

(19)



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(11)

**EP 0 580 120 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
**10.03.1999 Bulletin 1999/10**

(51) Int Cl.<sup>6</sup>: **C09B 69/06, B41M 5/26**

(21) Application number: **93111590.1**

(22) Date of filing: **20.07.1993**

**(54) Use of hydrophobic cationic dye in an ink layer of a thermal transfer ink ribbon**

Verwendung eines hydrophoben kationischen Farbstoffs in der Farbschicht eines Farbbandes für den  
Thermotransferdruck

Usage d'un colorant cationique hydrophobique pour la couche d'encre d'un ruban encré pour le  
transfert thermique

(84) Designated Contracting States:  
**DE FR GB**

(30) Priority: **23.07.1992 JP 217137/92**

(43) Date of publication of application:  
**26.01.1994 Bulletin 1994/04**

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**US-A- 4 602 263** **US-A- 4 748 149**

**EP 0 580 120 B1**

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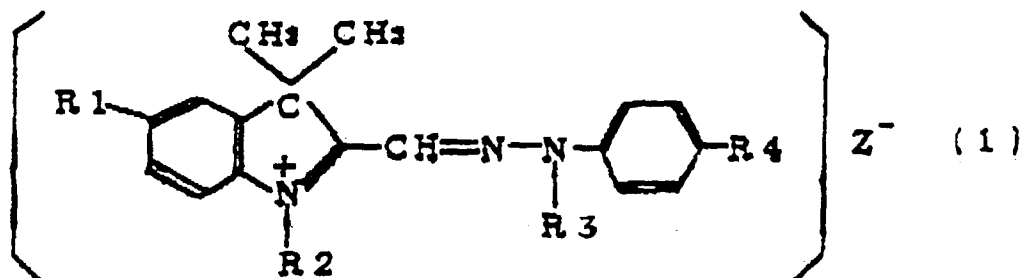
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$$\left[ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{R}_1 \text{---} \text{C}_6\text{H}_4 \text{---} \text{N}^+ \text{---} \text{CH}=\text{N} \text{---} \text{N} \text{---} \text{C}_6\text{H}_4 \text{---} \text{R}_4 \\ | \quad | \\ \text{R}_2 \quad \text{R}_3 \end{array} \right] \text{Z}^- \quad (1)$$

2

a cycloalkyl group, an alkoxy group, an aryl group, an aryloxy group, an aralkyl group, an aralkoxy group, an alkenyl group, an alkenoxy group, an alkoxycarbonyl group, an acyloxy group, or an acyl group which may be substituted, and Z<sup>-</sup> represents a counter ion in ink layers of thermal transfer ink ribbons.

[0009] According to another aspect of this invention, there is provided a thermal transfer ink ribbon which comprises a support and an ink layer formed on the support, wherein the ink layer comprises a hydrophobic cationic dye which is obtained by substituting, with an organic anion, a counter ion of a diazacarbocyanine cationic dye of the formula (1)



wherein R1, R2, R3 and R4 independently represent a hydrogen atom, a halogen atom, a cyano group, an alkyl group, a cycloalkyl group, an alkoxy group, an aryl group, an aryloxy group, an aralkyl group, an aralkoxy group, an alkenyl group, an alkenoxy group, an alkoxycarbonyl group, an acyloxy group, or an acyl group which may be substituted, and Z<sup>-</sup> represents a counter ion.

