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Thermal transfer image recording method.

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A thermal transfer image recording method is disclosed. The method comprises the steps of (1) imagewise exposing a recording element to high intensity light, which comprises a support having thereon a colorant layer, and a colorant barrier layer containing an infrared absorbing substance and being provided on said color material layer, to imagewise ablate said colorant barrier layer, (2) contacting the surface of said colorant barrier layer with the surface of image receiving layer of an image receiving element, and (3) transferring colorant of said colorant layer through ablated portion of said colorant barrier layer to said image receiving layer by applying heat or pressure.

EP 0 618 081 A1

Field of the Invention

This invention relates to a thermal-transfer image-recording method capable of providing a recorded image with a high resolving power.

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Background of the Invention

The thermal-transfer recording method have included, conventionally, a process in which a thermal-transfer recording element comprising a base member provided thereon with a thermally fusible colorant layer or a colorant layer containing a thermally sublimable dye is made opposite to an image-receiving element, and a heat source being controlled by an electric signal sent from a thermal head or an electricity feeding head is brought into pressure contact from the ink sheet, i.e., the recording element, so that an image can be transferred and then recorded. A thermal-transfer recording has such an advantage that a noiseless operation, a maintenance-free, a low cost, an easy colored recording and a digital recording can be performed, so that the thermal recording have been utilized in various fields such as a variety of printers, recorders, facsimiles and the terminals for computers.

In medical and printing fields, on the other hand, there have recently been the demands for a recording process capable of performing the so-called digital recording in which a high resolving powder, a high-speed recording and an image processing can be provided. However, in the thermal-transfer recording processes in which a conventional thermal head or an electricity feeding head has been used as a heat source, an exothermic element has been hardly able to have any high density and any highly resolving image, because of the life of the exothermic element of a head.

For solving the above-mentioned problems, there have been proposed for a thermal-recording technique in which laser beam is used as the heat source, in Japanese Patent Publication Open to Public Inspection (hereinafter referred to as JP OPI Publication) Nos. 49-15437/1974, 49-17743/1974, 57-87399/1982 and 59-143659/1984. In a thermal recording technique in which laser beam is used as the heat source, a resolving powder can be enhanced by narrowing a laser spot down. However, when recording an image with a laser beam, a recording time cannot be shortened unless the spots of a recording medium are scanned at a high speed, because it has been usual that a recording is carried out by scanning minute spots. In this case, it is generally disadvantageous to improve a recording speed, as compared to the case where a flood exposure is made or a line thermal head is used. It is also general that a heating given by light is relatively low as compared to a heating given by an exothermic element such as a thermal head. Also from this point, a heat mode recording of the light-heat conversion type utilizing a laser beam or the like is disadvantageous, in the present situation, for improving a recording speed.

On the other hand, JP OPI Publication Nos. 63-35385/1988 and 63-35387/1988 describe each the following technique; a sublimable ink layer and a protective layer containing a thermoplastic resin as a principal component are provided onto a support, and the protective layer is imagewise ablated by laser beam. Thereafter, the surface of the protective layer is brought into close contact with an image-receiving sheet and heat is applied by laser beam or a thermal head from the side of the support having the sublimable ink layer, so that an image information can thermally be transferred thereby to an image-receiving layer. The points of the above-mentioned technique are that a laser beam is output as few as possible, that a protective layer containing a thermoplastic resin as a principal component is fused, and that holes are made by the fused portions pulled to the circumferential portions by the surface tension of the fused thermoplastic resin.

JP OPI Publication No. 4-201486/1992 and EP 489972 (1992) disclose each a technique in which vacuum-evaporated metal layer is applied to a dye-barrier layer, that is equivalent to the aforementioned protective layer.

In these techniques, heating required for an image transfer shall not relatively be limited, because a colorant transfer itself is performed in another means, as compared to a system in which a colorant is transferred by heat applied from the aforementioned laser beam. However, in particular, the above-mentioned patents do not imply any clear cognizance of an exposure light intensity, nor of which layer, an ink layer or a protective layer, can serve as a layer capable of absorbing rays of light.

Furthermore, in the case of using an evaporated metal layer as a protective layer, the metal layer is evaporated on the colorant barrier layer in a vacuum. The evaporation process accompanies a problem that the dye in the colorant layer is sublimated at the time of evaporation.

On the other hand, US Patent Nos. 5,156,938 and 5,171,650 describe each the following technique as another technique; an explosion is produced by irradiating an extremely high power density laser beam to an ink layer or to a layer interposed between a support and an ink layer, and the ink layer is blown off to an

image-receiving medium by the explosive force, so that an image can be transferred to the image-receiving element.

Summary of the Invention

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It is an object of the invention to provide an image-recording process and the material for the same, each in which an image having a high resolving power can be recorded and the process can relatively be simplified.

10 The present inventors have discovered the following technique; a colorant barrier layer is so exploded as to be ablated by irradiating a high power density exposure light such as 100,000 w/cm² or more to the colorant barrier layer, and the colorant can be transferred to an image-receiving layer through the resulting minute holes by applying heat or pressure. The present inventors have also discovered a component effective to the above-mentioned colorant barrier layer, so that the invention could finally be completed. To be more concrete, the above-mentioned objects of the invention can be achieved with the following
15 constitution.

The thermal transfer image recording method of the invention comprises the steps of (1) imagewise exposing a recording element to high intensity light, which comprises a support having thereon a colorant layer containing a colorant, and a colorant barrier layer containing an infrared absorbing substance and being provided on said colorant layer, to imagewise ablate said colorant barrier layer, (2) contacting the
20 surface of said colorant barrier layer with the surface of image receiving layer of an image receiving element, and (3) transferring colorant of said colorant layer through ablated portion of said colorant barrier layer to said image receiving layer by applying heat or pressure.

Further in the above-mentioned thermal transfer recording process, it can be said to be a preferable embodiment of the invention when the following factors can be satisfied, because the effects of the invention can more be displayed. A high intensity exposure is to have a power density of not lower than
25 100000 W/cm²; an exposure speed is to be not slower than 1 m/second; a high intensity exposure is to be made with laser beam; a high intensity exposure is to be made from the side of a colorant barrier layer.

Brief Description of the Drawings

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Fig. 1 is a typical illustration of the time-sequential steps of a recording process in which a thermal-transfer type recording material of the invention; wherein

- 1 A support for a recording element;
- 2 A colorant layer;
- 35 3 A colorant barrier layer;
- 4 A support for an image-receiving element; and
- 5 An image-receiving layer

Detailed Description of the Invention

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As shown in Fig. 1, for example, a thermal transfer recording element of the invention, hereinafter sometimes simply referred to as a recording element, is basically comprised of support 1 laminated thereon with colorant layer 2 and colorant barrier layer 3 in this order.

The supports shall not particularly be limitative, provided that a support is excellent in dimensional
45 stability and durable against a heat source such as laser. The supports applicable thereto include, for example, a thin-leaf paper such as condenser paper and glassine paper; and a heat resistive plastic film such as those made of polyethylene terephthalate, polyamide, polycarbonate, polysulfone, polyvinyl alcohol, cellophane and polystyrene.

The supports are to have a thickness ordinarily within the range of, preferably, 2 to 200μm and, more
50 preferably, 25 to 100μm.

A colorant layer contains a binder besides a colorant. If required, an optional component such as an additive may also be contained therein.

In the invention, it is preferable that a colorant which is to be transferred to an image-receiving layer is to be a thermally diffusible dye. However, without limitation thereto, a colorant may also be other dyes or
55 pigments, and when they may be transferred, it is further allowed to take the so-called thermally fusible transfer system in which a colorant and the binder component thereof may be transferred together.

There is no special limitation to the thermally diffusible dyes, provided that they are thermally diffusible or sublimable. The thermally diffusible cyan dyes include, for example, those of the naphthoquinone type,

anthraquinone type and azomethine type, which are described in JP OPI Publication Nos. 59-78895/1984, 59-227948/1984, 60-24966/1985, 60-53563/1985, 60-130735/1985, 60-131292/1985, 61-19936/1986, 61-22993/1986, 61-31292/1986, 61-31467/1986, 61-35994/1986, 61-49893/1986, 61-148269/1986, 62-191191/1987, 63-91287/1988, 63-91288/1988 and 63-290793/1988.

5 The thermally diffusible magenta dyes include, for example, those of the anthraquinone type, the azo type and azomethine type, which are described in JP OPI Publication Nos. 59-78896/1984, 60-30392/1985, 60-30394/1985, 60-253595/1985, 61-262190/1986, 63-5992/1988, 63-205288/1988, 64-159/1989 and 64-63194/1989.

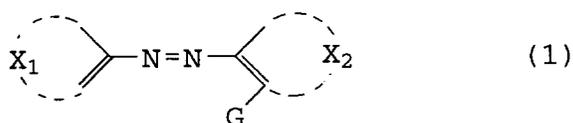
10 The thermally diffusible yellow dyes include, for example, those of the methine type, the azo type, the quinophthalone type and the anthraisothiazole type, which are described in JP OPI Publication Nos. 59-78896/1984, 60-27594/1985, 60-31560/1985, 60-53565/1985, 61-12394/1986 and 63-122594/1988.

15 As for a thermally diffusible dye, it is suitable to make use of an azomethine dye obtained upon making coupling reaction of a compound having an opened- or closed-chain type active methylene group with an oxidant of a p-phenylene diamine or p-aminophenol derivative, and an indoaniline dye obtained upon making reaction of a phenol or naphthol derivative with an oxidation product of a p-phenylene diamine or a p-aminophenol derivative.

Among these dyes, those each capable of forming a chelate compound with a metal ion are preferable.

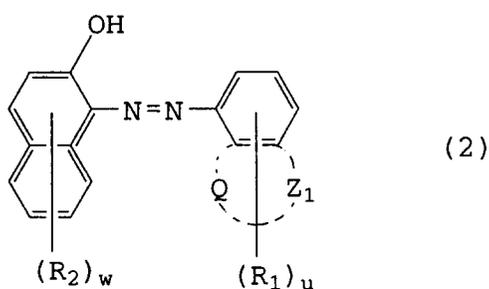
20 The dye capable of forming a chelate compound means a dye changeable into a chelate compound after chelating reaction with a metal ion, in more detail, a dye having at least two or more ligands, or a group capable of forming a chelating bond with a metal ion, in the molecule thereof and made these ligand present in a position where a cyclic structure such as 4-, 5-, 6- or 7-member ring can be taken after the ligands are each coordinate to a metal ion. The above-mentioned groups each capable of coordinating to a metal ion, i.e., a chelating group or a ligand, include a group having, for example, -OH, -COOH, -NH₂, -NH-, -N=, -CO-, -O-, -NHCO-, -S-, -SO-, -P=, -NO or -N=N-.

25 The preferable dyes capable of forming a chelating compound are ones represented by the following Formula 1.



35 In the above formula 1, X₁ is a group of 5 to 7 atoms necessary to complete an aromatic carbon ring or an aromatic heterocyclic ring provided that at least one atom adjacent to the carbon atom bonded to the nitrogen atom of the azo bonding, is a carbon atom having a substituent capable of forming a chelating bond with a metal ion or a nitrogen atom; X₂ is a group of 5 to 7 atoms necessary to complete an aromatic carbon ring or an aromatic heterocyclic ring; and G is a hydrogen atom or a group capable of forming a chelating bond with a metal ion.

40 The dyes represented by the above formula 1 include those represented by the following formulas 2 through 8.

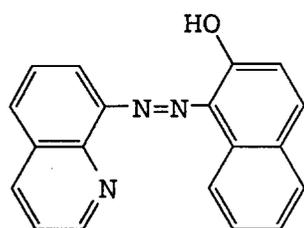


55 In formul 2, Z₁ is a group of atoms necessary to form a 5- or 6-member heterocyclic ring together with the two carbon atom of the benzene ring and Q; Q is -O-, -S-, -N= or -N(R)-, in which R is a hydrogen atom or an alkyl group; R₁ and R₂ are each a hydrogen atom or a monovalent group; and u and w are each an integer of 1 to 5.

The following are exemplified dyes represented by formula 2.

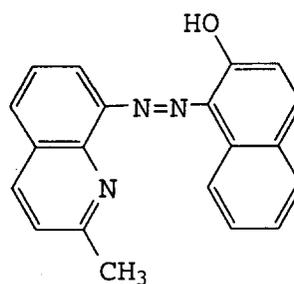
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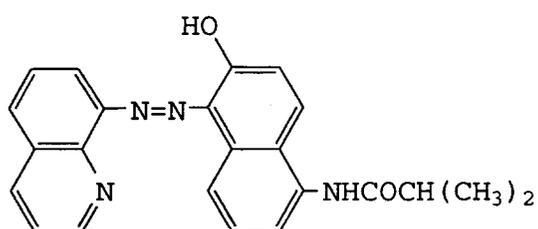
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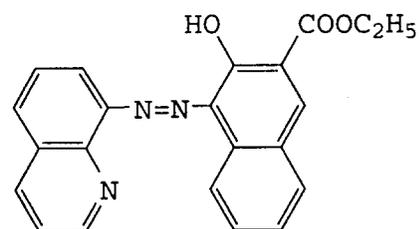
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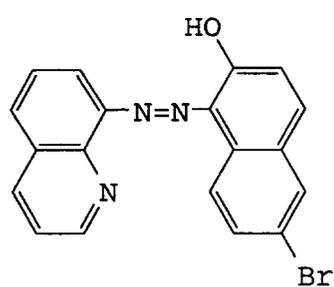
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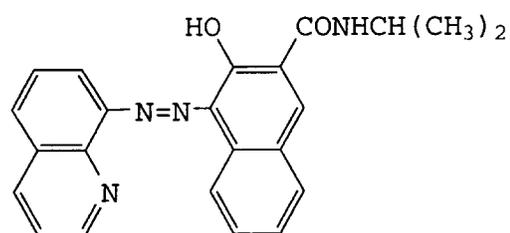
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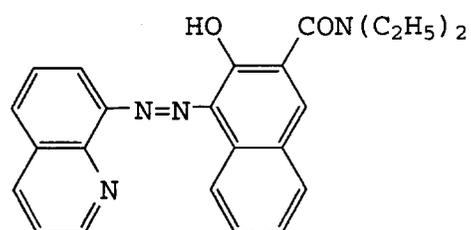
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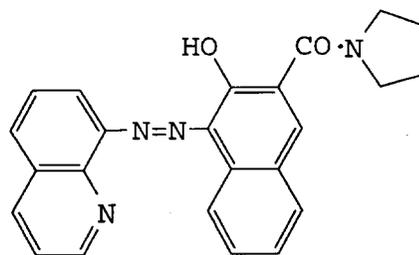
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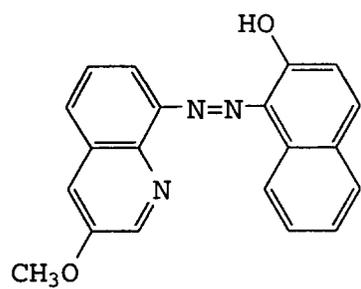


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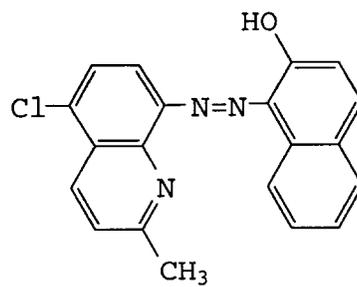
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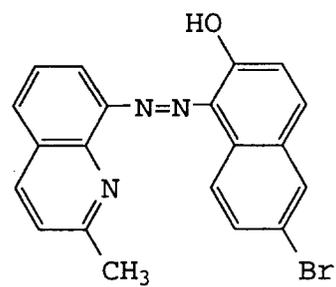
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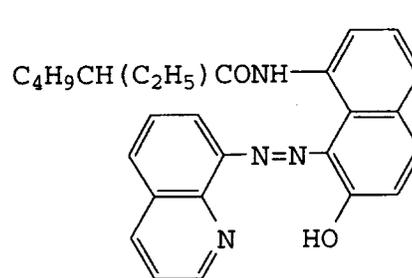
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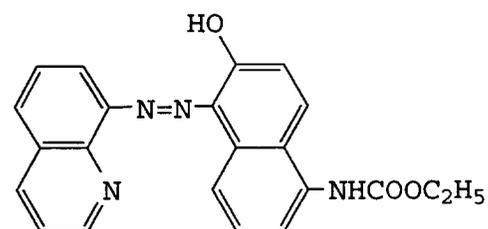
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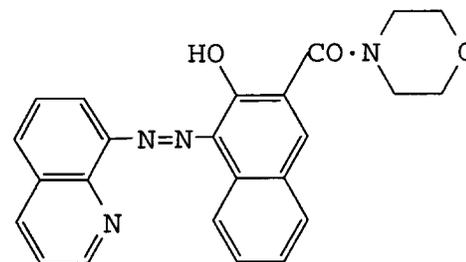
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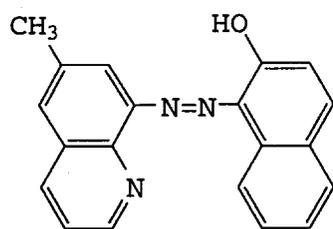
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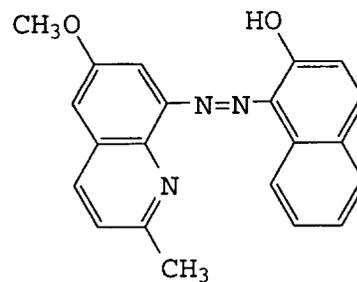
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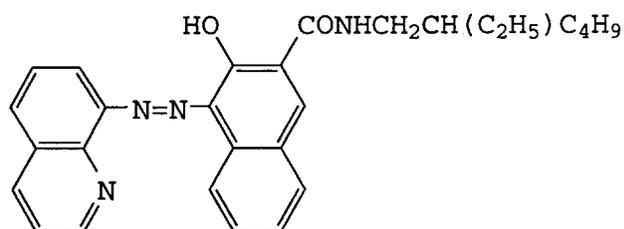
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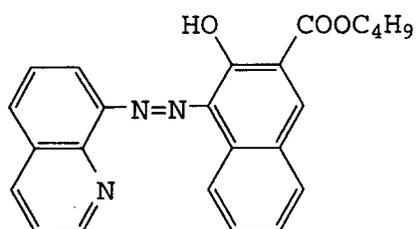
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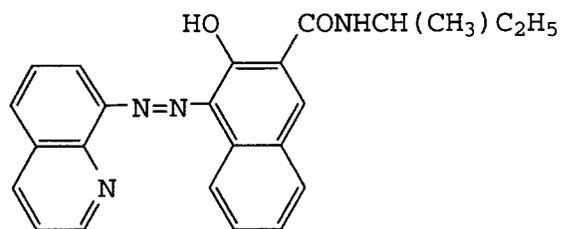
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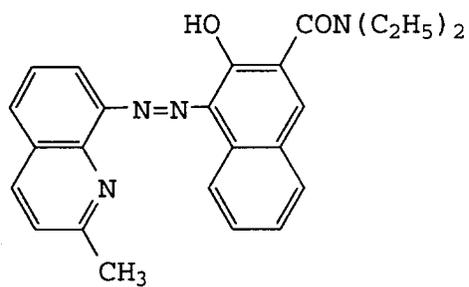
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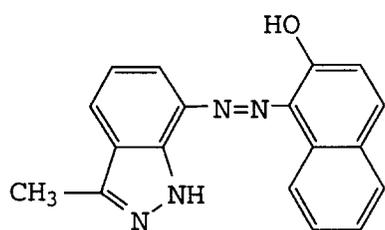
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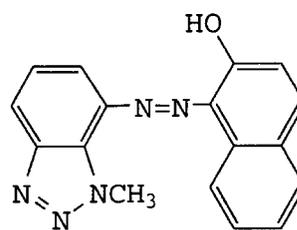
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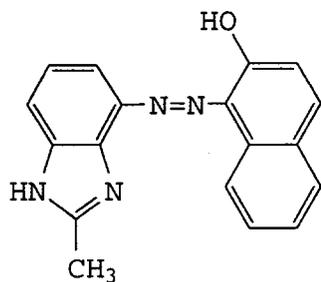
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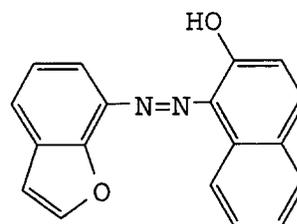
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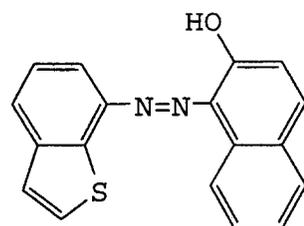
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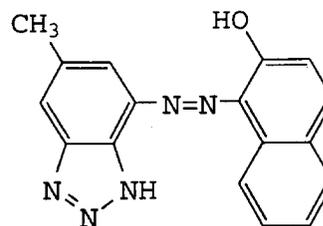
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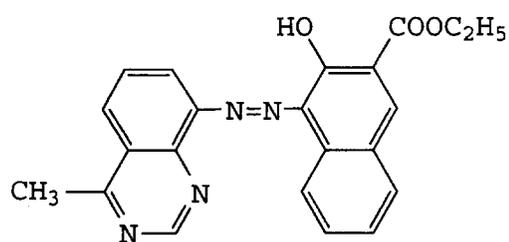


