	0.25 W/dot
Heating time for head:	10 msec

Color density was measured with densitometer TR-927 manufactured by Macbeth Corporation, U.S.A.

The light resistance of the recorded image obtained was examined by means of a carbon arc fade meter (manufactured by Suga Testing Machine Co., Ltd., Japan) at a black panel temperature of 63±2 °C. The degree of discoloration through a 40-hour irradiation in the light resistance test was shown in Table 3 in terms of ΔE^* value. Further, the transfer recording sheet and the print obtained were found to be stable to heat and moisture and show good storage stability in the dark.

The dyestuff used in this example had been synthesized by reacting 3-methoxy-N,N-di-isobutylaniline with tetracyanoethylene in N,N-dimethylformamide. Its maximum absorption wavelength in acetone was as

shown in Table 3 and its melting point was 116-117 °C.

EXAMPLES 2 TO 10

Inks and transfer recording sheets were prepared and transfer recording was conducted in the same manner as in Example 1 except that in place of the dyestuff used in Example 1, the dyestuffs shown in Table 3 were used. As a result, recorded images which were of a vivid magenta color and respectively had color densities shown in Table 3 could be obtained, and the light resistance of each recorded image was good as shown in Table 3.

EXAMPLE 11

An ink and a transfer recording sheet were prepared and transfer recording was conducted in the same manner as in Example 1 except that dyestuff No. 4 in Table 2 given hereinabove was used in place of the dyestuff used in Example 1. The results obtained are shown in Table 3.

The dyestuff used in this example had been synthesized by reacting 2,5-dimethoxy-N-isobutylaniline with tetracyanoethylene in N,N-dimethylformamide. Its maximum absorption wavelength in acetone was as shown in Table 3 and its melting point was 181-182 °C.

EXAMPLES 12 TO 20

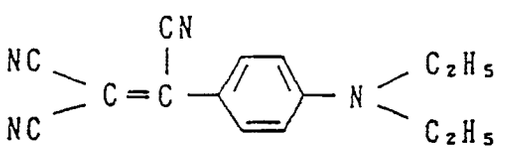
Inks and transfer recording sheets were prepared and transfer recording was conducted in the same manner as in Example 1 except that in place of the dyestuff used in Example 1, the dyestuffs shown in Table 3 were used. As a result, recorded images which were of a vivid magenta color and respectively had color densities shown in Table 3 could be obtained, and the light resistance of each recorded image was good as shown in Table 3.

COMPARATIVE EXAMPLES 1 TO 8

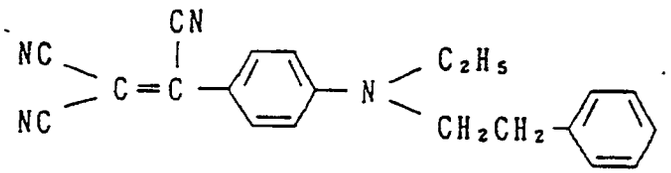
Inks and transfer recording sheets were prepared and transfer recording was conducted in the same manner as in Example 1 except that the dyestuffs shown below were used in place of the dyestuff used in Example 1. The results obtained are summarized in Table 3.

Dyestuffs used in Comparative Examples

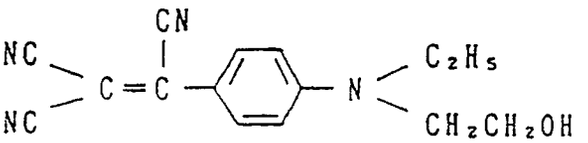
Comparative Example 1 (Example 1 of JP-A-59-78896)



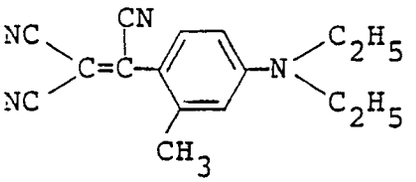
Comparative Example 2 (Example 1 of JP-A-60-31563)



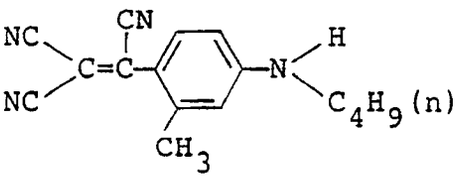
Comparative Example 3 (Reference Example 1 of JP-A-63-203393)