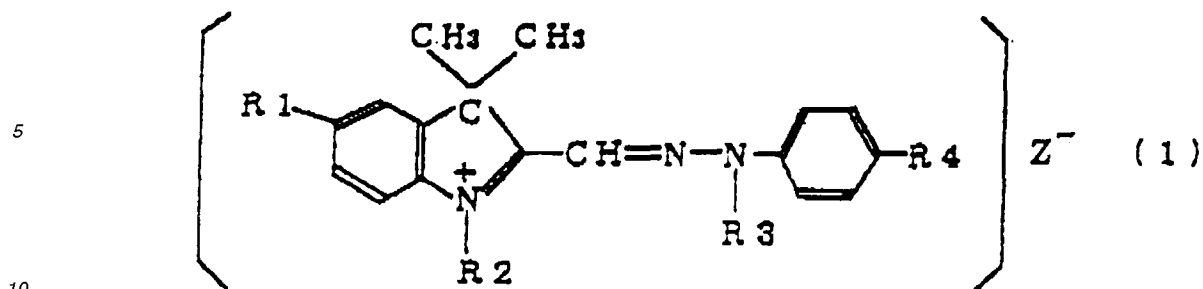
#### Brief Description of the Drawings

- [0010] Figure 1 shows a sectional view of a thermal transfer ink ribbon of the invention.
- [0011] Figure 2 is a dynamic sensitivity characteristic graph of an ink ribbon of the invention.
- [0012] Figure 3 is a dynamic sensitivity characteristic graph of another ink ribbon of the invention.
- [0013] Figure 4 is a dynamic sensitivity characteristic graph of another ink ribbon of the invention.
- [0014] Figure 5 is a dynamic sensitivity characteristic graph of still another ink ribbon of the invention.
- [0015] Figure 6 is a dynamic sensitivity characteristic graph of another ink ribbon of the invention.
- [0016] Figure 7 is a dynamic sensitivity characteristic graph of another ink ribbon of the invention.
- [0017] Figure 8 is a dynamic sensitivity characteristic graph of yet another ink ribbon of the invention.
- [0018] Figure 9 is a dynamic sensitivity characteristic graph of another ink ribbon of the invention.
- [0019] Figure 10 is a dynamic sensitivity characteristic graph of another ink ribbon of the invention.
- [0020] Figure 11 is a dynamic sensitivity characteristic graph of another ink ribbon of the invention.
- [0021] Figure 12 is a dynamic sensitivity characteristic graph of another ink ribbon of the invention.
- [0022] Figure 13 is a dynamic sensitivity characteristic graph of another ink ribbon of the invention.

#### Description of the Preferred Embodiments

[0023] We have found that the substitution of a counter ion, such as a halogen, of cationic dyes with an organic anion enables the cationic dyes to be imparted with hydrophobicity and that specific type of dyes have good gradation properties with respect to yellow, magenta and cyan colors necessary for the formation of full color images. The invention is accomplished based on this finding.

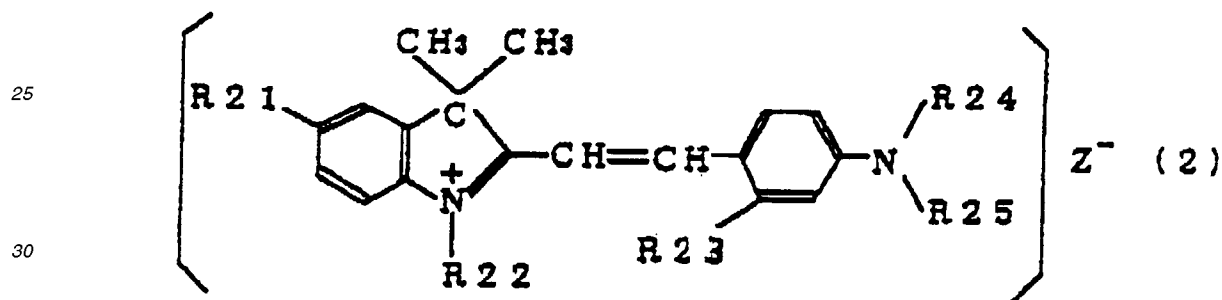
[0024] The invention makes use of a yellow dye, a hydrophobic cationic dye which is obtained by substituting, with an organic anion, a counter ion of a diazacarbocyanine cationic dye of the formula (1)



wherein R1, R2, R3 and R4 independently represent a hydrogen atom, a halogen atom, a cyano group, an alkyl group, a cycloalkyl group, an alkoxy group, an aralkoxy group, an alkenyl group, an alkenoxy group, an alkoxy carbonyl group, an acyloxy group, or an acyl group which may be substituted, and Z- represents a counter ion. Examples of the cationic dyes not substituted with an organic anion include C.I. Basic Yellow 28 and 51.