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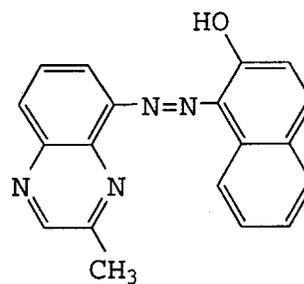
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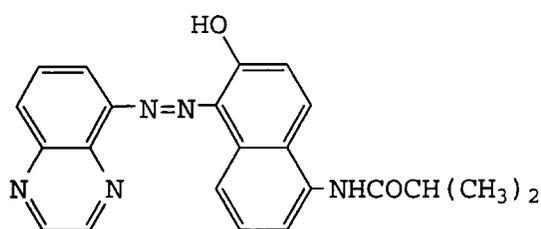
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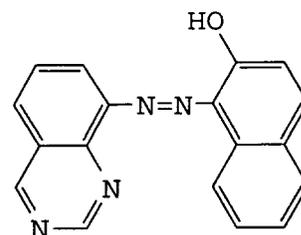
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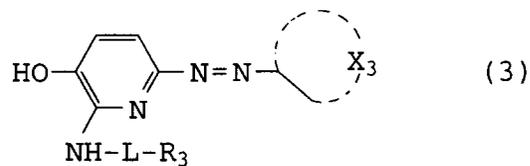


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In formula 3, L is $-\text{CON}(\text{R}')-$, $-\text{COO}-$ or $-\text{SO}_2-$, in which R' is an alkyl group or a hydrogen atom; X_3 is a nitrogen-containing heterocyclic ring or an aromatic carbon ring, provided that the atom adjacent to the carbon atom linked to the azo group is a nitrogen atom or a carbon atom having a group capable of forming chelating bond with a metal ion; and R_3 is a hydrogen atom, an aliphatic group or a heterocyclic group.

Exemplified dyes represented by the above formula 3 are as follows:

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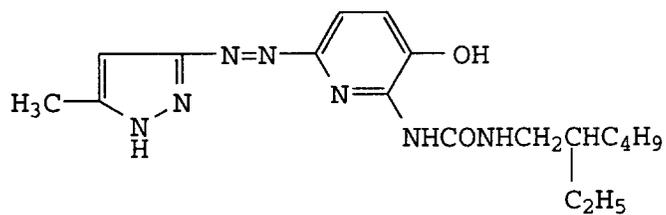
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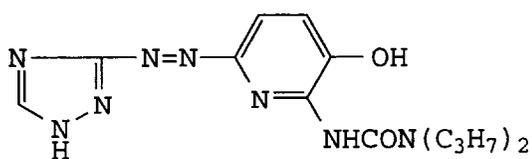
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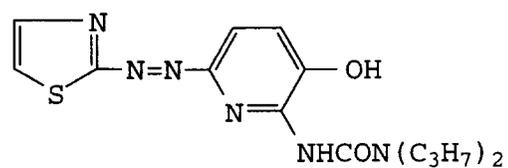
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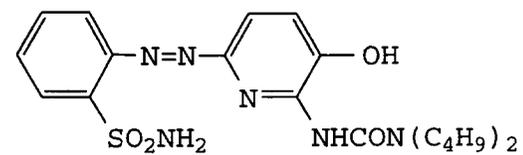
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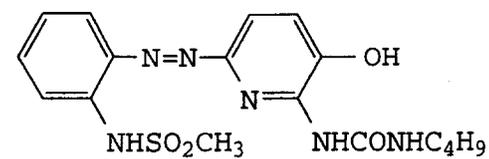
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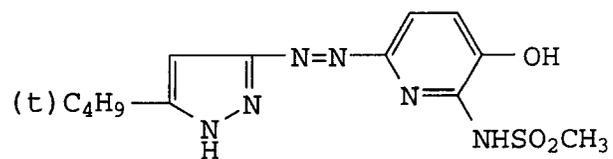


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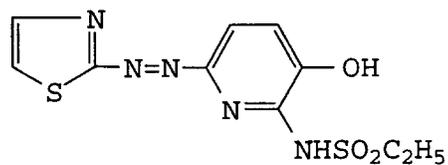
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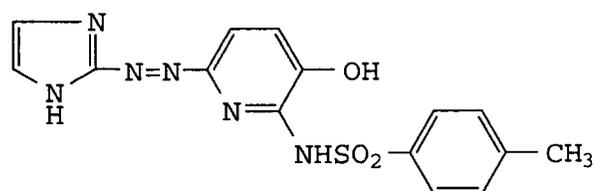
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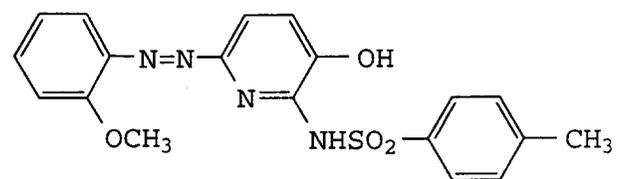
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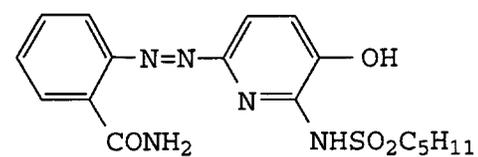
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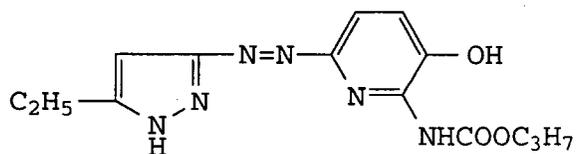


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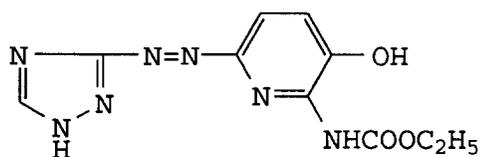
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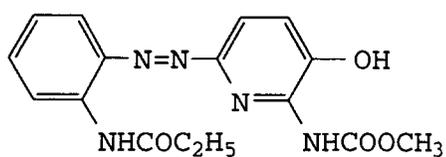
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3-13

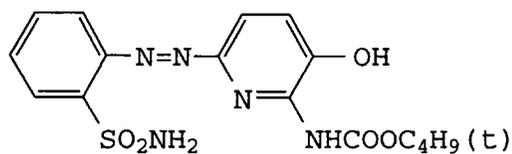
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3-14

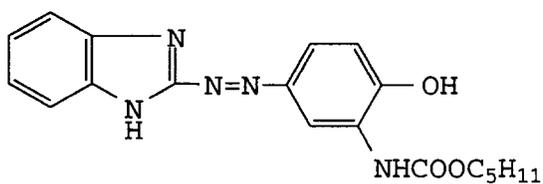
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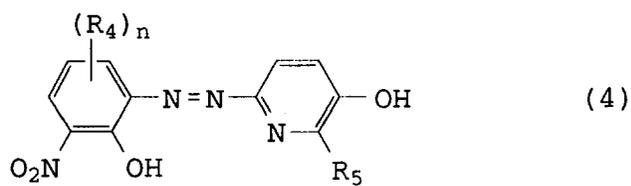
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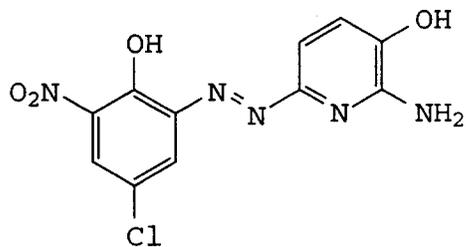
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In formula 4, R_4 is a substituent; n is an integer of 0 to 3, the plurality of R_4 s may be the same or different when n is 2 or 3; and R_5 is a hydroxyl group or an amino group.

Exemplified dyes represented by Formula 4 are as follows:

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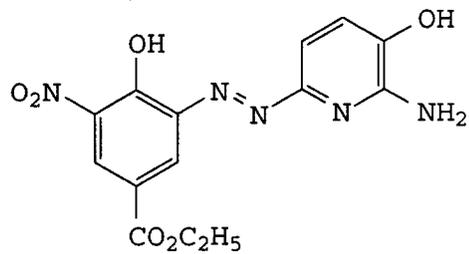
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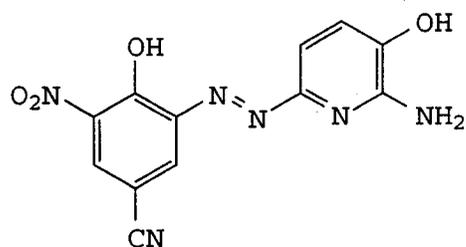
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4-2



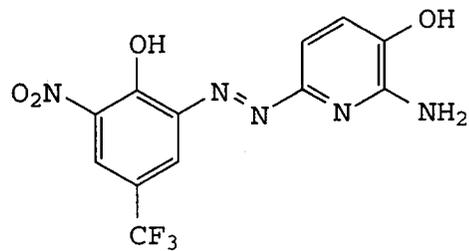
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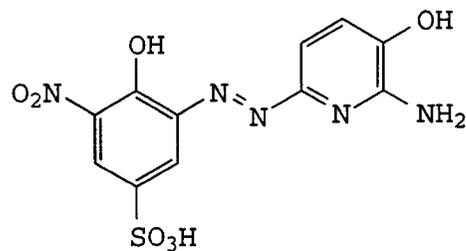
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4-4



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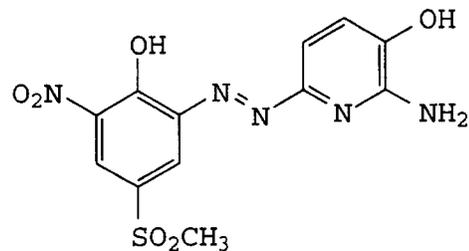
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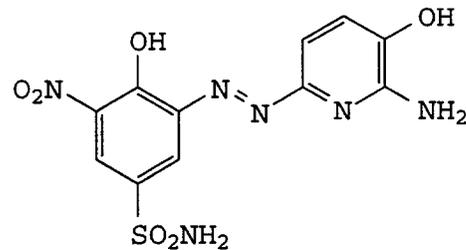
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4-6



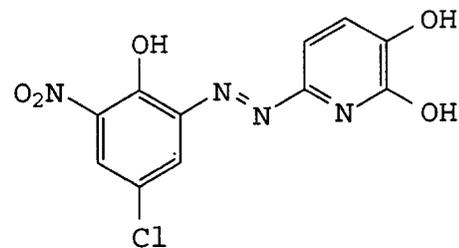
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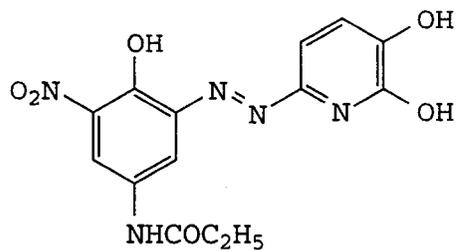
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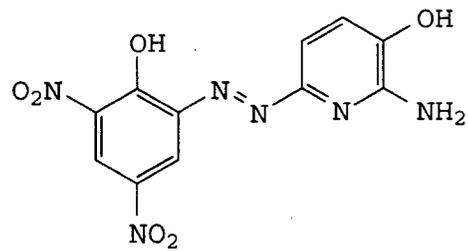
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4-9

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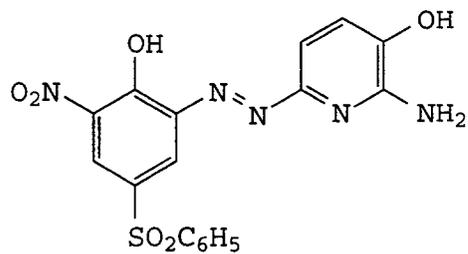


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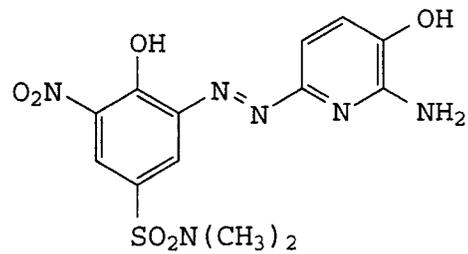


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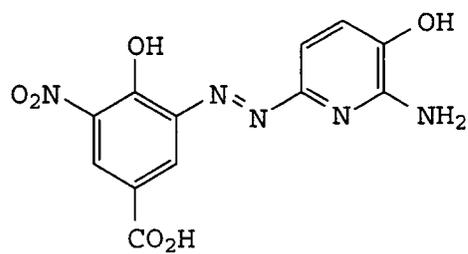


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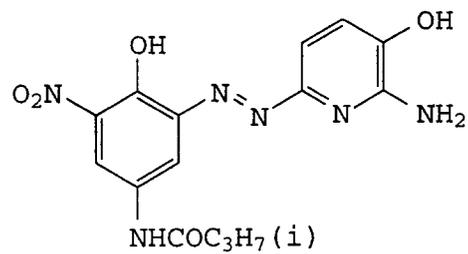


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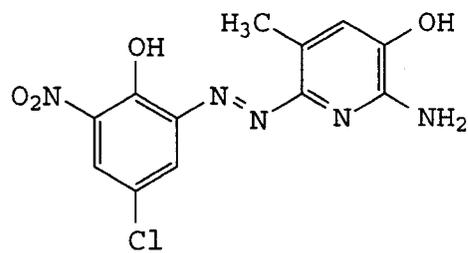


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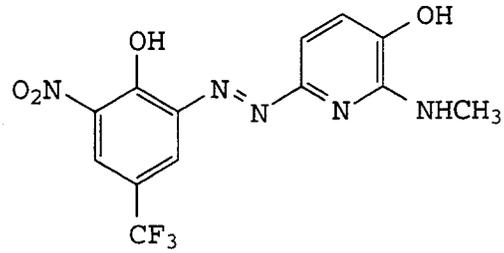


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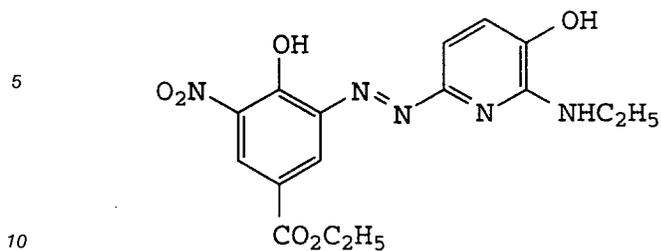
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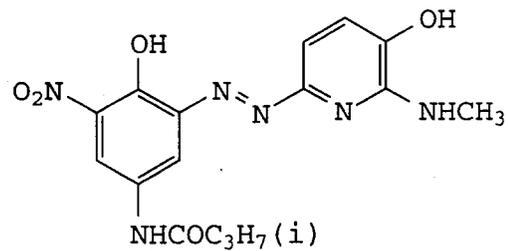
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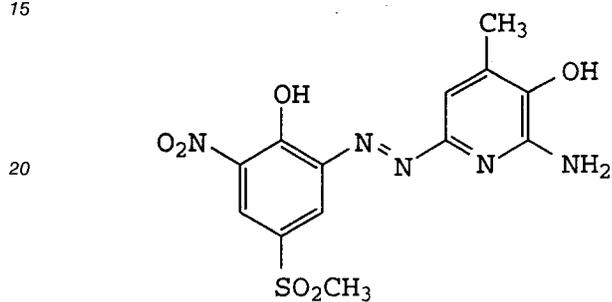
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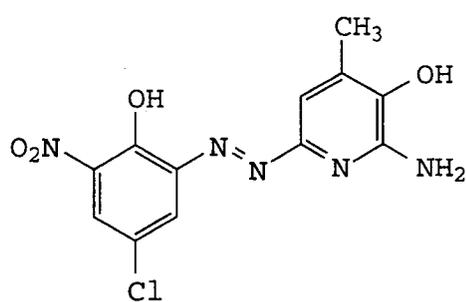
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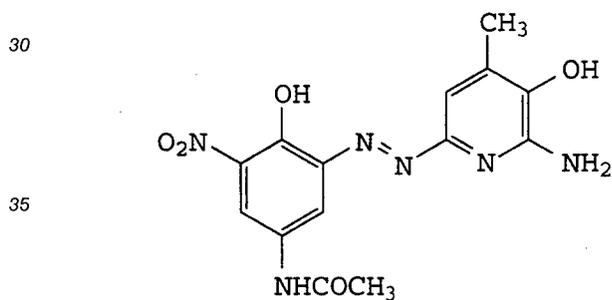
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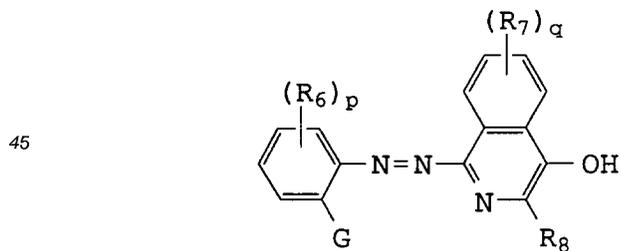
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(5)

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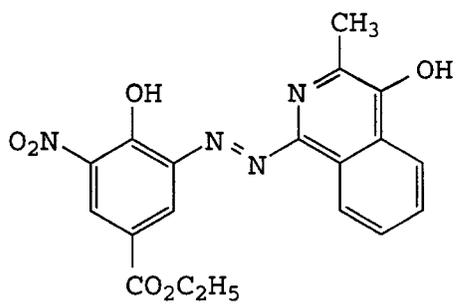
In formula 5, R_6 and R_7 are each a substituent of the benzene ring and the isoquinoline ring, respectively; p and q are each an integer of 0 to 4, when p and q are each 2 or more, the plurality of R_6 s and R_7 s may be each the same or different and may link to form a ring, respectively; R_8 is a hydrogen atom, a halogen atom or a monovalent substituent; and G is a group capable of forming chelating bond with a metal ion.