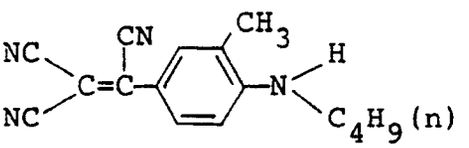
Comparative Example 4



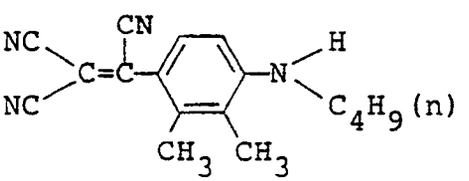
Comparative Example 5



Comparative Example 6



Comparative Example 7



Comparative Example 8

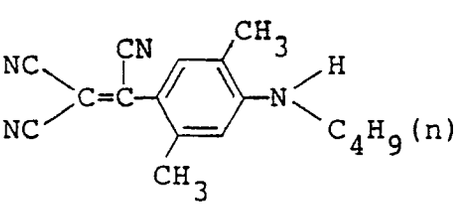


TABLE 3

	Dye No. (Table No.)	Maximum absorption wavelength* (nm)	Color density	Light resistance(ΔE^*)
Example 1	4 (1)	523	2.03	6.11
Example 2	3 (1)	501	1.98	3.85
Example 3	2 (1)	523	2.05	4.52
Example 4	6 (1)	518	2.01	7.21
Example 5	13 (1)	518	1.92	6.85
Example 6	15 (1)	524	1.98	6.23
Example 7	17 (1)	518	1.92	6.51
Example 8	19 (1)	520	1.93	6.37
Example 9	37 (1)	520	1.98	6.32
Example 10	38 (1)	524	1.91	6.51
Example 11	4 (2)	542	2.05	3.12
Example 12	3 (2)	542	2.02	5.21
Example 13	5 (2)	543	1.88	5.35
Example 14	6 (2)	538	2.01	5.51
Example 15	15 (2)	544	1.95	4.15
Example 16	13 (2)	538	1.90	4.22
Example 17	17 (2)	540	1.95	4.05
Example 18	20 (2)	540	1.91	4.02
Example 19	37 (2)	541	1.95	4.32
Example 20	38 (2)	543	1.86	3.85

(continued)

TABLE 3 (continued)

	Dye No. (Table No.)	Maximum absorption wavelength* (nm)	Color density	Light resistance(ΔE^*)
Comparative Example 1	-	520	2.05	32.70
Comparative Example 2	-	521	1.95	30.51
Comparative Example 3	-	521	1.75	44.65
Comparative Example 4	-	540	2.06	25.5
Comparative Example 5	-	520	1.80	42.1
Comparative Example 6	-	510	1.88	27.5
Comparative Example 7	-	524	1.44	33.2
Comparative Example 8	-	526	1.92	29.1

Note: * The maximum absorption wavelength was measured in acetone.

EXAMPLE 21

A transfer recording sheet was prepared and transfer recording was conducted in the same manner as in Example 1 except that an ink prepared according to the following formulation was used in place of the ink used in Example 1. As a result, a recorded image which was of a vivid magenta color and had a uniform color density of 2.15 could be obtained. Further, the recorded image was subjected to a light resistance test and the transfer recording sheet and recorded image were subjected to a storage stability test in the dark. As a result, good results were obtained in each test.

Preparation of Ink

Same dyestuff as that in Example 1 (dyestuff No. 4 in Table 1)	5 g
AS resin**	10 g
Toluene	90 g
Cyclohexanone	10 g
Total	115 g

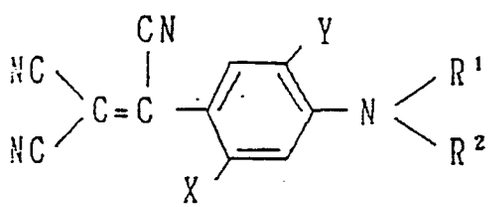
** AS resin: trade name, "Denka AS-S"; manufactured by Denki Kagaku Kogyo K.K., Japan; Vicat softening point (JIS K-6870) 105°C.