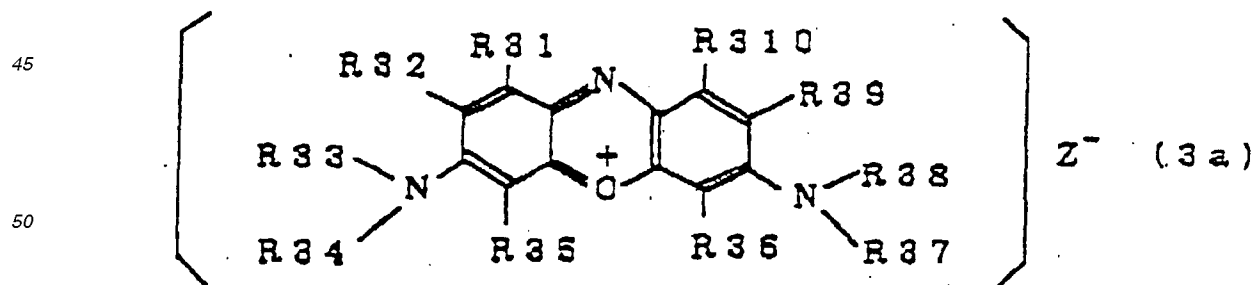
[0025] Another type of yellow dye provided for use according to the invention includes hydrophobic cationic dyes which are obtained by substituting the counter ion of a cationic dye such as C.I. Basic Yellow 21, 36, 67 or 73 with an organic anion.

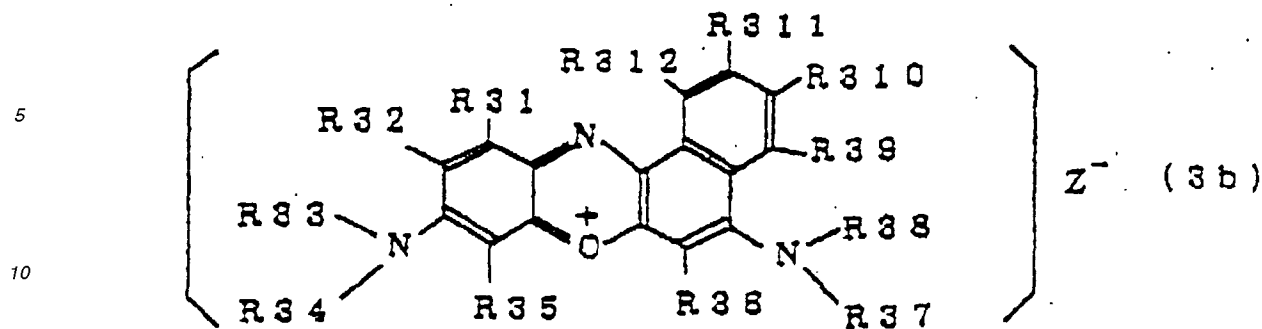
[0026] The invention also makes use of a magenta dye, a hydrophobic cationic dye which is obtained by substituting, with an organic anion, a counter ion of a hemicyanine cationic dye of the formula (2)



wherein R21, R22, R23, R24 and R25 independently represent a hydrogen atom, a halogen atom, a cyano group, an alkyl group, a cycloalkyl group, an alkoxy group, an aryl group, an aryloxy group, an aralkyl group, an aralkoxy group, an alkenyl group, an alkenoxy group, an alkoxy carbonyl group, an acyloxy group, or an acyl group which may be substituted, provided that R24 and R25 may join together to form a ring, and Z- represents a counter ion. Examples of the cationic dyes prior to substitution with an organic anion include C.I. Basic Red 13, 14, C.I. Basic Violet 7, 16, C.I. 48025 and 48030.

[0027] Moreover, the invention makes use of, as a cyan dye, a hydrophobic cationic dye which is obtained by substituting, with an organic anion, a counter ion of an oxazine cationic dye of the formula (3a) or (3b).





15 wherein R31, R32, R33, R34, R35, R36, R37, R38, R39, R310, R311 and R312 independently represent a hydrogen atom, a halogen atom, a cyano group, an alkyl group, a cycloalkyl group, an alkoxy group, an aryl group, an aryloxy group, an aralkyl group, an aralkoxy group, an alkenyl group, an alkenoxy group, an alkoxycarbonyl group, an acyloxy group, or an acyl group which may be substituted, provided that R31 and R32, R33 and R34, R37 and R38, R39 and R310, R310 and R311, and R311 and R312 may, respectively, join together to form a ring, and Z- represents a counter ion. Examples of the cationic dyes prior to the substitution with the organic anion include C.I. Basic Blue 3, 6, 10, 12, 49, 75, 87, 95, 96, 101, 104, 107, 108, 114 122, 124, 141, 151 155 and C.I. 51015.