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Exemplified dyes represented by Formula 5 are as follows:

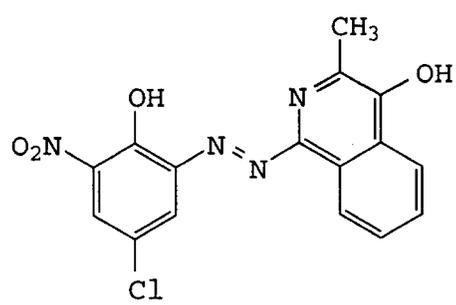
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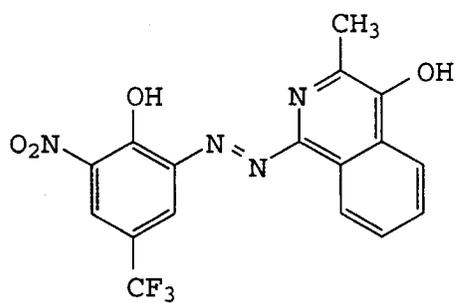
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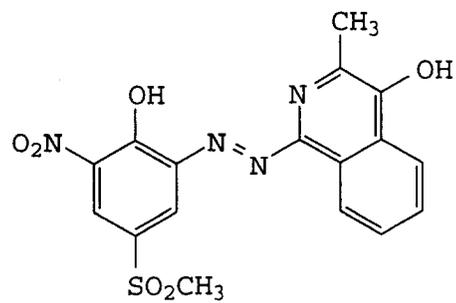
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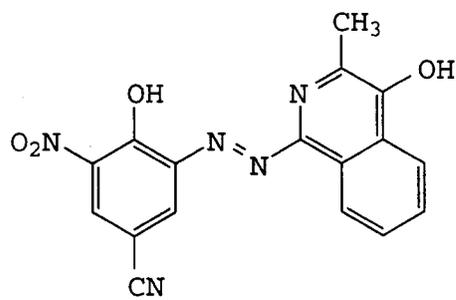
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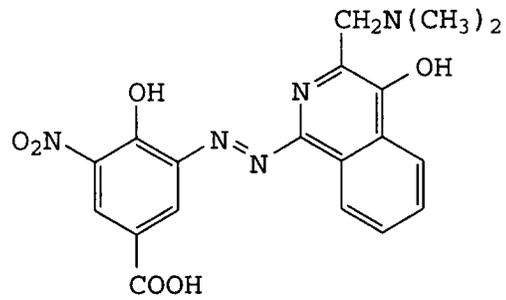
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5-6



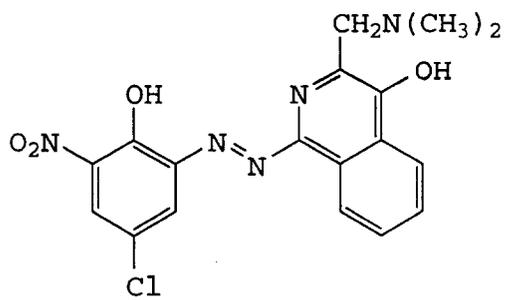
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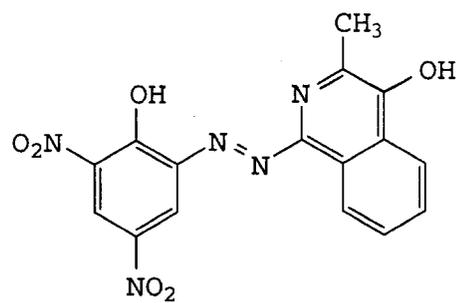
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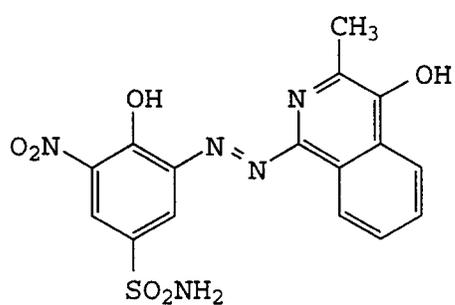
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5-8



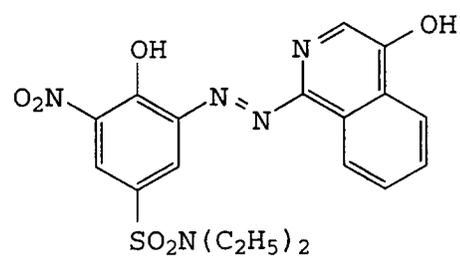
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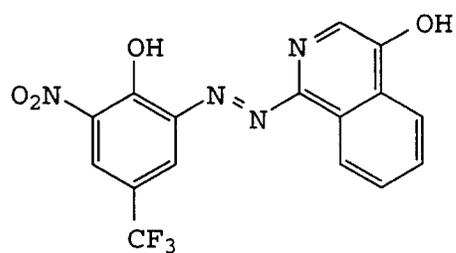
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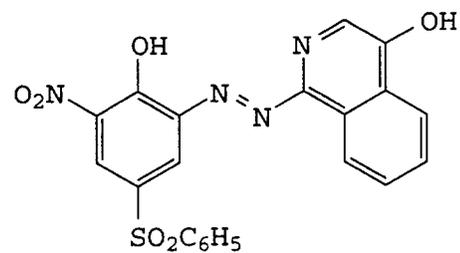
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5-12



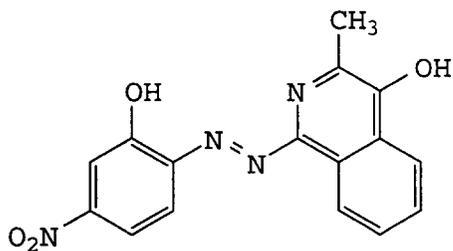
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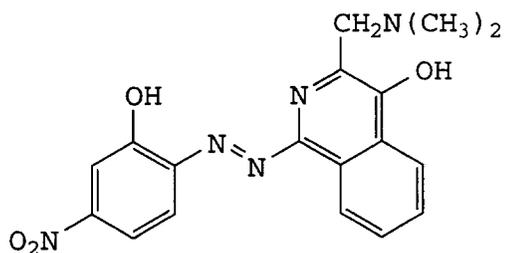
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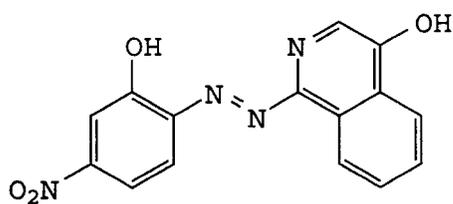
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5-14



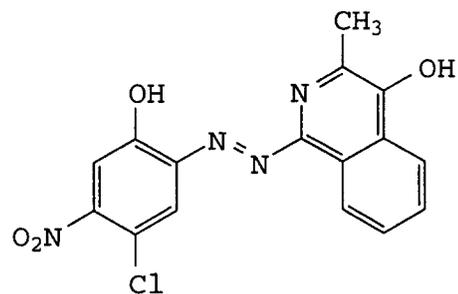
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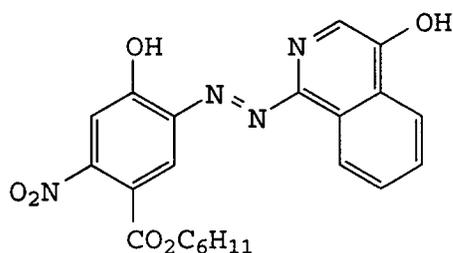
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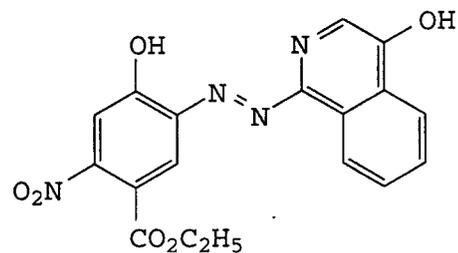
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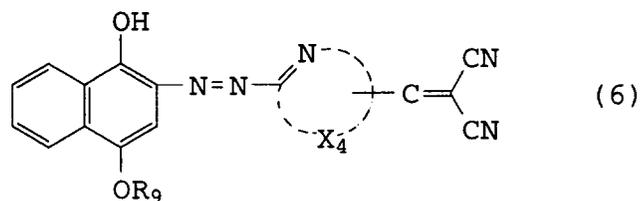


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5-18



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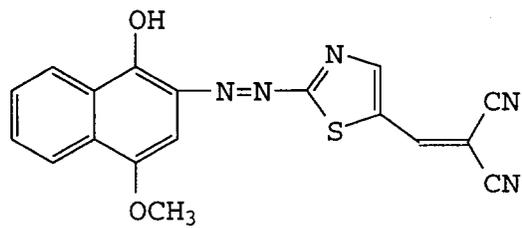
In formula 6, R₉ is an alkyl group or a cycloalkyl group; X₄ is a group of atoms necessary to form a 5- or 6-member nitrogen-containing heterocyclic ring together with the carbon atom linked with the azo group and the nitrogen atom linked with said carbon atoms; the heterocyclic ring may have a substituent which may form a 9- or 10-member condensed ring.

Exemplified dyes represented by Formula 6 are as follows:

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6-1

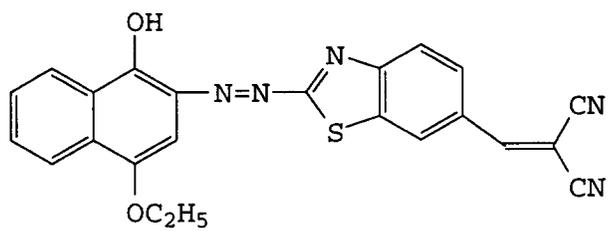
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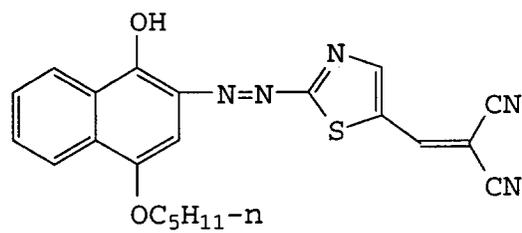


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6-3

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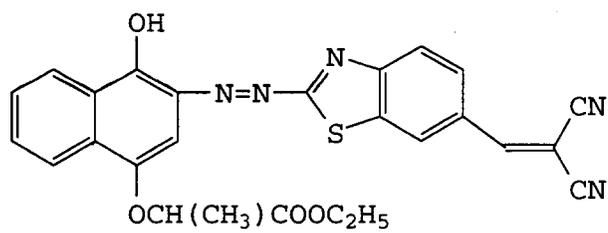
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6-4

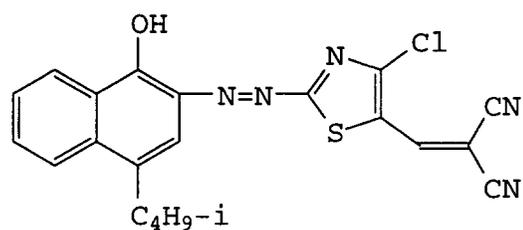
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6-5

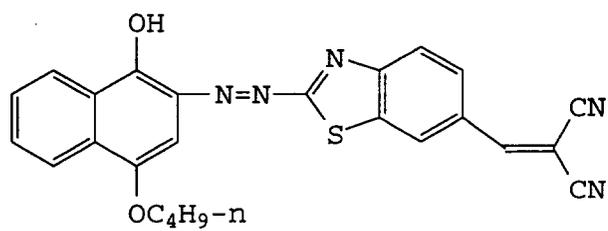
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6-6

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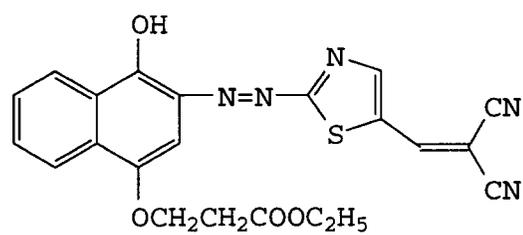


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6-7

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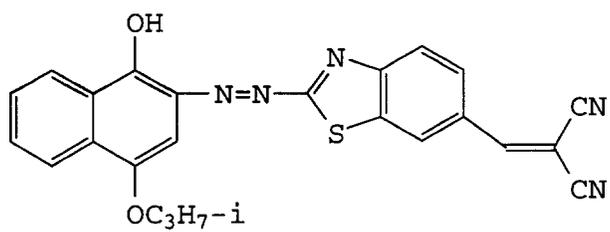
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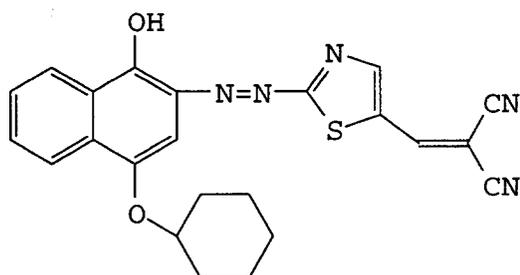
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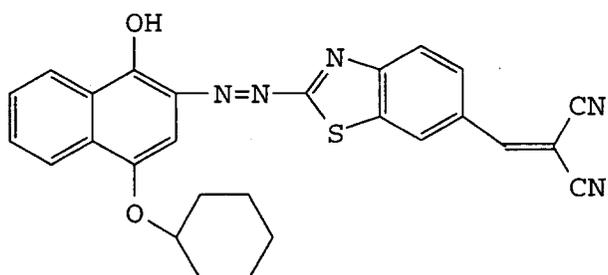


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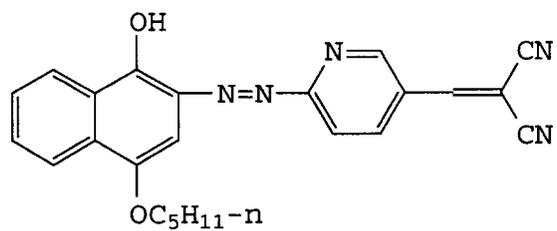


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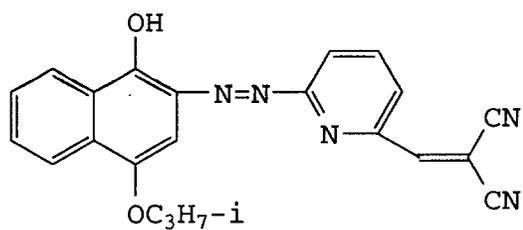


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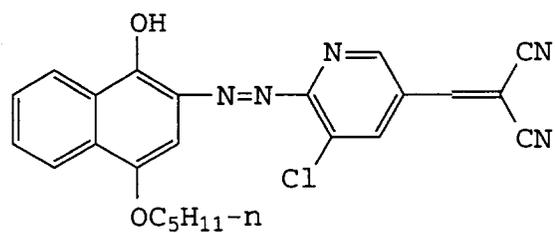
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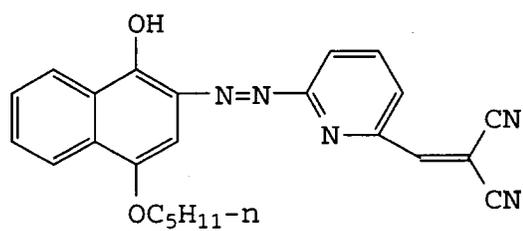
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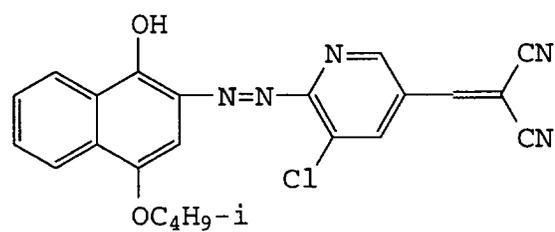