EXAMPLE 22

A transfer recording sheet was prepared and transfer recording was conducted in the same manner as in Example 21 except that in place of the dyestuff used in Example 21, the same dyestuff as that used in Example 11, i.e., dyestuff No. 4 in Table 2, was used. As a result, a recorded image which was of a vivid magenta color and had a uniform color density of 2.15 could be obtained. Further, the recorded image was subjected to a light resistance test and the transfer recording sheet and recorded image were subjected to a storage stability test in the dark. As a result, good results were obtained in each test.

Claims

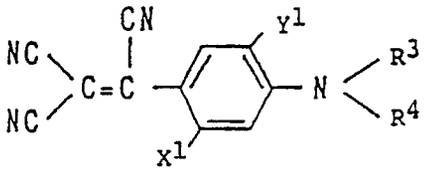
1. A thermal transfer recording sheet comprising a substrate having thereon a colorant layer, said colorant layer comprising a binder and a dyestuff represented by the following general formula (I):



(I)

wherein X and Y independently represent a hydrogen atom, a lower alkyl group, or a lower alkoxyl group, provided that either of X and Y represents a lower alkoxyl group; and R^1 and R^2 independently represent a hydrogen atom, a substituted or unsubstituted alkyl group, a cycloalkyl group, an allyl group, or a substituted or unsubstituted phenyl group, provided that in the case where both of X and Y represent a lower alkoxyl group, R^1 represents a hydrogen atom.

2. A sheet as claimed in claim 1, wherein said dyestuff is represented by the following general formula (II)



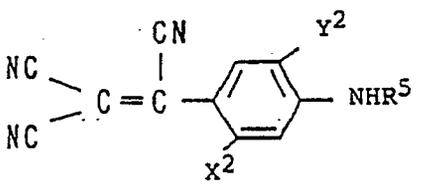
(II)

wherein R^3 and R^4 independently represent a hydrogen atom, a substituted or unsubstituted alkyl group, a cycloalkyl group, allyl group, or a substituted or unsubstituted phenyl group; and X^1 and Y^1 independently represent a hydrogen atom, a lower alkyl group, or a lower alkoxyl group, provided that either of X^1 and Y^1 represents a lower alkoxyl group and the remaining one represents another group.

3. A sheet as claimed in claim 1, wherein said dyestuff is represented by general formula (I) in which R^1 represents a hydrogen atom.

4. A sheet as claimed in claim 1, wherein said dyestuff is represented by general formula (I) in which one of X and Y is a lower alkoxyl group and the other is a lower alkoxyl group or a lower alkyl group.

5. A sheet as claimed in claim 1, wherein said dyestuff is represented by the following general formula (III)



(III)

wherein R^5 represents a substituted or unsubstituted alkyl group, a cycloalkyl group, allyl group, or a substituted or unsubstituted phenyl group, and X^2 and Y^2 independently represent a lower alkoxyl group.

6. A sheet as claimed in claim 1, wherein said dyestuff is represented by general formula (I) in which R^1 and R^2 independently represent a hydrogen atom; a straight-chain or branched alkyl group which has 1 to 8 carbon atoms and which may be substituted with a substituent selected from the group consisting of phenyl group which may be substituted with hydroxyl group, carboxyl group, cyano group, amino group, or a halogen atom, an alkoxyl group, an alkoxyalkoxyl group, allyloxy group, an aryloxy group, an aralkyloxy group, an acyl group, a substituted or unsubstituted alkoxycarbonyl group, a substituted or unsubstituted alkoxycarbonyloxy group, and a heterocyclic group; cyclohexyl or cyclopentyl group; allyl group; or phenyl group which may be substituted with a substituent selected from the group consisting of a straight-chain or branched alkyl group having 1 to 8 carbon atoms, a straight-chain or branched alkoxyl group having 1 to 4 carbon atoms, a halogen atom, nitro group, cyano group, and trifluoromethyl group.

7. A sheet as claimed in claim 1, wherein said dyestuff is represented by general formula (I) in which R^1 and R^2 independently represent a hydrogen atom, a straight-chain or branched alkyl group having 1 to 8 carbon atoms, or an alkoxyalkyl group having 3 to 8 carbon atoms.