20 **[0028]** The present invention also provides a thermal transfer ink ribbon which comprises a support and an ink layer formed thereon, characterized in that the ink layer comprises any of these hydrophobic cationic dyes.

25 **[0029]** The organic anions used in the present invention are those which can render the hydrophilic cationic dyes hydrophobic by substituting the counter ion of the cationic dye therewith. Such organic anions are those ions of anionic surface active agents indicated below. It will be noted here that these organic anions may be available as salts of alkali metals prior to the substitution with the counter ion of the hydrophilic cationic dyes.

(1) Carboxylic acid anions

30 (1a) Soaps (RCOO-)

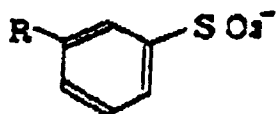
(1b) N-Acylamino acids (RCON-COO-)

(1c) Alkyl ether carboxylic acids (RO(C<sub>2</sub>H<sub>4</sub>O)<sub>n</sub>COO-)

35 (2) Sulfonic acid anions

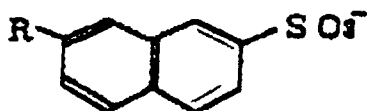
(2a) Alkylsulfonates ((RSO<sub>3</sub>-)

(2b) Alkylbenzenesulfonates (formula (4))



(4)

45 (2c) Alkyl naphthalenesulfonates (formula (5))



(5)

55 (2d) Sulfosuccinates (formula (6))



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(2e) a -Olefinsulfonates

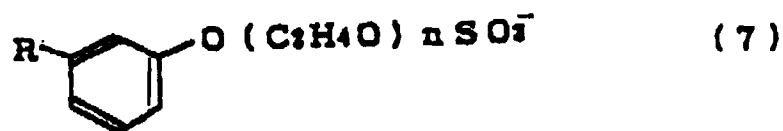
(2f) N-acylsulfonates (-CON-SO<sub>3</sub><sup>-</sup>)

(3) Sulfuric ester anions

(3a) Sulfated oil

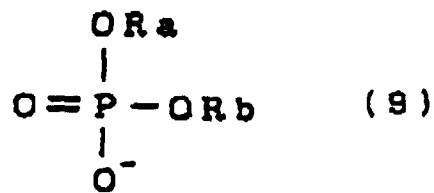
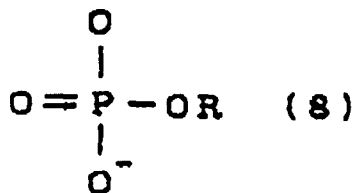
(3b) Alkylsulfates (ROSO<sub>3</sub><sup>-</sup>)(3c) Alkyl ether sulfates (RO(C<sub>2</sub>H<sub>4</sub>O)<sub>n</sub>SO<sub>3</sub><sup>-</sup>)

(3d) Alkyl aryl ether sulfates (formula (7))

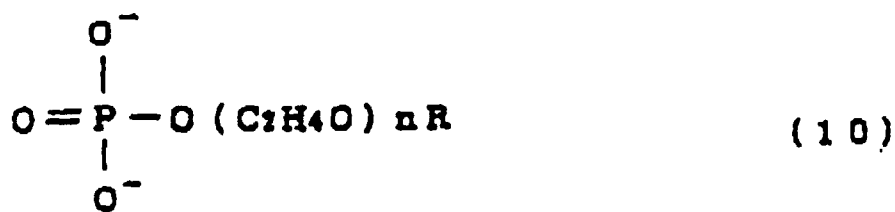
(3e) Alkylamidosulfates (RCONH-OSO<sub>3</sub><sup>-</sup>)

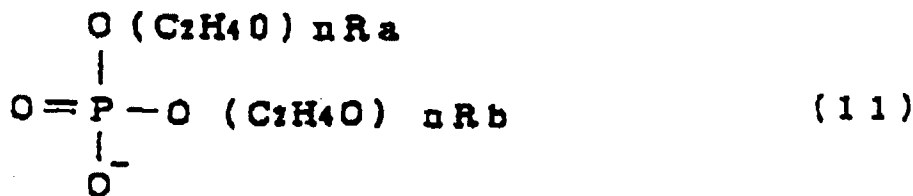
(4) Phosphoric ester anions

(4a) Alkylphosphates (formulas (8), (9))



(4b) Alkyl ether phosphates (formulae (10), (11))





## (4c) Alkyl aryl ether phosphates

**[0030]** In the above organic anions, it is preferred that R, Ra and Rb, respectively, represent a linear or branched alkyl or alkenyl group having 5 - 20 carbon atoms from the viewpoint of the ease in availability and costs.