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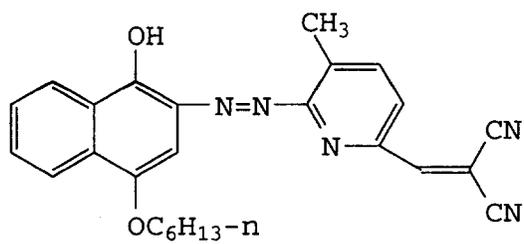
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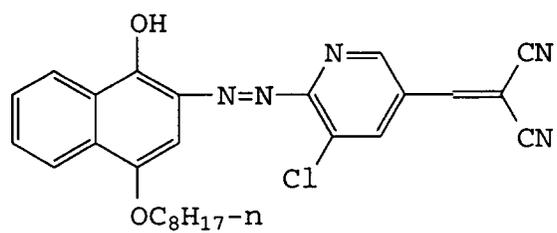
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6-17

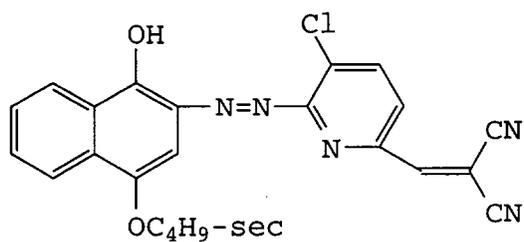
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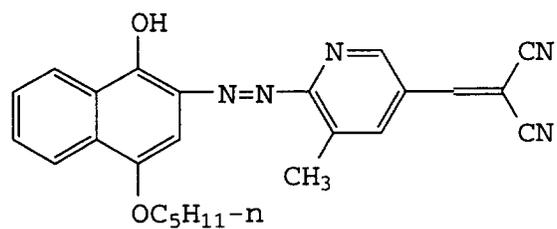


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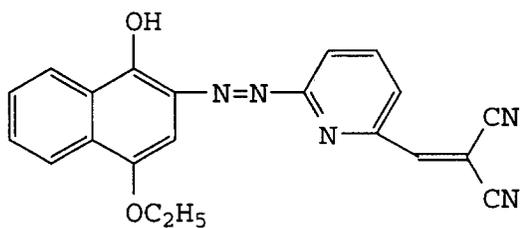
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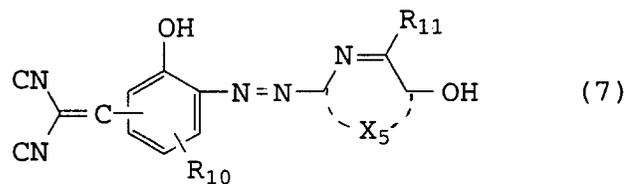
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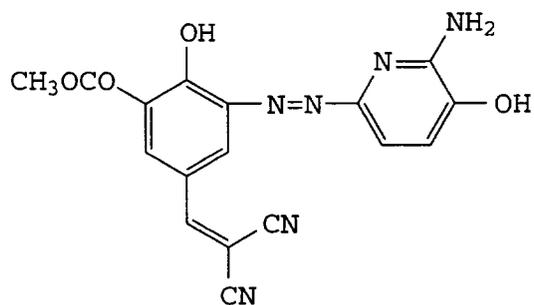
In formula 7 R_{10} and R_{11} is a hydrogen atom or a substituent; X_5 is a group of atoms, necessary to form a 6-member nitrogen-containing heterocyclic ring together with the carbon atom linked with the azo group and the carbon group linked with the hydroxyl group; the heterocyclic ring may have a substituent which may form a condensed ring.

Exemplified dyes represented by Formula 7 are as follows:

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7-1

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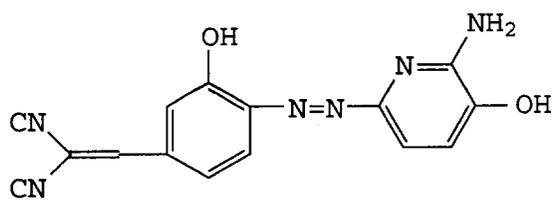
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7-2

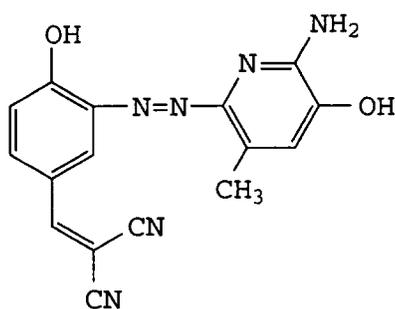
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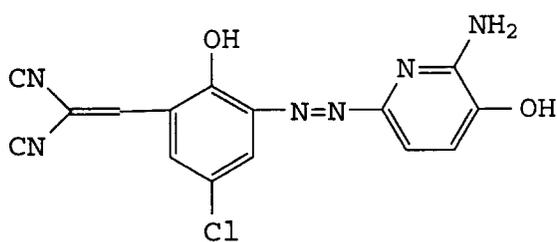


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7-4

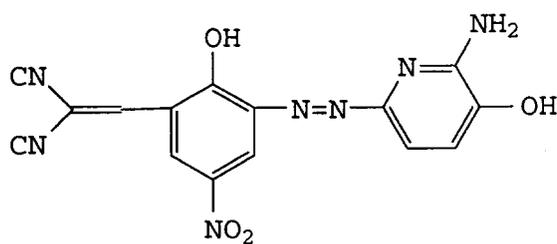
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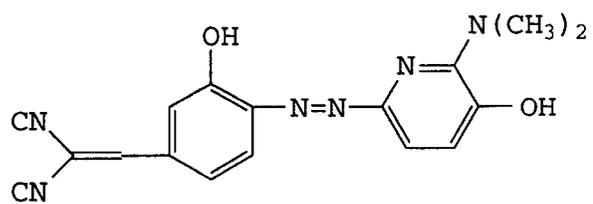
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7-6

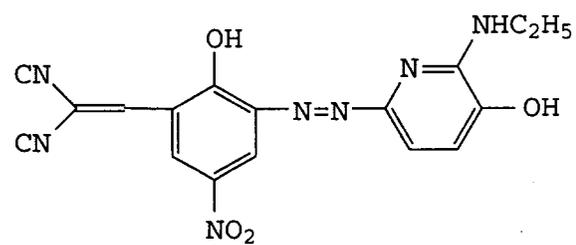
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7-7

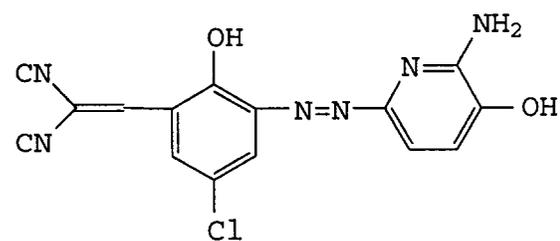
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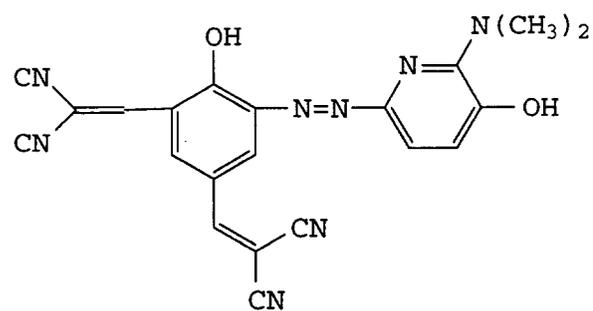


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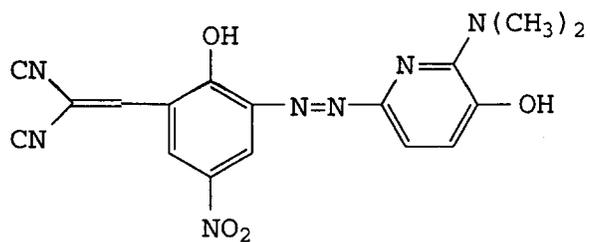
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7-10

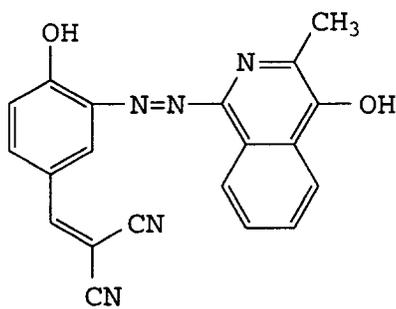
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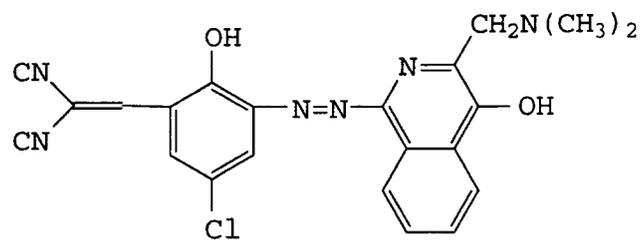


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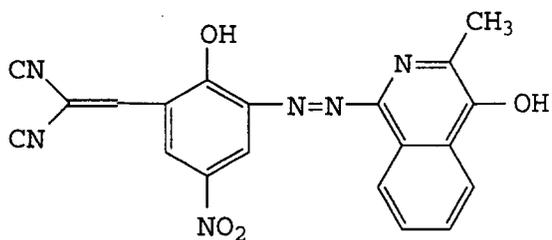


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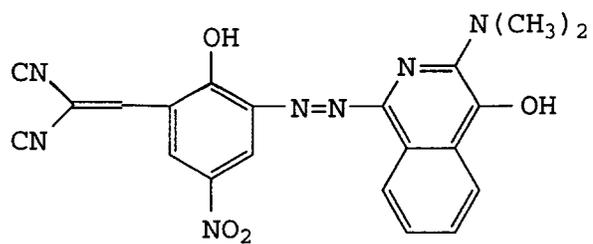


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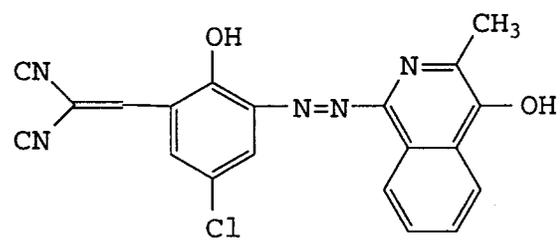
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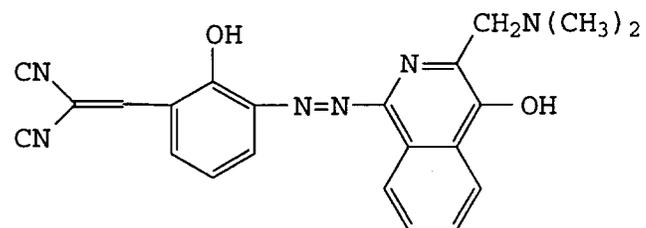


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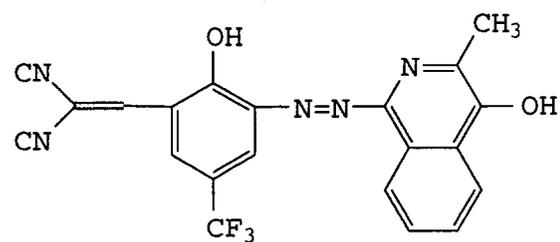
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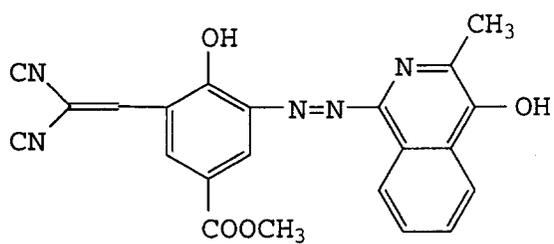
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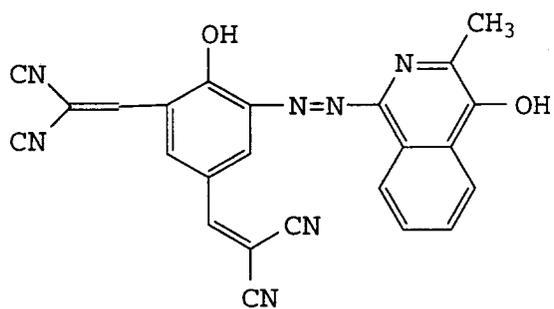


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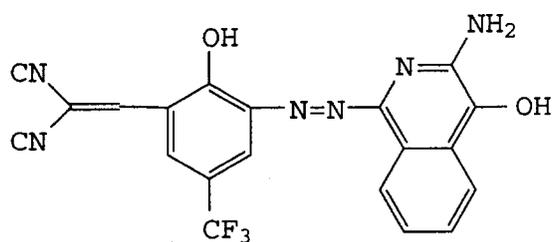
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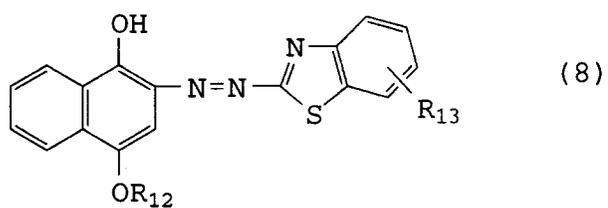
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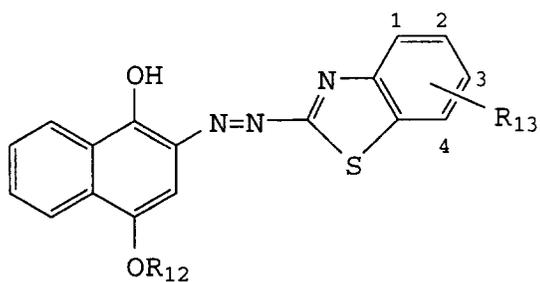


In formula 8, R_{12} is an alkyl group; and R_{13} is a hydrogen atom or a substituent.
Exemplified dyes represented by Formula 8 are as follows:

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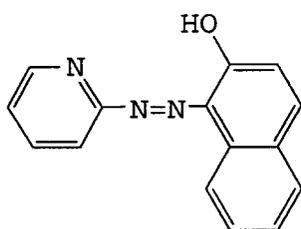
	R ₁₂	R ₁₃		R ₁₂	R ₁₃
8-1	n-C ₅ H ₁₁	3-CH ₃	8-2	n-C ₃ H ₇	3-CH ₃
8-3	n-C ₆ H ₁₃	3-CH ₃	8-4	n-C ₄ H ₉	3-CH ₃
8-5	i-C ₃ H ₇	3-CH ₃	8-6	CH ₂ CH(C ₂ H ₅)C ₄ H ₉	3-CH ₃
8-7	n-C ₅ H ₁₁	H	8-8	C ₂ H ₄ OC ₂ H ₅	3-CH ₃
8-9	CF ₂ CF ₃	3-CH ₃	8-10	n-C ₄ H ₉	2-F
8-11	n-C ₄ H ₉	3-OCH ₃	8-12	CF ₃	3-C ₂ H ₅

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Other than the above dyes, the following thermally diffusible dyes, for example, can be use in the invention.

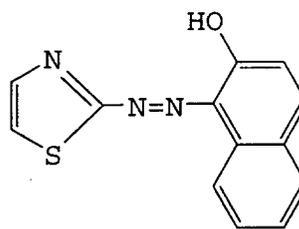
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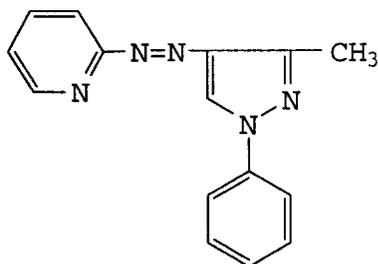
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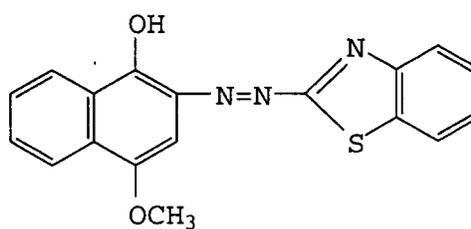


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The thermally diffusible dyes may be used in an amount within the range of, ordinarily, 0.1 to 20 g per m² of a support used and, preferably, 0.2 to 5 g per m² thereof. In a colorant layer, the thermally diffusible dye content is within the range of, ordinarily, 5 to 70% by weight and, preferably, 30 to 70% by weight.

As for the binders applicable to a colorant layer, any resins known in the thermal-transfer recording field may be used. For this purpose, the following polyvinyl acetal type resins and cellulose type resins may preferably be used, provided, however, that the binders of the invention shall not be limited thereto.

The polyvinyl acetal type resins include various kinds of compounds according to the acetalized degrees and the contents of an acetyl group, and a residual group such as hydroxyl group. The typical examples thereof may include polyvinyl acetoacetal, polyvinyl butyral.

The cellulose type resins include, for example, nitrocellulose, ethyl cellulose, hydroxyethyl cellulose, ethylhydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, cellulose acetate and cellulose butyrate. Among them, nitrocellulose is particularly preferable.

Besides the above, the other resins may be used which are known in the thermal-transfer recording field include, for example, acrylic resin, methacrylic resin, polycarbonate, polyvinyl alcohol, polyvinyl formal, polyvinyl ether, polyvinyl pyrrolidone, polystyrene, a polystyrene copolymer and ionomer resin.

From the above-given binders, one or more kinds of them can suitably be selected to be used. It is preferable to compound the above-mentioned binders in a proportion within the range of, ordinarily, 30 to 70% by weight of the whole colorant layer. In a colorant layer, the weight ratio of the binder thereof to the thermally diffusible dye thereof is to be within the range of, preferably, 1:10 to 10:1 and, particularly, 2:8 to 8:2.

A colorant layer may have any thickness, provided that the colorant layer can be controlled to be peeled off from an image receiving element and that the colorant thereof can be controlled to be transferred by applying heat energy. The thickness of a colorant layer is to be within the range of, ordinarily, 0.2 to 10 μm and, preferably, 0.4 to 5 μm.

In the invention, an additive to be added to a colorant layer include, for example, fluororesin, a surfactant, wax, higher aliphatic acid, higher aliphatic alcohol, higher aliphatic ether, fine metal powder, silica gel, carbon black, organic filler, inorganic filler, and a hardener reactive with a binder component, such as a radiation-active compound, e.g., isocyanate, acrylic acid and epoxy, as well as modified silicone resin. For the purpose of promoting a transfer, it is further allowed to make use of a thermally fusible substance such as higher aliphatic ester described in, for example, JP OPI Publication No. 59-106997/1984.

The amounts of the additives to be added cannot be determined without distinction, because of the various kinds of additives and the various purposes for adding them. Usually, as the whole of them, it is preferable to add them in a proportion of not more than 50% by weight of a binder used.