8. A sheet as claimed in claim 1, wherein said binder is a resin selected from the group consisting of water-soluble resins which are cellulose resins, acrylic acid-based resins, polyvinyl alcohols, polyethylene oxides, and starches and organic solvent-soluble resins which are acrylic resins, methacrylic resins, polystyrenes, polycarbonates, polysulfones, AS resins, polyethersulfones, epoxy resins, polyvinyl acetals, phenoxy resins, polyvinyl butyrals, polyesters, ethyl celluloses, and acetyl celluloses.

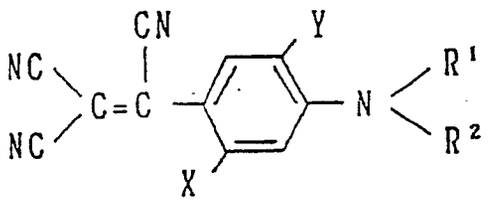
9. A sheet as claimed in claim 1, wherein said substrate is a sheet of paper selected from capacitor paper and glassine paper or a film of a heat-resistant plastic selected from the group consisting of polyesters, polycarbonates, polyamides, polyimides, and polyaramids, and has a thickness in the range of from 1

to 50 μm.

10. A sheet as claimed in claim 1, wherein said substrate is a polyethylene terephthalate film.

11. A sheet as claimed in claim 1, wherein said substrate has a heat-resistant resin layer on the side thereof opposite to the colorant layer.

12. An ink composition for use in producing a thermal transfer recording sheet, said ink composition comprising a dyestuff represented by the following general formula (I), a binder resin, and a medium:



(I)

wherein X and Y independently represent a hydrogen atom, a lower alkyl group, or a lower alkoxyl group, provided that either of X and Y represents a lower alkoxyl group; and R^1 and R^2 independently represent a hydrogen atom, a substituted or unsubstituted alkyl group, a cycloalkyl group, an allyl group, or a substituted or unsubstituted phenyl group, provided that in the case where both of X and Y represent a lower alkoxyl group, R^1 represents a hydrogen atom.

13. An ink composition as claimed in claim 12, wherein said medium is water, an organic solvent, or a mixture thereof.

14. An ink composition as claimed in claim 13, wherein said organic solvent is a single compound or a mixture of two or more compounds, said compound and compounds being selected from the group consisting of alcohols which are methyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, and isobutyl alcohol, Cellosolves which are methyl Cellosolve, ethyl Cellosolve and butyl Cellosolve, aromatics which are toluene, xylene, and chlorobenzene, esters which are ethyl acetate and butyl acetate, ketones which are acetone, methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone, chlorine-containing solvents which are methylene chloride, chloroform, and trichloroethylene, ethers which are tetrahydrofuran and dioxane, N,N-dimethylformamide, and N-methylpyrrolidone.

15. An ink composition as claimed in claim 12, wherein said binder is a resin selected from the group consisting of water-soluble resins which are cellulose resins, acrylic acid-based resins, polyvinyl alcohols, polyethylene oxides, and starches and organic solvent-soluble resins which are acrylic resins, methacrylic resins, polystyrenes, polycarbonates, polysulfones, AS resins, polyethersulfones, epoxy resins, polyvinyl acetals, phenoxy resins, polyvinyl butyrals, polyesters, ethyl celluloses, and acetyl celluloses.

16. An ink composition as claimed in claim 12, wherein the content of said binder is in the range of from 1 to 40% by weight based on the total amount of the ink composition.

17. An ink composition as claimed in claim 12, wherein the content of said dyestuff of general formula (I) is in the range of from 1 to 30% by weight based on the total amount of the ink composition.

18. An ink composition as claimed in claim 12, which further contains organic or inorganic non-sublimable fine particles, a dispersant, an anti-static agent, an anti-blocking agent, an anti-foaming agent, an antioxidant, a viscosity modifier, and a release agent.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 1766

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X,A	EP-A-0 258 856 (BASF AG.) * page 3, line 39 - page 5, line 4 * Table 1, pages 11,12 *	1-3,5-18, 4	B 41 M 5/38
A	GB-A-2 159 971 (MITSUBISHI CHEMICAL INDUSTRIES LIMITED) * page 2, lines 40 - 50; claims 3, 6 * * page 33; figure 7 *	1-18	
A	EP-A-0 279 467 (DAI NIPPON INSATSU KABUSHIKI KAISHA) * page 9, lines 40 - 54 *	1-18	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

B 41 M

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	19 April 91	BACON,A.J.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
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