**[0031]** Of these organic anions, it is preferable to use sulfosuccinate anions of (2d) such as diethylhexylsulfosuccinate anion, alkylbenzenesulfonate anions of (2b) such as dodecylbenzenesulfonate anion, alkylsulfate anions of (3b) such as lauryl sulfate anion, and soap anions of (1a).

**[0032]** The hydrophobic cationic dyes used according to the invention can be obtained by dropping an aqueous solution of salts containing the above-indicated organic anions in an aqueous solution of a hydrophilic cationic dye under agitation, extracting the resulting mixture with an organic solvent such as toluene, and removing the solvent from the organic phase to obtain a hydrophobic dye as a residue insoluble or sparingly soluble in water.

**[0033]** As a matter of course, the hydrophobic cationic dyes used according to the invention are hydrophobic in nature, so that they can be uniformly, stably, mixed with hydrophobic resins which would not be otherwise used along with known hydrophilic cationic dyes. For instance, the above hydrophobic cationic dyes can be uniformly, stably mixed with hydrophobic polymer binders for use in the ink layer of a thermal transfer ink ribbon and are thus suitable for use as the dye of thermal transfer ink ribbons.

**[0034]** Accordingly, a thermal transfer ink ribbon composed of a support and an ink layer formed thereon wherein the ink layer contains the above hydrophobic cationic dye is within the scope of the invention.

**[0035]** The ink layer of the thermal transfer ink ribbon of the invention may be constituted of the above hydrophobic cationic dye alone. If necessary, other ingredients such as hydrophobic polymer binders, melting point adjusting agents, plasticizers, solvents, binders, and pigments and dyes other than the hydrophobic cationic dyes used according to the invention can be used.

**[0036]** The support of the thermal transfer ink ribbon of the invention may be, for example, polyethylene terephthalate films, nylon films, triacetyl cellulose films, moistureproof cellophane sheets, capacitor paper, thin paper, cloth the like.

**[0037]** The thermal transfer ink ribbon of the invention may be fabricated by a usual manner. For instance, an ink composition comprising the above hydrophobic cationic dye is applied onto a support by use of a wire bar coater to obtain a ribbon.

**[0038]** In order to form color images on a transfer material by the use of the thermal transfer ink ribbon of the invention, the ink layer of the ink ribbon and the dye-receiving layer of the transfer material are placed in face-to-face relation, under which an image-forming portion is heated from the support side of the ink ribbon by means of a thermal head of a laser beam of a printer, thereby causing the dye ingredient in the ink layer to be transferred on the image-receiving layer by sublimation or thermal diffusion.

**[0039]** The hydrophobic cationic dyes used according to the invention are rendered hydrophobic by substitution of the counter ion of the hydrophilic cationic dye with an organic anion, making it possible to enhance miscibility with non-aqueous solvents and hydrophobic polymers. Thus, the above dyes are usable as a dye for the thermal transfer ink ribbon.

**[0040]** The invention is more particularly described by way of examples.

Example 1 - Preparation of a diethylhexylsulfosuccinate of C.I. Basic Yellow 28

**[0041]** 1 g of C.I. Basic Yellow 28 (commercial name: Kayacryl Golden Yellow GL available from Nippon Kayaku K. K.) which is a diazacyanocyanine cationic dye for dyeing acrylic fibers from which additives such as sodium sulfate were removed by a Soxhlet apparatus using ethanol was dissolved in 100 ml of water. While agitating the dye solution, 50 g of a 2 wt% sodium diethylhexylsulfosuccinate aqueous solution was dropped in the dye solution to substitute the counter ion with an organic anion (diethylhexylsulfosuccinate anion).

**[0042]** The resultant solution was evaporated to dryness under reduced pressure. Toluene was added to the resultant residue for extraction of the dye. The toluene solution of the dye was filtered to remove an unreacted matter and side products (inorganic salts). The filtrate was concentrated to dryness under reduced pressure. As a result, about 1.6 g of the captioned hydrophobic cationic dye with a dark orange in the form of a tar was obtained.