The typical examples of the above-mentioned modified silicone resins include polyester-modified silicone resin, acryl-modified silicone resin, urethane-modified silicone resin, cellulose-modified silicone resin, alkyd-modified silicone resin and epoxy-modified silicone resin. They may be used independently or in combination.

The above-mentioned modified silicone resins may be compounded in a proportion within the range of, ordinarily, 0.01 to 10% by weight of a colorant layer and, preferably, 0.01 to 2.0% by weight thereof.

A colorant layer can be formed by the following manner. The foregoing thermally diffusible dye, binder and, if required, an additive are each dissolved or dispersed in a solvent, so that a coating solution can be prepared, and the resulting coating solution is coated over a support and then dried up.

The binders may be used not only by dissolving one or more kinds thereof in a solvent, but also by latex-dispersing them.

The solvents include, for example, water, an alcohol such as ethanol, propanol and butanol, cellosolve, an ester such as ethyl acetate and butyl acetate, an aromatic compound such as toluene, xylene and chlorobenzene, a ketone such as acetone and methyl ethyl ketone, an ether such as tetrahydrofuran and dioxane and a chlorine-containing solvent such as chloroform and trichloroethylene. These solvents may be used independently or in combination.

The coating solution may be coated by a commonly known coating process such as a sequentially coating process in which a gravure-roll is used, an extrusion coating process, a wire-bar coating process and a roll coating process.

A barrier layer is to be provided at least with a property that it cannot be permeated with the colorant or the thermally diffusible dye of a colorant layer even when applying heat or pressure and another property that it can absorb any high intensity exposure light. For providing it with the properties, it is preferable that a colorant barrier layer is to contain a resin, in which (1) a water-soluble resin, (2) a resin having an ion bond, or (3) a resin having a T_g (or a glass-transition point) of not lower than 120 °C, preferably not lower than 150 °C and, more preferably not lower than 200 °C, is contained as the principal component.

The water soluble resin which may be used in the invention is a resin capable of being dissolved in water in a concentration of not less than 1 % by weight, preferably not less than 2 %. The above solubility of the resin is not limited that at an ordinary temperature. Temperature for dissolving the resin can be changed according to necessity. A resin can be used which can be dissolved in water with a concentration of not less than 1 % by weight at a temperature 0 to 100 °C.

The water-soluble resins include, for example, gelatin, polyvinyl alcohol, water-soluble polyvinyl formal, water-soluble polyvinyl acetal, water-soluble polyvinyl butyral, polyvinyl pyrrolidone, water-soluble polyester, water-soluble nylon, polyacrylic acid, water-soluble polyurethane, methyl cellulose, hydroxyethylcellulose, hydroxypropyl cellulose, and carboxyl cellulose. It is also allowed to use the copolymers of the monomer components constituting the above-given resins. At the time of preparation of coating solution, it is preferable to dissolve gelatin at a temperature of not lower than 40 °C and to dissolve methyl cellulose at a temperature of not higher than 10 °C.

The term, a resin having a ion-bond, means a resin having an ion-bonded group that is, an acidic or basic group, in the principal or side chain of a macromolecule.

The acidic groups include, for example, $-\text{COO}^-$, $-\text{SO}_3^-$ and $-\text{PO}_3^-$. The basic groups include, for example, $-\text{NH}_2$,



and $-\text{N}=\text{}$.

The resins each having an ion-bond include, for example, those having both of an acidic group and a basic group, and those each having an acidic group, containing a divalent metal ion and having a cross-linking structure through the metal ion. It is preferred that a resin having an ion bond, that is related to the invention, has at least one or more of the ion-bonded groups per 100 repetition monomer units. However, a resin not always having such a repetition monomer unit as mentioned above can also suitably be used.

The resins having an ion bond include, for example, a resin containing styrene substituted with a sulfo group, acrylic acid, methacrylic acid, phthalic anhydride, or the like, each added with Na^+ , K^+ , Ca^{2+} , NH_4^+ or the like as a counter ion, besides an ionomer resin and so forth. Further, gelatin and casein may also be used preferably.

The resins each having a Tg of not lower than 120 °C include, for example, polyvinyl chloride, polystyrene, polyaryl methacrylate, polybenzyl methacrylate, polycarbonate, nylon, polyphenylene oxide, polyphenylene sulfide, gelatin and polyparabanic acid. A resin having a Tg of not lower than 120 °C is also preferably used, that is, a copolymer of a monomer component of styrene, vinyl chloride, methyl methacrylate, aryl methacrylate, acrylonitrile, ethylene oxide, benzyl methacrylate or cyclohexyl methacrylate. It is further preferable to use a thermosetting resin without having any glass transition point.

Among these resin usable for the colorant barrier layer, water soluble ones are preferable. As the water soluble resin, gelatin, polyvinylpyrrolidone, methylcellulose, hydroxyethylcellulose, hydroxypropyl-cellulose, carboxylcellulose are particularly preferable. These water-soluble resin is well mixed with a water-soluble infrared absorbing dye after-mentioned.

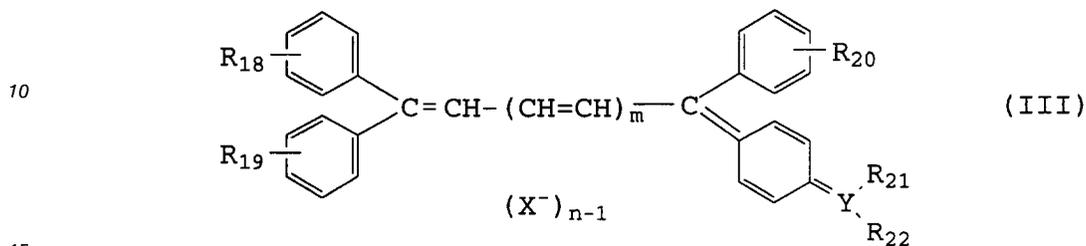
The proportion of a resin component to a colorant barrier layer is preferably within the range of 50 to 99% by weight of a colorant barrier layer. Among the resin components, the proportion of the foregoing resin component (1), (2) or (3) of to the whole resin component is preferably not less than 50% by weight, more preferably not less than 70% by weight and, most preferably not less than 90% by weight based on the total weight of the barrier layer.

A colorant barrier layer contains an infrared absorbable substance for absorbing a high intensity exposure light and convert the absorbed light to heat. The infrared absorbable substances are preferably ones which absorb infrared having a wavelength of not shorter than 650 nm.

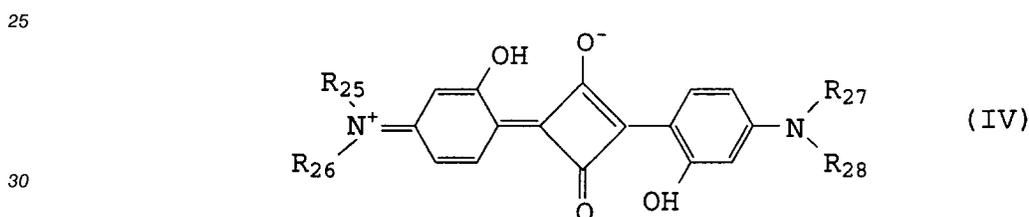
As for the infrared absorbing dyes, anyone of them can be used, provided that they can absorb infrared rays of not lower than 700nm. However, for effectively achieving the invention, it is preferable to make use of a dye having a molar distination coefficient of not less than 50,000 and, preferably, not less than 100,000, in a wavelength showing the most strongest absorption within the range of 700nm to 1200nm.

An infrared absorbing dye applicable to the invention is preferable to have a good compatibility to a binder for a colorant barrier layer of the invention. An infrared absorbable dye of the invention is also preferable to be dissolved, in a proportion of not less than 0.1% and, particularly, not less than 1%, in at least water or an organic solvent, provided that there shall not exclude those capable of being mixed with a binder for a colorant barrier layer, by dispersing them in at least water or an organic solvent.

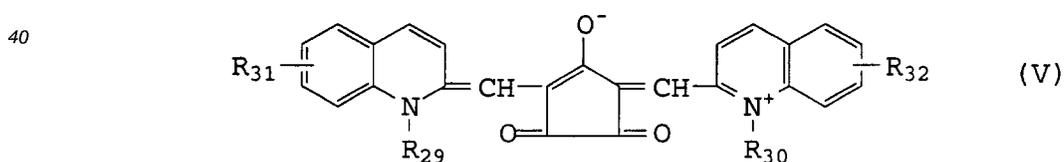
substituted or unsubstituted alkyl group, a halogen atom or a hydrogen atom; R₇ and R₁₇ are each independently a substituted or unsubstituted alkyl group or a hydrogen atom; and X⁻, m and n are each the same as X⁻, m and n defined in formula 1, respectively. Among the dyes represented by the above formula, ones in which at least one of the groups represented by R₇ to R₁₇ has a sulfo group, a carboxyl group or a phosphono group are preferable. Ones having a sulfo group is particularly preferable.



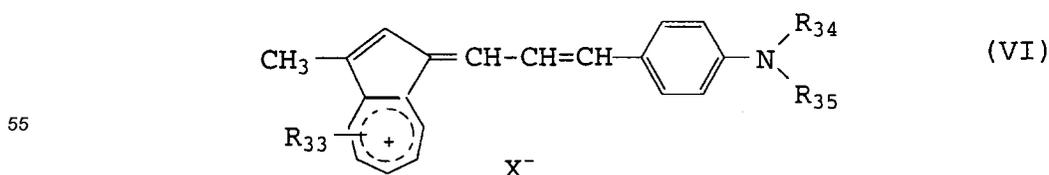
In formula III, R₁₈, R₁₉ and R₂₀ are each independently a hydrogen atom, a substituted or unsubstituted alkyl group -N(R₂₃)(R₂₄), =N⁺(R₂₃)(R₂₄) or a sulfo group, in which R₂₃ and R₂₄ are each independently a substituted or unsubstituted alkyl group; Y is a carbon atom or a nitrogen atom; R₂₁ and R₂₂ are each independently a hydrogen atom or a substituted or unsubstituted alkyl group; X⁻ an anion; m is 0 to 5 and n is 1 or 2. Among the dyes represented by formula III, ones in which at least one of the groups represented by R₁₈ to R₂₄ has a sulfo group, a carboxyl group or a phosphono group, particularly a sulfo group, are preferable.



In the above formula IV, R₂₅, R₂₆, R₂₇ and R₂₈ are each independently a hydrogen atom or a substituted or unsubstituted alkyl group. Among the dyes represented by formula IV, ones in which at least one of the groups represented by R₂₅ to R₂₈ has a sulfo group, a carboxyl group or a phosphono group, particularly sulfo group, are preferable.

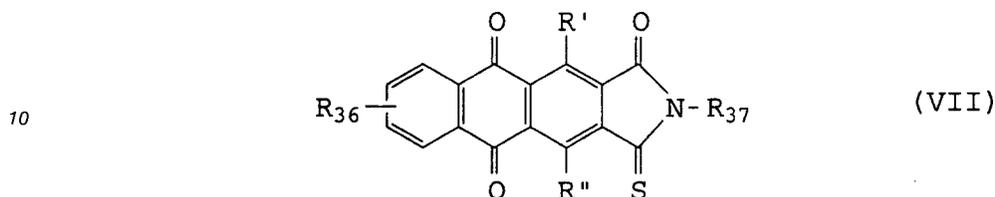


In the above formula V, R₂₉ and R₃₀ are each independently a substituted or unsubstituted alkyl group; and R₃₁ and R₃₂ are each independently a hydrogen atom or a substituted or unsubstituted alkyl group. Among the dyes of formul V, ones in which at least one of the groups represented by R₂₉ to R₃₀ has a sulfo group, a carboxyl group or a phosphono group, particularly sulfo group, are preferable. Further, R₃₁ and R₃₂ may be substituted with a sulfo group, a carboxyl group or a phosphono group.



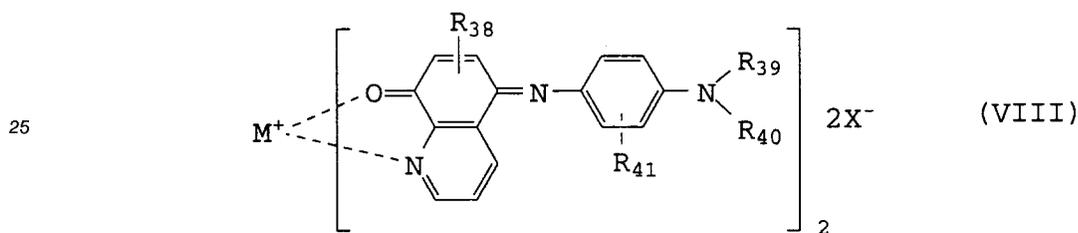
In formula VI, R_{33} , R_{34} and R_{35} are each independently a hydrogen atom, a substituted or unsubstituted alkyl group; and X^- is an anion. Among the dyes of formula VI, ones in which at least one of the groups represented by R_{33} to R_{35} has a sulfo group, a carboxyl group or a phosphono group, particularly sulfo group, are preferable.

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15 In formula VII, R_{36} and R_{37} are each independently a hydrogen atom, a sulfo group, a carboxyl group, a phosphono group or a substituted or unsubstituted alkyl group; and R' and R'' are each independently a hydrogen atom, a substituted or unsubstituted amino group or a substituted or unsubstituted alkyl group. As the substituted alkyl group represented by R_{36} and R_{37} , those substituted with a sulfo group, a carboxyl group or a phosphono group,

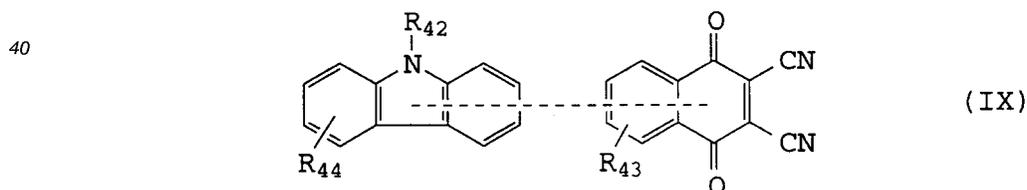
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35 In formula VIII, R_{38} is a hydrogen atom, a substituted or unsubstituted amino group, a substituted or unsubstituted amido group or a substituted or unsubstituted alkyl group; R_{39} and R_{40} are each independently a hydrogen atom or a substituted or unsubstituted alkyl group; and R_{41} is a hydrogen atom, a sulfo group, a carboxyl group, a phosphono group or a substituted or unsubstituted alkyl group, M is a metal atom; and X^- is an anion. As the above substituted alkyl group represented by R_{38} to R_{41} , those substituted with a sulfo group, a carboxyl group or a phosphono group are preferable. As the metal represented by M , Cu and Ni are preferable.

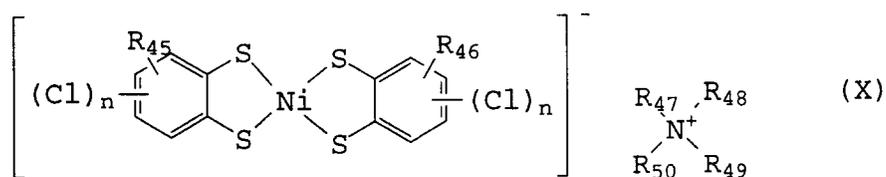
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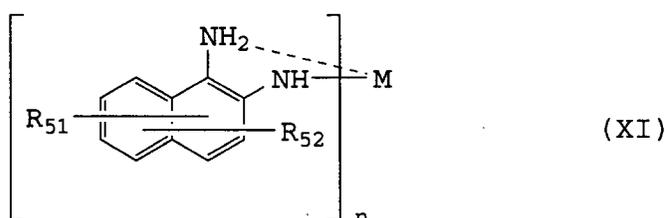
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50 In formula IX, R_{42} is a hydrogen atom or a substituted or unsubstituted alkyl group; R_{43} is a hydrogen atom, an amido group, a nitro group, a sulfo group, a carboxyl group, a phosphono group or a substituted or unsubstituted alkyl group; and R_{44} is a hydrogen atom, a sulfo group, a carboxyl group, a phosphono group or a substituted or unsubstituted alkyl group. As the substituted alkyl group represented by R_{42} to R_{44} , those substituted with a sulfo group, a carboxyl group or a phosphono group are preferable.

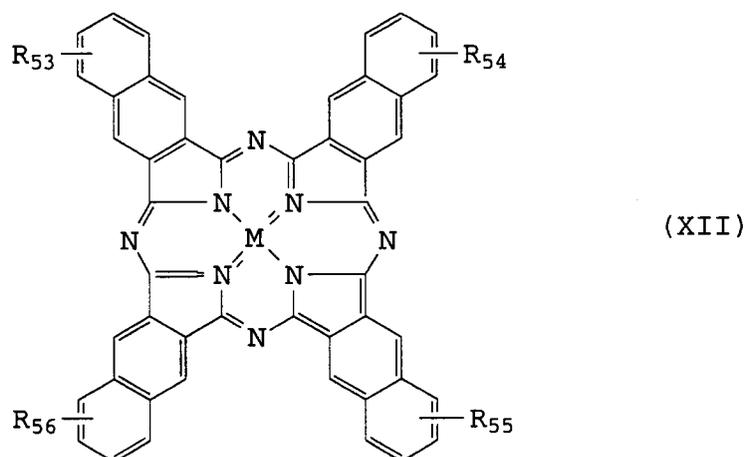
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10 In the above formula X, R₄₄ and R₄₅ are each independently a hydrogen atom a sulfo group, a carboxyl group, a phosphono group or a substituted or unsubstituted alkyl group; R₄₆, R₄₇, R₄₈ and R₄₉ are each independently an alkyl group which may be the same or different; and n is 0 to 4. As the substituted alkyl groups represented by R₄₄ and R₄₅, those substituted with a sulfo group, a carboxyl group or a phosphono group are preferable.



25 In formula XI, R₅₁ and R₅₂ are each independently a hydrogen atom, a sulfo group, a carboxyl group, a phosphono group or a substituted or unsubstituted alkyl group; M is a divalent or trivalent metal atom; and n is 2 or 3. As the substituted alkyl groups represented by R₅₁ and R₅₂, those substituted with a sulfo group, a carboxyl group or a phosphono group are preferable.

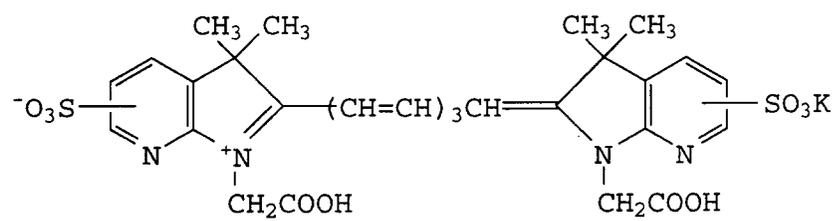


50 In formula XII, R₅₃, R₅₄, R₅₅ and R₅₆ are each independently a hydrogen atom, a sulfo group, a carboxyl group, a phosphono group or a substituted or unsubstituted alkyl group; and M is a divalent metal atom. Preferable substituents of the alkyl groups represented by R₅₃ to R₅₆ are each a sulfo group, a carboxyl group or a phosphono group. Among these infrared absorbing dyes, cyanine dyes represented by formulas I or II, anthraquinone dyes represented by formula VII, and chelate dyes represented by formula VIII, X, XI or XII are preferable. Cyanine dyes of formula I or II each having a sulfo group are particularly preferable.

55 Among these infrared absorbing dyes, cyanine dyes represented by formula I or II, anthraquinone dyes represented by formula VII, and chelate dyes represented by formula VIII, X, XI or XII are preferable. Cyanine dyes of formula I or II each having a sulfo group are particularly preferable.

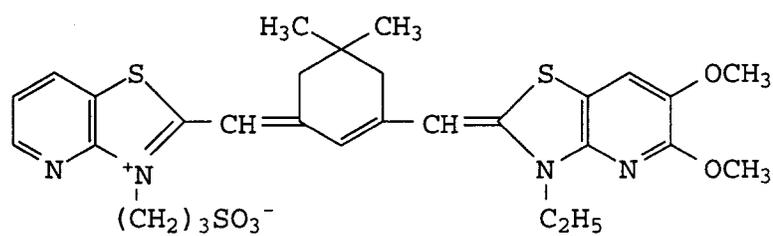
The followings are exemplified water-soluble infrared absorbing dye represented by Formula I to XI or XII.

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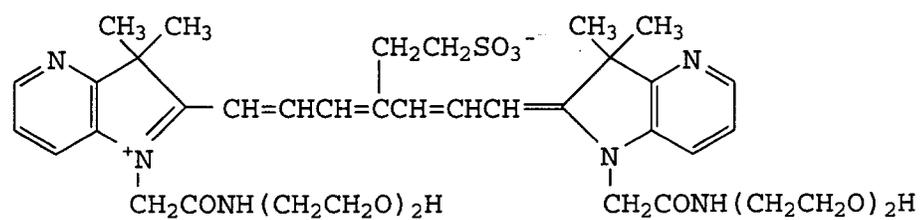
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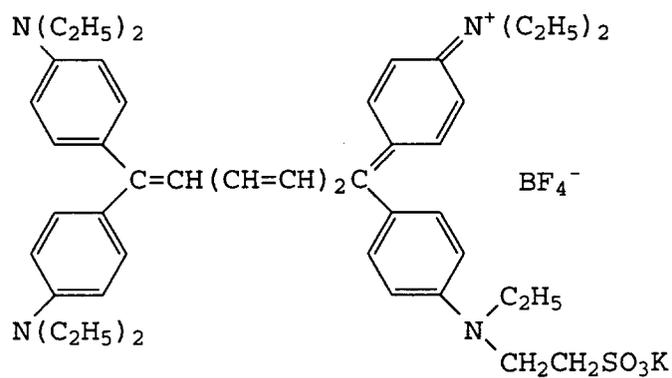
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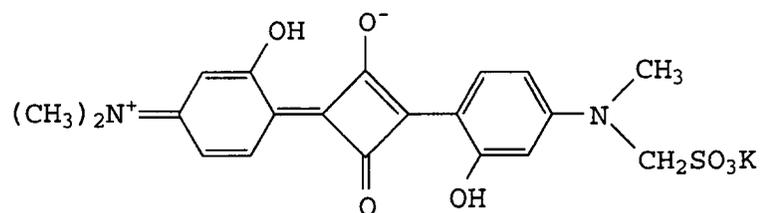
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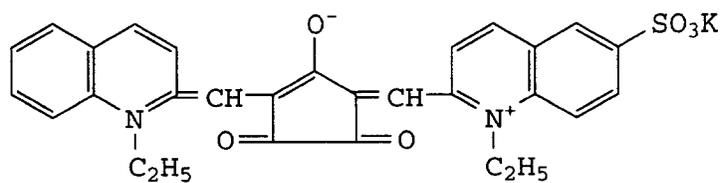


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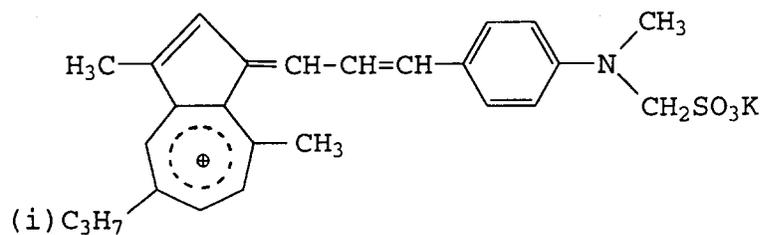
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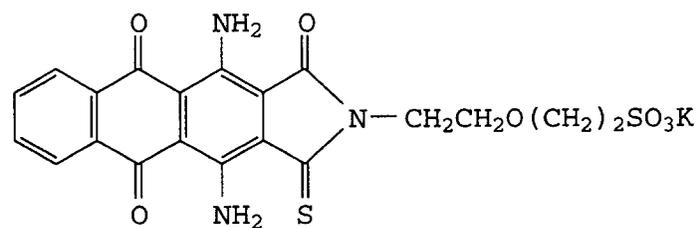
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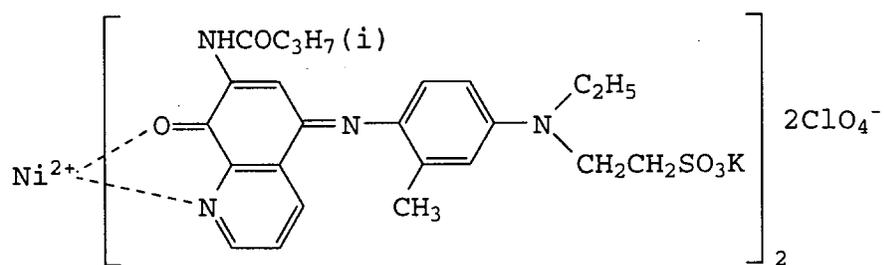


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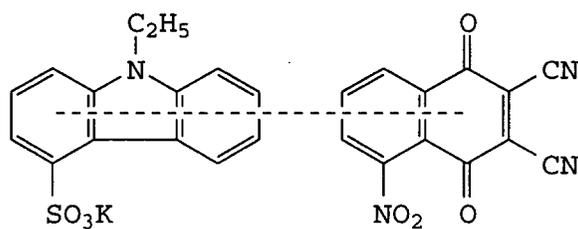
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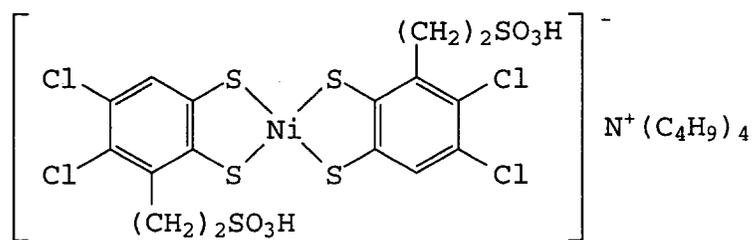
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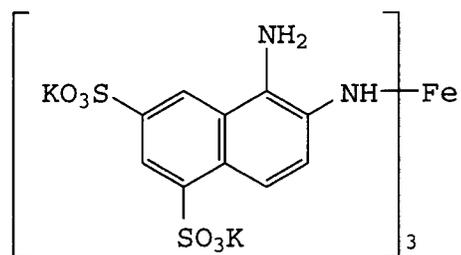


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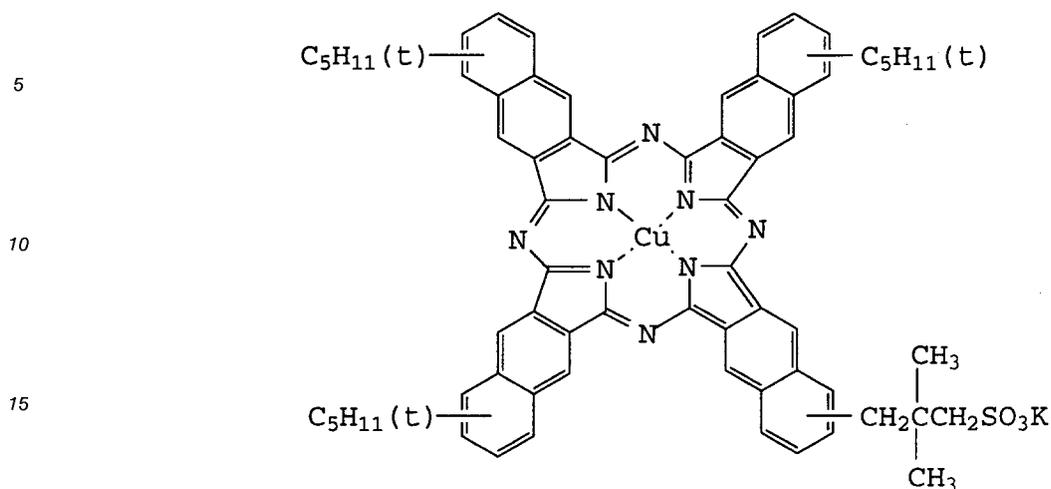
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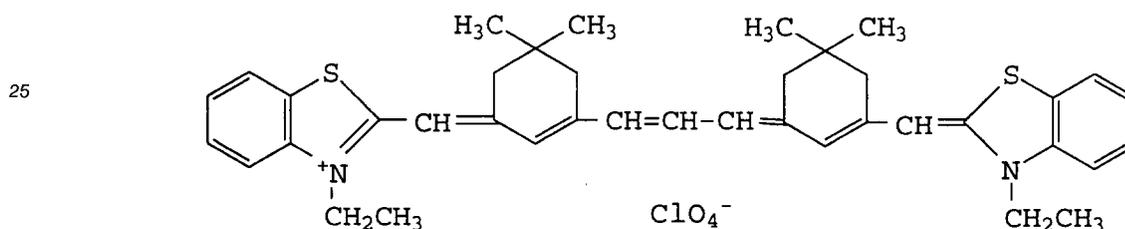
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(13)



(14)



Further, dyes represented by formulas each the same as Formulas I to XII except that which do not have neither sulfo group, carboxyl group nor phosphono group are also may be used.

When the colorant barrier layer comprises a water-insoluble resin, infrared absorbing dyes described in JP O.P.I. Publications 62-12345 (1987) and 3-146565 (1991) can be used.

When the wavelength of an exposure light is in an infrared region, it is preferable that the light-absorbable substance is to contain the foregoing infrared absorbing dye in a proportion within the range of 1 to 50% by weight in the colorant barrier layer. If the infrared absorbable substance does not deteriorate the barrier function of the foregoing infrared absorbable dye of a colorant barrier layer, the near infrared absorbable dye can further be added in a further amount.

Besides the above a colorant barrier layer can also contain, if required, additives such as a surfactant for improving a coatability, a conductive compound for an antistatic agent, and a releasing agent for preventing a blocking and a matting agent.

The layer thickness of a colorant barrier layer is to be as thinner as possible, provided that the barrier function cannot be deteriorated. To be more concrete, the thickness thereof is to be within the range of 0.1 to 2.0 μ m and, preferably, 0.1 to 1.0 μ m, provided, however, that the layer thickness thereof shall not be limited thereto, because an ablation can be made even if the layer thickness is thicker, when an exposure light intensity is satisfactorily high.

If required, a colorant barrier layer may be formed of a plurality of layers by which the functions are separated. The functions to be separated thereby include, for example, a colorant barrier property, a conductivity, a light absorbability and a blocking resistance. These functions may be provided separately to a plurality of layers.

A colorant barrier layer can be coated in the same manner as in the case of the foregoing colorant layer.

In the invention, if required, besides the colorant layer and colorant barrier layer, the other layers may be provided. For example, between a support and a colorant layer, a sublayer can be interposed for enhancing a adhesion and so forth. A intermediate layer may be provided between the colorant layer and the colorant barrier layer, which has a heat insulating or an adhering effect. And, to the rear side of a

support, (that is, the opposite side thereof to a colorant layer), a backing layer may also be provided for the purposes of endowing a running stability, heat resistance, antistaticity. The above-mentioned backing layer is preferable to have a layer thickness within the range of 0.1 to 1 μ m.

Further to a recording element, a series of perforations, a detection mark for detecting the positions of every area having different hues, and so forth may be provided, so as to meet the convenience for use.

Now, an image-receiving materials applicable together with a recording material of the invention will be detailed below.

An image-receiving element is comprised of a support and an image-receiving layer. However, an image-receiving material may also be formed of an image-receiving layer which is self-supportable by itself.

The supports include, for example, those made of the following materials; paper, coated paper, synthetic paper such as those made of polypropylene and polystyrene, and those made of the compounded materials thereof pasted on a paper or a plastic film, those made of a white or transparent polyethylene terephthalate film, those made of a white or transparent polyvinyl chloride sheet, and those made of polyolefin-coated paper. The thicknesses of the supports are to be within the range of, normally, 20 to 300 μ m and, preferably, 30 to 200 μ m.

An image-receiving layer is formed of a binder for image-receiving layer and a variety of additives. The binders for image-receiving layer include, for example, a polyvinyl chloride resin, a copolymeric resin of vinyl chloride and other monomer such as alkyl vinyl ether and vinyl acetate, a polyester resin, a polyacrylate, polyvinyl pyrrolidone, polycarbonate, cellulose triacetate, a styrene acrylate resin, a vinyl toluene acrylate resin, a polyurethane resin, a polyamide resin, a urea resin, a polycaprolactone resin, a styrene-maleic anhydride resin and a polyacrylonitrile resin.

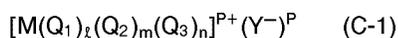
The above-given resins may be synthesized afresh. However, those available on the market may also be used. In any case, from the viewpoint of physical properties, a resin having a Tg within the range of -20 to 150 $^{\circ}$ C and, particularly, 30 to 120 $^{\circ}$ C is preferable as a binder for image-receiving layers. Also, a resin having an average molecular weight by weight within the range of 2,000 to 100,000 is preferable.

When forming an image-receiving layer, a variety of the above-mentioned resins may also be cross-linked or hardened by utilizing the reaction active sites thereof (provided, when there is no reaction active site, the reaction active sites are endowed) and then by applying radiation, heat, moisture, a catalyst or the like. When this is the case, it is allowed to make use of a radiation active monomer such as epoxy and acryl, and a cross-linking agent such as isocyanate.

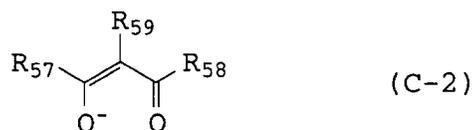
It is preferable that the image-receiving layer contains a metal ion-containing compound as a metal source to form a chelate compound with a diffusible dye transferred from a image recording element. As for the metal ion-containing compounds, anyone of organic and inorganic compound each have a metal ion bonded with ion bonding or coordinate bonding thereto. Generally from the view points of a solubility and a handling convenience, a salt or complex of a low-molecular organic compound are preferably used, however, the metal ion-containing compound are limited hereto.

As the above metal, monovalent or polyvalent metal of Groups I to VIII of the Periodic Table can be used. Among them, Al, Co, Cu, Fe, Mg, Mn, Mo, Ni, Sn, Ti and Zn, particularly Cu, Cr, Co and Zn, are preferable. Examples of the metal ion-containing compound suitably used include salts of Ni²⁺, Cu²⁺, Cr²⁺, Co²⁺ or Zn²⁺ with an aliphatic acid such as acetic acid and stearic acid, and salts of these metal ions with an aromatic carboxylic acid such as benzoic acid and salicylic acid.

Further, complexes represented by the following formula C-1 are particularly preferably used.



wherein M is a metal ion; preferably Ni²⁺, Cu²⁺, Cr²⁺, Co²⁺ or Zn²⁺; Q₁, Q₂ and Q₃ are each independently a ligand compound capable of forming a coordinate bond with a metal ion represented by M, which may be the same or different. The above ligand compound represented by Q₁ to Q₃ may be selected from ligand compounds described in "Chelate Chemistry (5)", p.p. 1-372, Konando 1975. Y⁻ is an anion, preferably an organic anion, such as tetraphenylboron anion and alkylbenzene-sulfonate anion. l is 1, 2 or 3; m is 1, 2 or 0; and n is 1 or 0, and these numbers are defined according to the number of ligand of the compound represented by Q₁, Q₂ and Q₃, or the number of coordinate, 4-coordinate or 6-coordinate, of the complex. P is 0, 1 or 2. When the ligand compound represented by Q is an anionic compound, and cation of metal ion of M is neutralized by anion of compound Q, P is 0. The anionic compounds preferable be used are those represented by the following formula C-2:



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wherein R_{57} and R_{58} are each a hydrogen atom an alkyl group or an aryl group which may be the same or different; and R_{59} is a hydrogen atom, an alkyl group, an alkoxy group, a halogen atom or an alkoxy carbonyl group.