**[0043]** The hydrophobic cationic dye was placed in a water-toluene phase and shaken, whereupon it was found most of the dye remained in the toluene phase. On the other hand, the dye which had not been subjected to the substitution treatment with the organic anion was kept in the aqueous phase when treated in a similar manner as set out above. This reveals that the substitution treatment contributes to drastic improvement of miscibility with organic solvents.

#### Fabrication of thermal transfer ink ribbon

**[0044]** Using the thus obtained hydrophobic cationic dye, a thermal transfer ink ribbon 10 shown in Fig. 1 was fabricated in the following manner.

**[0045]** A 6  $\mu\text{m}$  thick polyethylene terephthalate (PET) film which had a heat-resistant, lubricating layer 1 on the one side thereof was provided as a support 2. The support 2 was applied with 25 g/m<sup>2</sup> of a thermal transfer ink composition with the following formulation on a side opposite to the side of the heat-resistant lubricating layer 1 of the support 1 and dried. By this, there was obtained a thermal transfer ink ribbon 10, as shown in Fig. 1, which had the PET film support 2 and the ink layer 3 with a thickness of about 1  $\mu\text{m}$ .

| Thermal transfer ink composition                                  |                    |
|-------------------------------------------------------------------|--------------------|
| Hydrophobic cationic dye of the invention                         | 1 part by weight   |
| Polyvinylbutyral<br>(6000-CS, made by Denki Chem. Ind. Co., Ltd.) | 1 part by weight   |
| Toluene                                                           | 12 parts by weight |
| Methyl ethyl ketone                                               | 12 parts by weight |

**[0046]** The thermal transfer ink ribbon obtained above was set in a ribbon cassette (not shown). A color video printer (commercial name: CVP-G500, made by Sony Co., Ltd.) was used for single color printing on a printing sheet whose image-receiving layer was made of a vinyl chloride-vinyl acetate copolymer resin (commercial name: UPC-3010, made by Sony Co., Ltd.), a printing sheet whose dye-receiving layer was made of a polyester resin (commercial name: VPM-30ST, made by Sony Co., Ltd.), and a printing sheet whose dye-receiving layer was made of a cellulose ester resin (commercial name: VPM-30STA, made by Sony Co., Ltd.) As a result, there was obtained an image with a good yellow color and good gradation properties.

**[0047]** Fig. 2 shows a so-called dynamic sensitivity (color-development) characteristic of the ink ribbon. The abscissa axis indicates a gradation (step) which shows an energy added for image printing in a stepwise manner. As shown in the figure, the ink ribbon fabricated in this example ensures gradation printing by the thermal transfer with respect to all the printing sheets.

#### Example 2 - Preparation of dodecylbenzenesulfonate of C.I. Basic Yellow 28

**[0048]** In the same manner as in Example 1, 1 g of C.I. Basic Yellow 28 and 1 g of sodium dodecylbenzenesulfonate were reacted to obtain about 1.8 g of crystals of the captioned hydrophobic cationic dye. The hydrophobic cationic dye was placed in a water-toluene phase and shaken, whereupon the dye mostly remained in the toluene phase. This reveals that the substitution with the organic anion contributes to drastically improved miscibility with the organic solvent.

**[0049]** In the same manner as in Example 1, the resultant hydrophobic cationic dye was used to make a thermal transfer ink ribbon, followed by a similar printing, test. As a result, there was obtained an image which assumed a good yellow color and good gradation properties. Fig. 3 shows a so-called dynamic sensitivity (color-development) characteristic of the ink ribbon. As shown in the figure, the ink ribbon obtained in this example ensures gradation printing by the thermal transfer on the printing sheets.

#### Example 3 - Preparation of laurylsulfate of C.I. Basic Yellow 28

**[0050]** In the same manner as in Example 1, 1 g of C.I. Basic Yellow 28 and 1 g of sodium laurylsulfate were reacted to obtain about 1.5 g of crystals of the captioned hydrophobic cationic dye. The hydrophobic cationic dye was placed in a water-toluene phase and shaken, whereupon the dye mostly remained in the toluene phase. This reveals that the substitution with the organic anion contributes to drastically improved miscibility with the organic solvent.