10 A metal source $M^{2+}(X^-)_2$ is formed from the above anionic compound (X^-) of formula C-2 and a metal ion M^{2+} . Compounds each having $-COOCH_3$ or $-COOC_2H_5$ as the group represented by R_{46} are preferable. As metal represented by the above M is preferably Ni. The metal ion-containing compound is contained in the image receiving layer in a content of 0 to 80 % by weight. The content can be varied depending on the

15 The followings are the examples of the anionic compound represented by formula C-2.

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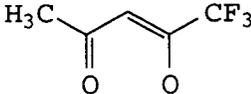
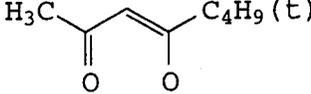
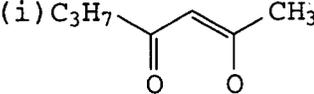
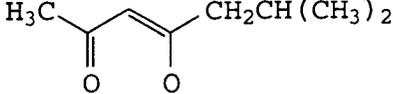
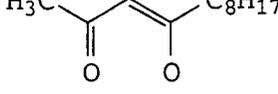
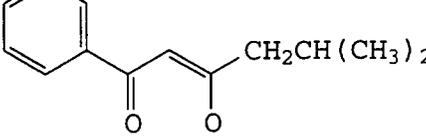
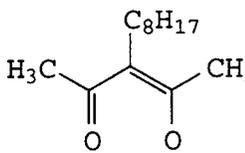
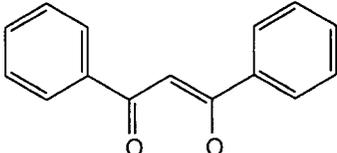
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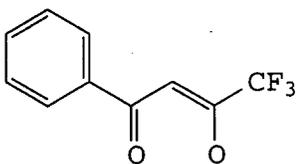
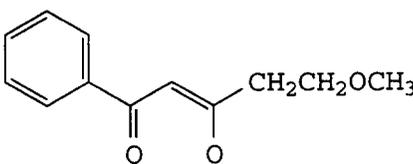
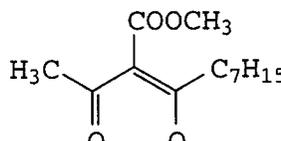
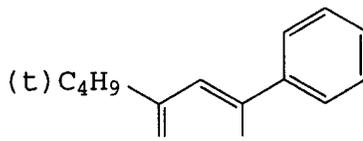
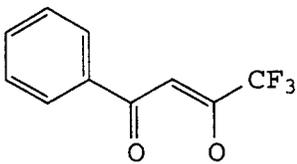
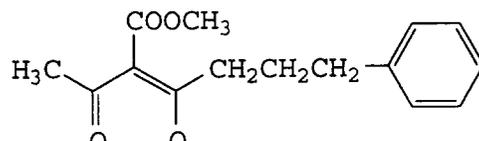
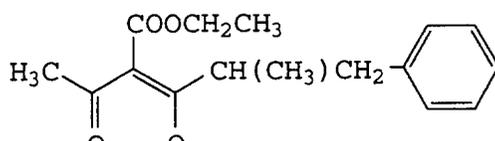
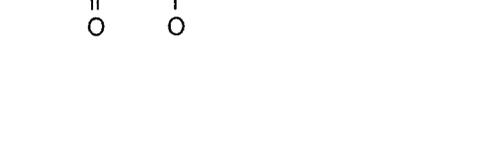
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No.	M	X
5	Ni	 <chem>CC(=O)C=C(C(F)(F)F)C(=O)O</chem>
10	Ni	 <chem>CC(=O)C=C(C(C)(C)C)C(=O)O</chem>
15	Ni	 <chem>CC(C)C(=O)C=C(C)C(=O)O</chem>
20	Ni	 <chem>CC(=O)C=C(CC(C)C)C(=O)O</chem>
25	Ni	 <chem>CC(=O)C=C(CCCCCC)C(=O)O</chem>
30	Ni	 <chem>CC(=O)C=C(CC(C)C)C(=O)c1ccccc1</chem>
35	Ni	 <chem>CC(=O)C(C)C=C(C)C(=O)O</chem>
40	Ni	 <chem>O=C(c1ccccc1)C=C(c2ccccc2)C(=O)O</chem>

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No.	M	X
5	Ni	 <chem>C1=CC=C(C=C1)C(=O)C=C(C(=O)C(F)(F)F)</chem>
10	Ni	 <chem>C1=CC=C(C=C1)C(=O)C=C(C(=O)OCC)</chem>
15	Ni	 <chem>CC(=O)C=C(C(=O)OC)C(=O)C7H15</chem>
20	Ni	 <chem>CC(C)(C)C(=O)C=C(C(=O)C1=CC=CC=C1)</chem>
25	Zn	 <chem>C1=CC=C(C=C1)C(=O)C=C(C(=O)C(F)(F)F)</chem>
30	Ni	 <chem>CC(=O)C=C(C(=O)OC)C(=O)CCc1ccccc1</chem>
35	Ni	 <chem>CC(=O)C=C(C(=O)OCC)C(=O)C(C)Cc1ccccc1</chem>
40	Ni	 <chem>CC(=O)C=C(C(=O)OCC)C(=O)C(C)Cc1ccccc1</chem>
45	Ni	 <chem>CC(=O)C=C(C(=O)OCC)C(=O)C(C)Cc1ccccc1</chem>
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55		

No.	M	X
5	16	Ni
10	17	Ni
15	18	Ni
20		
25	19	Ni

30 To an image-receiving layer, a peeling agent, an antioxidant, a UV absorbent, a light stabilizer, a filler and a pigment may be added. And, a plasticizer, a heat solvent and so forth may also be added to serve as a sensitizer.

35 A peeling agent is capable of improving a recording material peeling property. For example, they include silicone oil including the so-called silicone resin; a solid wax such as polyethylene wax, alkyd wax and Teflon powder; and a fluorine type or phosphoric acid ester type surfactant. Among them, silicone wax may preferably be used.

The amounts of a simply-adding type silicone oil to be added may not be determined uniformly, because they are so added as to meet the various kinds thereof. However, they may be added in a proportion within the range of 0.5 to 50% by weight and, preferably, 1 to 20% by weight to a binder for an image-receiving layer to be used.

40 As for a reaction-setting type silicone oil, there include, for example, those prepared by reaction-setting an amino-denatured silicone oil with an epoxy-denatured silicone oil. As for a catalyst-setting type or a light-setting type silicone oil, there include, for example, those of KS-705F-PS, KS-705F-PS-1 and KS-770-PL-3 which are catalyst-setting type silicone oils manufactured by Shinetsu Chemical Industrial Co.; and KS-720 and KS-774-PL-3, which are light-setting type silicone oils manufactured by Shinetsu Chemical Industrial Co..

45 The above-mentioned light-setting type silicone oils are to be added preferably in a proportion within the range of 0.5 to 30% by weight to a binder for an image-receiving layer to be used.

50 It is also allowed that the above-mentioned peeling agent is dissolved or dispersed in a suitable solvent, and the resulting solution or dispersion is then coated on a part of the surface of an image-receiving layer and then dried, so that a peeling layer can be provided.

As for the above-mentioned antioxidants, there may include, for example, the compounds given in JP OPI Publication Nos. 59-182785/1984, 60-130735/1985 and 1-127387/1989; and a compound well-known as a compound capable of improving an image durability of photographs or other image-recording elements.

55 As for the above-mentioned UV absorbents and Light stabilizers, there may include, for example, the compounds given in JP OPI Publication Nos. 59-158287/1984, 59-196292/1984, 61-283595/1986, 62-229594/1987, 63-74686/1988, 63-145089/1988, 63-122596/1988 and 1-204788/1989; and the compounds well-known as a compound capable of improving an image-durability of photographs and other image-recording elements.

As for the fillers, there may include, for example, inorganic or organic fine particles. As for the inorganic particles include, for example, those of silica gel, calcium carbonate, titanium oxide, acid clay, active clay or alumina. As for the organic particles include, for example, resin particles such as those of fluororesin, guanamine resin, acrylic resin and silicone resin.

5 These inorganic or organic fine particles are preferably added in a proportion within the range of 0.1 to 70% by weight, provided, however, that the amounts thereof to be added may be varied according to the specific gravities thereof.

As for the above-mentioned pigments, there may include, for example, those of titanium white, calcium carbonate, zinc oxide, barium sulfate, silica, talc, clay, kaolin, activated clay and acid clay.

10 As for the above-mentioned plasticizers, there may include, for example, those of a phthalic acid ester, a trimellitic acid ester, a pyromellitic acid ester, an adipic acid ester, other oleic acid esters, a succinic acid ester, a maleic acid ester, a sebacic acid ester, a citric acid ester, epoxidated soybean oil, epoxidated linseed oil, epoxystearic acid, an orthophosphoric acid ester, a phosphorous acid ester and a glycol ester.

15 The whole additive is to be added in a proportion ordinarily within the range of 0.1 to 50% by weight to a binder for an image-receiving layer used.

An image-receiving layer can be formed in the following process; for example, a coating process in which a coating solution is prepared by dispersing or dissolving the components of the image-receiving layer in a solvent, and the resulting coating solution is coated on the surface of a support and then dried; or a lamination process in which a mixture comprising the components of the image-receiving layer is fused to be extruded, so that the extrusion thereof is laminated on the surface of a support.

As for the solvents applicable to the above-mentioned coating processes, there may include, for example, tetrahydrofuran, methyl ethyl ketone, toluene, xylene, chloroform, dioxane, acetone, cyclohexane and butyl acetate.

25 When making use of the above-mentioned lamination process, a co-extrusion process may also be used in the case where a support is made of a synthetic resin.

An image-receiving layer may be formed over the whole surface of a support, or may also be formed on a part of the surface of the support.

30 The thickness of an image-receiving layer is of the order within the range of, generally, 1 to 50 μm and, preferably, 2 to 10 μm . On the other hand, when a self-supportable image-receiving layer itself forms an image-receiving material, the thickness thereof is of the order within the range of, generally, 60 to 200 μm and, preferably, 90 to 150 μm .

35 On the surface of an image-receiving layer, an over-coat layer may also be laminated with the purposes of preventing any fusion, improving an image preservability, and so forth. The over-coat layer may be formed in a gravure-coating process, a wire-bar coating process, a roll coating process, other well-known coating processes, or a lamination process. The thickness of the layer is ordinarily within the range of 0.05 to 3 μm .

40 When an image-receiving element comprises a support and an image-receiving layer, a cushion layer may be interposed between the support and the image-receiving layer, with the purposes of reducing a noise, and transferring and recording an image, with an excellent image-reproducibility, so as to correspond an image information.

The materials for a cushion layer may include, for example, a urethane resin, an acrylic resin, an ethylene type resin, an epoxy resin and a butadiene rubber. The thickness of a cushion layer is preferably within the range of 5 to 25 μm .

Now, a thermal transfer-recording process for forming an image of the invention will be detailed below.

45 As shown in Fig. 1, an image-forming process is comprised of a step in which a colorant barrier layer is ablated imagewise by making a high intensity exposure from the side of a recording element and, preferably, from a colorant barrier layer, and another step in which the ablated recording element and an image-receiving element is so put one upon another as to make the colorant barrier layer and an image-receiving layer face to face, and heat or pressure is then applied to the whole surfaces thereof.

50 As for the light sources for making a high intensity exposure, there may include, for example, those of Xenon light, halogen light, semiconductive laser beam, He-Ne laser beam, Ar laser beam, YAG laser beam and carbonic acid gas laser beam. From the viewpoint of the handling convenience, semiconductive laser beam is preferably used as the Light source. However, the light sources shall not be limited thereto.

55 The power density of an exposure is, preferably, not lower than 100,000 W/cm^2 and, more preferably, not lower than 200,000 W/cm^2 , each on the focal plane. An exposure speed is, preferably, not slower than 1 m/sec . and, more preferably, not slower than 2 m/sec .

A preferable example of the exposure conditions may be given as follows. However, the exposure conditions shall not be limited thereto.

Output power (mW)	Optical efficiency (%)	Exposure spot diameter (μm)	Power density on focal plane (W/cm^2)
100	50	6	177000
150	70	10	134000
500	50	10	318000
2000	30	10	764000

An ablation produced by making a high intensity exposure may be in the halftone dot form or may also be in the continuously ablation form.

When applying heat to the whole surface of a recording material and an image-receiving material each put one upon another, the heat energy may be applied from any side of the image-receiving material, recording material or both of the materials. By applying the above-mentioned heat, the thermally diffusible dye of a colorant layer is diffused to be transferred to the image-receiving layer of the image-receiving material from a colorant layer through the foregoing ablation of a colorant barrier layer, so that an image can be formed. There is no special limitation to a heating temperature. However, it is to be within the range of, ordinarily, 60 to 200 °C and, preferably, 80 to 150 °C.

EXAMPLES

In the following descriptions, the term, "a part" or "parts", herein means "a part by weight" or "parts by weight".

Example 1

Preparation of a recording element

The following compositions were mixed up and dispersed together, so that a colorant layer coating solution containing a thermally diffusible dye could be prepared.

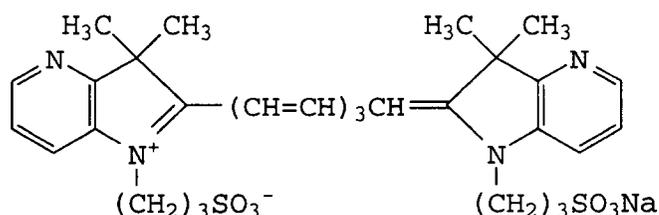
Colorant layer coating solution	
Thermally diffusible dye (Kayaset-blue 714 manufactured by Nihon Kayaku Co.)	4 parts
Polyvinyl butyral resin (Eslec BX-1 manufactured by Sekisui Chemical Co.)	4 parts
Methyl ethyl ketone	90 parts
Cyclohexanone	10 parts

The above-mentioned colorant layer coating solution was coated on a 100 μm -thick polyethylene terephthalate (PET) film by making use of a wire-bar and then dried up, so that a 4 μm -thick colorant layer was formed. On the rear side of the PET film, there formed a nitrocellulose layer containing a silicone-denatured urethane resin (SP-2105 manufactured by Dai-Nichi Seika Co.).

Next, a recording element was prepared in the following manner. A colorant barrier layer having the following composition was coated on the above-mentioned colorant layer by making use of a wire-bar and then dried up, so that a 0.5 μm -thick colorant barrier layer was formed.

Composition of the colorant barrier layer	
Gelatin	3.5 parts
A infrared absorbable dye (IR-1)	1.5 parts
Pure water	95 parts

IR-1



Preparation of an image-receiving element

An image-receiving material was prepared in the following manner. On a 150 μ m-thick synthetic paper (Upo FPG-150 manufactured by Oji Yuka Synthetic Paper Co.), a coating solution for forming an image-receiving layer, which has the following composition, was coated by making use of a wire-bar. The resulting coated synthetic paper was preliminarily dried by making use of a drier, and was then dried up in an oven at 100 °C for one hour, so that a 5 μ m-thick image-receiving layer was formed on the synthetic paper.

Coating solution for forming an image-receiving layer	
Vinyl chloride-vinyl isobutylether copolymer (Laroflex MP25 manufactured by BASF)	9 parts
A polyester-denatured silicone resin (X-24-8300 manufactured by Shinetsu Silicone Co.)	1 part
Methyl ethyl ketone	40 parts
Cyclohexanone	10 parts

(Formation of an image)

(Ablation of the colorant barrier layer)

The colorant barrier layer was ablated in the following manner. A laser beam of a semiconductive laser LT090MD/MF, having a wavelength of 830nm and the maximum beam output of 100mW, manufactured by Sharp Corp., was so condensed as to be a beam having an approximately 6 μ m-diameter. The resulting laser beam was applied at a scanning speed of 2m/sec. to the colorant barrier layer of the resulting recording material. At that time, the optical efficiency was 60%. The dot size in the portions where the ablation was made dotwise was 8 μ m.

(Transfer of the colorant)

As mentioned above, the recording element of which the colorant barrier layer was ablated and the image-receiving material were put one upon another so that the colorant barrier layer and the image-receiving layer could be brought into contact with each other. Then, only the colorant, that was the diffusible dye, in the ablated portion were transferred to the image-receiving layer through a heat roll capable of applying heat of 120 °C and pressure of 2 kg/cm².

When measuring the red reflection density in the over-all solid transferred portion, or the over-all solid density, it was proved to be 2.3. When measuring the reflection density in the unablated portion or the white background density, it was proved to be 0.06. The above-mentioned reflection density was also proved to remain unchanged from the reflection density of the image-receiving element measured before it was passed through the heat roll.

Example 2

The preparation steps from the beginning to the preparation of the colorant layer were quite the same as in Example 1. However, three kinds of the recording elements of the invention and one kind of the comparative recording element were prepared by changing only the composition of the colorant barrier layers as given below. The colorant barrier layers were each made to have a thickness of 0.5 μ m.

EP 0 618 081 A1

Recording element 2-1	
Polycarbonate resin (w/Tg 140 ° V) (IUPILON S2000 manufactured by Mitsubishi Gas-Chemical Co.)	4 parts
Near-infrared absorbable dye (IR-2)	1 part
Methylene chloride	95 parts

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Recording element 2-2	
Water-soluble polyester resin (w/anionic property and pH=3 to 5), (Pesresin 200 in an aqueous 20% solution, manufactured by Takamatsu Yushi Co.)	20 parts
Infrared absorbable dye (IR-3)	1 part
Pure water	79 parts

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Recording material 2-3	
Methyl cellulose resin (SM400 manufactured by Shinetsu Chemical Co.)	3 parts
Infrared absorbable dye (IR-4)	2 parts
Pure water	95 parts

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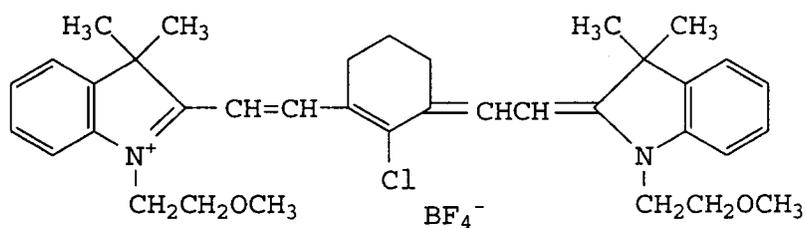
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Recording element for comparison	
An ethylene-vinyl acetate copolymer (w/Tg ≤ -20 ° C), (EV40X manufactured by Mitsui-DuPont Co.)	4 parts
Methyl ethyl ketone	96 parts

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IR-2

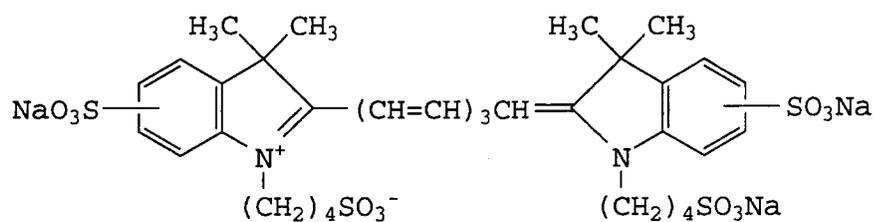
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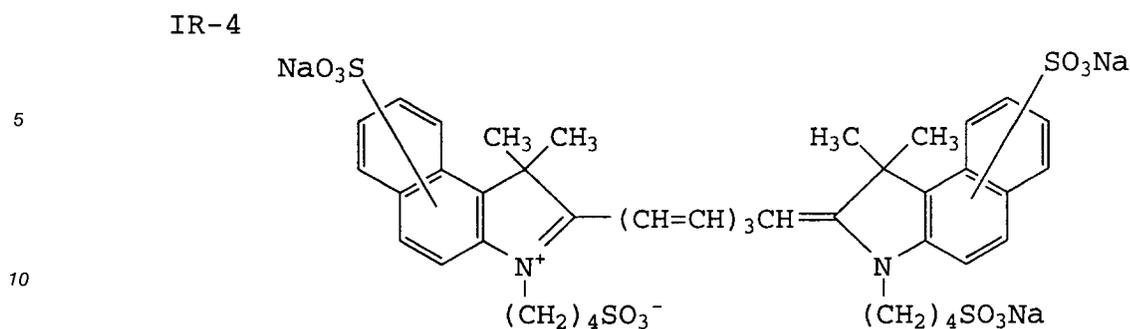
IR-3

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15 By making use of the above-mentioned recording elements and the same image-receiving material as in Example 1, the ablation of the colorant layers and the thermal transfer to the image-receiving layers each quite the same as in Example 1 were carried out, respectively. The results thereof will be given below.

20

Recording element	Solid density	White background density	Spot size in the ablated portion (μm)
2-1	2.4	0.06	4.5
2-2	2.5	0.07	6.0
2-3	2.3	0.06	6.0
Comparison	-	2.0	0

25

In the comparative recording element, any infrared absorbable substance was not contained. Therefore, no ablation could be found out. In the colorant barrier layer, there was no barrier effect. Therefore, the dye having a considerable density was transferred to the image-receiving layer.

30 Example 3

Preparation of a recording element

35 A recording element the same as that in Example 1 was prepared.

An image-receiving element was prepared in the following manner. On a $150\mu\text{m}$ -thick synthetic paper (Upo FPG-150 manufactured by Oji Yuka Synthetic Paper Co.), a coating solution for forming an image-receiving layer, which has the following composition, was coated by making use of a wire-bar. The resulting coated synthetic paper was preliminarily dried by making use of a drier, and was then dried up in an oven at 100°C for one hour, so that a $5\mu\text{m}$ -thick image-receiving layer was formed on the synthetic paper.

40

Coating solution for an image-receiving layer	
Vinyl chloride-vinyl isobutylether copolymer (Laroflex MP25 manufactured by BASF)	8.5 parts
Globular-shaped fine particles of polymethyl methacrylate (w/particle size of $12\text{-}15\mu\text{m}$)	0.5 parts
Polyester-denatured silicone resin (X-24-8300 manufactured by Shinetsu Silicone Co.)	1 part
Methyl ethyl ketone	40 parts
Cyclohexanone	10 parts

45

50 The resulting recording element and the image-receiving element were contacted at the colorant barrier surface and image receiving layer surface and unified into a body at 90°C through a heat roll with a pressure of 1 kg/cm^2 .

55

(Formation of an image)

⟨Ablation of the colorant barrier layer⟩

5 The colorant barrier layer was ablated in the following manner. A laser beam of a semiconductive laser
 LT090MD/MF (having a wavelength of 830nm and the maximum beam output of 100mW, manufactured by
 Sharp Corp.) was so condensed to the colorant barrier layer as to be a beam having an approximately 6
 μm-diameter at the time of the maximum output. The resulting laser beam was applied, at a scanning pitch
 10 of 10μm and a scanning speed of 2m/second, to the colorant barrier layer of the resulting recording
 element. (At that time, the optical efficiency was 60%).

⟨Transfer of a colorant⟩

15 The elements unified into a body, of which the colorant barrier layer was ablated, was passed through a
 heat roll capable of applying heat of 130 °C and a pressure of 3 kg/cm², so that only the colorants in the
 ablated portions, which were diffusible dyes, were transferred to the image-receiving layer.

The unified two elements were peeled off

20 When measuring the red reflection density in the transferred solid image portion comprised of 8μm-
 sized dots or the solid density, it was proved to be 3.1. When measuring the reflection density in the
 unablated portion (or the white background density), it was proved to be 0.06, that was also proved to
 remain unchanged from the reflection density of the image-receiving material measured before it was
 passed through the heat roll.

Example 4

25

Preparation of a recording element

A colorant layer coating solution containing a thermally diffusible dye was prepared by mixing and
 dispersing the following compositions.

30

Colorant layer coating solution	
Thermally diffusible dye (D-1)	25 parts
Ditto (D-2)	15 parts
Ditto (D-3)	40 parts
Polyvinyl butyral resin (Eslec BX-1)	20 parts
Methyl ethyl ketone	700 parts
Cyclohexanone	200 parts

35

40

The above-mentioned colorant layer coating solution was coated on a 100μm-thick PET film by making
 use of a wire-bar and then dried up, so that a 4μm-thick colorant layer could be prepared.

45 Next, a recording material was prepared in the following manner. A colorant barrier layer coating
 solution having the following composition was coated on the above-mentioned colorant layer by making use
 of a wire-bar and then dried up, so that a 0.15μm-thick colorant barrier layer could be so prepared as to
 complete the recording element.

45

Colorant barrier layer coating solution	
Gelatin	2.5 parts
Infrared absorbable dye (IR-3)	2.0 parts
Colloidal silver	0.5 parts
Pure water	95 parts

50

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Preparation of an image-receiving element

A 100 μ m-thick PET film of which the rear surface was treated in an antistaticity prevention process, and the surface resistance thereof was set to be $10^{10}\Omega$. An image-receiving layer coating solution having the following composition was coated, by making use of a wire-bar, on the surface of the PET film opposite to the antistaticity prevented surface thereof, and then dried up at 120 °C for 30 minutes, so that a 4 μ m-thick image-receiving layer was formed.

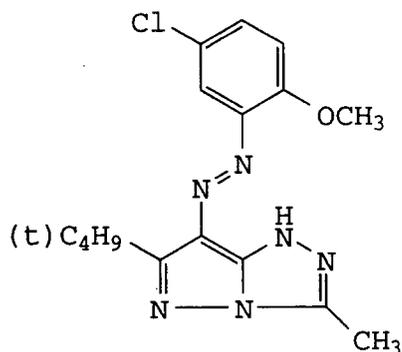
Image-receiving layer coating solution	
Polyvinyl butyral (Eslec BL-1 manufactured by Sekisui Chemical Co.)	40 parts
Metal source (D-4)	50 parts
Amino-modified silicone (KF-393 manufactured by Shinetsu Silicone Co.)	5 parts
Epoxy-modified silicone (X-22-343 manufactured by Shinetsu Silicone Co.)	5 parts
Methyl ethyl ketone	300 parts
Cyclohexanone	100 parts

D-1

5

10

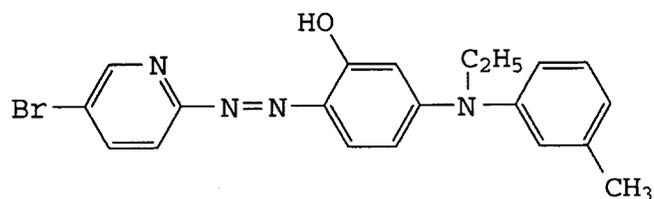
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D-2

20

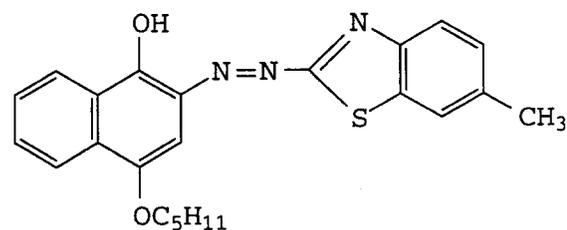
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D-3

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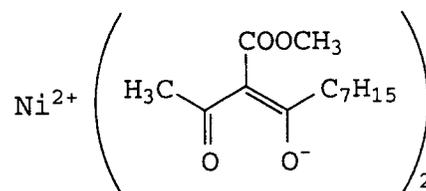
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D-4

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50 Formation of an image

<Ablation of the colorant barrier layer>

55 The colorant barrier layer of the above-mentioned recording material was exposed to light when a semiconductive laser beam having a wavelength of 810nm and the maximum beam output of 150mW was condensed so that a beam diameter of the half-band width could be 5μm at the time of the maximum output having an approximately 6μm-diameter. The exposure was made by 16 semiconductive laser beams.

When making the exposure, the light output on the focal plane was proved to be 101 mW in average per semiconductive laser. The exposure energy density, obtained by calculating out from the exposure light scanning speed, was proved to be 150 mJ/cm², when making an over-all solid exposure.

5 (Transfer of a colorant)

As mentioned above, the colorant barrier layer of a recording material, of which the colorant barrier layer was ablated, and the image-receiving layer of an image-receiving material were put one upon another so that the layers could be brought into contact with each other. Then, only the colorants in the ablated
 10 portion were transferred to the image-receiving layer through a heat roll capable of applying heat of 180 °C and pressure of 2 kg/cm².

The transmission densities were proved to be 0.02 of the PET film, 0.04 in the unexposed portions, and 3.28 in the over-all solid exposed portions, respectively. Further for the purpose of confirming the preservability of the resulting images, the images were preserved at 50 °C for one month. Resultingly, the
 15 preservability was excellently displayed without any image bleeding, even as compared to the reference to a preservation at room temperature.

Example 5

20 A recording material was prepared on a 12μm-thick PET film in the same manner as in Example 4, except that only the composition of the colorant layer coating solution was changed as follows. Also, the following image-receiving element was prepared.

25

Colorant layer coating solution	
Thermally diffusible dye (D-1)	22 parts
Ditto (D-2)	13 parts
Ditto (D-3)	35 parts
Matting agent (MR-20G having an average particle size of 17μm, manufactured by Soken Chemical Co.)	10 parts
30 Polyvinyl butyral resin (Eslec BX-1)	20 parts
Methyl ethyl ketone	700 parts
Cyclohexanone	200 parts

35

(Preparation of an image-receiving element)

A 175μm-thick PET film, of which the rear surface was treated in an antistaticity prevention process and the surface resistance thereof was set to be 5×10⁹Ω. A cushion layer coating solution having the following
 40 composition was coated, by making use of a doctor-blade, on the surface of the PET film opposite to the staticity prevented surface thereof, so that a 10μm-dried-thick cushion layer was formed.

45

Cushion layer coating solution	
Ethylene-vinyl acetate resin (Evaflex EV-40Y manufactured by Mitsui-DuPont Polychemical Co.)	30 parts
Toluene	60 parts
Methyl ethyl ketone	10 parts

50 Next, apart from the above, a 25μm-thick PET film was provided with a peelability by applying a silicone surface treating agent. On the surface treating agent coated surface thereof, an image-receiving layer coating solution having the following composition was coated by making use of a wire-bar, so that a 3μm-dried-thick image-receiving layer was formed.

55

Image-receiving layer coating solution	
Vinyl chloride resin (TK-300 manufactured by Shinetsu Chemical Co.)	40 parts
Metal source (D-4)	50 parts
Amino-modified silicone (KF-393 manufactured by Shinetsu Silicone Co.)	5 parts
Epoxy-modified silicone (X-22-343 manufactured by Shinetsu Silicone Co.)	5 parts
Methyl ethyl ketone	300 parts
Cyclohexanone	100 parts

The surface of the image-receiving layer provided onto the 25 μ m-thick peelable PET film and the surface of the previously formed cushion layer of the 175 μ m-thick PET film were each made face to face and were then applied with a pressure of 3 kg/cm² by a laminator at room temperature, so that the two sheets thereof were pasted together. Thereafter, the peelable PET film was peeled off, so that an image-receiving element comprising a cushion layer and an image-receiving layer each formed in this order on a 175 μ m-thick PET film could be prepared.

Unification process

Now, the surface of the barrier layer of the recording element and the surface of the image-receiving layer of the image-receiving element were made face to face and they were then applied with a pressure of 0.5 kg/cm² by making use of a laminator at room temperature, so that the recording material and the image-receiving element were unified into a body.

Formation of an image

The colorant barrier layer was ablated in the same manner as in Example 4, and the unified material was applied with a heat of 180 °C and a pressure of 5 kg through a laminator. Thereafter, the both of the materials were separated from each other. The transmission densities were proved to be 0.02 of the PET film, 0.04 in the unexposed portions, and 3.14 in the over-all solid exposed portions, respectively.

Comparative Example 1

A colorant layer coating solution for a recording element, to which a colorant layer whole can be exploded to be transferred, was prepared by mixing and dispersing the following compositions. The resulting coating solution was coated in an aluminium-evaporated layer which was evaporated on a 100 μ m-thick polyester film so as to have a transmission density of 50%.

Colorant layer coating solution	
Carbon black	7 parts
Phenol resin (Tamanol 510 manufactured by Arakawa Chemical Co.)	3 parts
Methyl ethyl ketone	40 parts

As for the image-receiving material, an unprocessed polyester film was used as it was.

Image recording

The foregoing recording material and the image receiving material were put on upon another, and then the air remaining in the interspace between the two sheets of the material was evacuated by making close contact under reduced pressure so as to bring them into close contact with each other. From the rear side of the recording material, an aluminium-evaporated layer was exposed to a semiconductive laser beam condensed (to have a wavelength of 810 μ m and the maximum beam output of 150mW) so that the beam diameter of the half-band width could be 5 μ m at the time of the maximum output. When making an exposure, 16x16 dots (that is, 256 dots in total) each having a spot diameter of 5 μ m were taken as a pixel unit, and an image was formed in terms of 80 μ m square units. At that time, the exposure surface power was proved to be 101mW. The over-all solid densities in the over-all solid portions were obtained as relatively high as could be 2.85. However, there were may pin-holes, so that image uniformity was not

satisfactory.

Claims

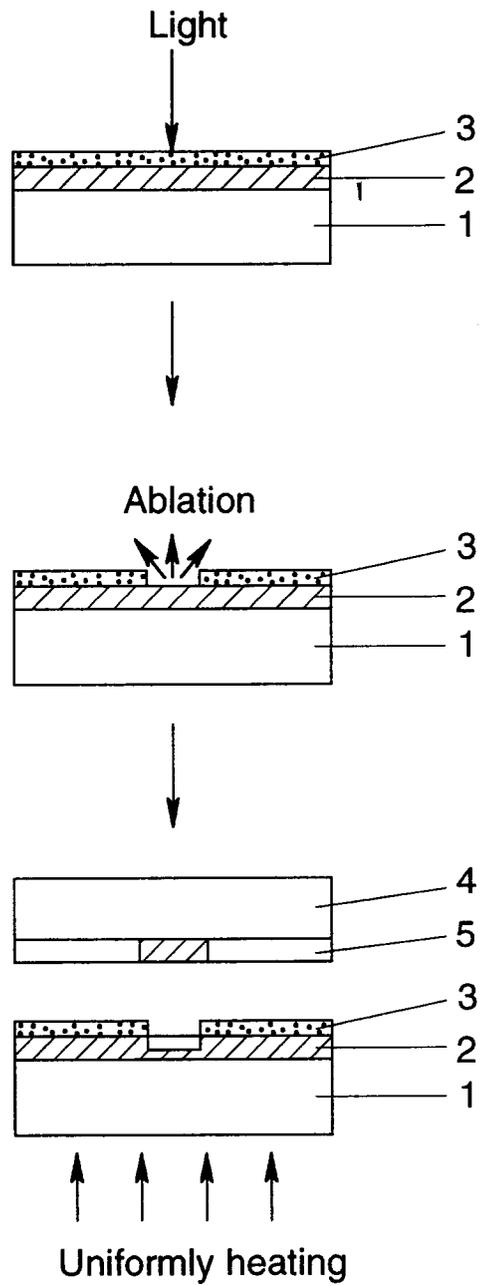
- 5 1. A thermal transfer image recording method comprising the steps of
 imagewise exposing a recording element to high intensity light, which comprises a support having
 thereon a colorant layer containing a colorant, and a colorant barrier layer containing an infrared
 absorbing substance and being provided on said colorant layer, to imagewise ablate said colorant
 barrier layer
 10 contacting the surface of said colorant barrier layer with the surface of image receiving layer of an
 image receiving element, and
 transferring colorant of said colorant layer through ablated portion of said colorant barrier layer to
 said image receiving layer by applying heat or pressure.
- 15 2. The method of claim 1, wherein said colorant barrier layer comprises a resin in an amount of 50 % to
 99 % by weight of the total weight of said colorant barrier layer.
3. The method of claim 1, wherein said colorant barrier layer comprises a water-soluble resin.
- 20 4. The method of claim 3, wherein said water-soluble resin is selected from the group consisting of
 gelatin, polyvynyl alcohol, water-soluble polyvinylformal, water-soluble polyvinylacetal, water-soluble
 polyvinylbutyral, polyvinylpyrrolidone, watr-soluble polyester, water-soluble nylon, polyacrylic acid,
 watersoluble polyurethane, methylcellulose, hydroxyethylcellulose, hydroxypropylcellulose and carbox-
 ylcellulose.
- 25 5. The method of claim 1, wherein said colorant barrier layer comprises a resin having an ionic bond.
6. The method of claim 1, wherein said colorant barrier layer comprises a resin having a glass transition
 point of not lower than 120° C.
- 30 7. The method of claim 1, wherein said colorant layer comprises a dye capable of forming a chelate
 compound.
8. The method of claim 1, wherein said infrared absorbing substance is a dye having a absorption
 35 maximum within the range of from 700 nm to 1200 nm and a molar extinction coefficient of 50,000 or
 more at the maximum absorption wavelength.
9. The method of claim 1, wherein said image receiving layer contains a metal ion-containing compound.
- 40 10. The method of claim 1, wherein said exposing step is carried out by high intensity light having a power
 density of not less than 100000W/cm² with a exposing speed of not less than 1m/sec.

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FIG. 1





European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 10 5080

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,D	EP-A-0 489 972 (AGFA-GEVAERT N.V.) * page 2, line 43 - line 47; claims 1-11; example 1 * -----	1	B41M5/24 B41M5/38 B41M5/035 B41M5/025
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			B41M
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		12 July 1994	Bacon, A
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X : particularly relevant if taken alone		T : theory or principle underlying the invention	
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