**[0051]** In the same manner as in Example 1, the resultant hydrophobic cationic dye was used to make a thermal transfer ink ribbon, followed by a similar printing test. As a result, there was obtained an image which assumed a good yellow color and good gradation properties. Fig. 4 shows a so-called dynamic sensitivity (color-development) characteristic of the ink ribbon. As shown in the figure, the ink ribbon obtained in this example ensures gradation printing by

the thermal transfer on the printing sheets.

#### Example 4 - Preparation of laurylsulfate of C.I. Basic Yellow 51

**[0052]** In the same manner as in Example 1, 1 g of C.I. Basic Yellow 51 (commercial name: Diacryl Yellow 3G-N, made by Mitsubishi Chem. Hoechst Co., Ltd.) and 1 g of sodium dodecylbenzenesulfonate were reacted to obtain about 1.5 g of crystals of the captioned hydrophobic cationic dye. The hydrophobic cationic dye was placed in a water-toluene phase and shaken, whereupon the dye mostly remained in the toluene phase. This reveals that the substitution with the organic anion contributes to drastically improved miscibility with the organic solvent.

**[0053]** In the same manner as in Example 1, the resultant hydrophobic cationic dye was used to make a thermal transfer ink ribbon, following by a similar printing test. As a result, there was obtained an image which assumed a good lemon yellow color and good gradation properties. Fig. 5 shows a so-called dynamic sensitivity (color-development) characteristic of the ink ribbon. As shown in the figure, the ink ribbon obtained in this example ensures gradation printing by the thermal transfer on the printing sheets.

#### Example 5 - Preparation of laurylsulfate of C.I. Basic Yellow 21

**[0054]** In the same manner as in Example 1, 1 g of C.I. Basic Yellow 21 (commercial name: Aizen Cathilon Yellow 7GLH, made by Hodogaya Chem. Inc. Co., Ltd.) and 1 g of sodium dodecylbenzenesulfonate were reacted to obtain about 1.6 g of crystals of the captioned hydrophobic cationic dye. The hydrophobic cationic dye was placed in water-toluene phase and shaken, whereupon the dye mostly remained in the toluene phase. This reveals that the substitution with the organic anion contributes to drastically improved miscibility with the organic solvent.

**[0055]** In the same manner as in Example 1, the resultant hydrophobic cationic dye was used to make a thermal transfer ink ribbon followed by a similar printing test. As a result, there was obtained an image which assumed a good lemon yellow color and good gradation properties. Fig. 6 shows a so-called dynamic sensitivity (color-development) characteristic of the ink ribbon. As shown in the figure, the ink ribbon obtained in this example ensures gradation printing by the thermal transfer on the printing sheets.

#### Example 6 - Preparation of diethylhexylsulfosuccinate of C.I. Basic Yellow 36

**[0056]** In the same manner as in Example 1, 1 g of C.I. Basic Yellow 36 (commercial name: Aizen Cathilon Yellow K-3RLH, made by Hodogaya Chem. Inc. Co., Ltd.) and 1 g of sodium diethylhexylsuccinate were reacted to obtain about 1.8 g of a tar-like captioned hydrophobic cationic dye. The hydrophobic cationic dye was placed in a water-toluene phase and shaken, whereupon the dye mostly remained in the toluene phase. This reveals that the substitution with the organic anion contributes to drastically improved miscibility with the organic solvent.

**[0057]** In the same manner as in Example 1, the resultant hydrophobic cationic dye was used to make a thermal transfer ink ribbon, followed by a similar printing test. As a result, there was obtained an image which assumed a good yellow color and good gradation properties. Fig. 7 shows a so-called dynamic sensitivity (color-development) characteristic of the ink ribbon. As shown in the figure, the ink ribbon obtained in this example ensures gradation printing by the thermal transfer on the printing sheets.

#### Example 7 - Preparation of laurylsulfate of C.I. Basic Yellow 67

**[0058]** In the same manner as in Example 1, 1 g of C.I. Basic Yellow 67 (commercial name: Kayacryl Yellow 3RL, made by Nippon Kayaku K.K.) and 1 g of sodium laurylsulfate were reacted to obtain about 1.8 g of a tar-like captioned hydrophobic cationic dye. The hydrophobic cationic dye was placed in a water-toluene phase and shaken, whereupon the dye mostly remained in the toluene phase. This reveals that the substitution with the organic anion contributes to drastically improved miscibility with the organic solvent.

**[0059]** In the same manner as in Example 1, the resultant hydrophobic cationic dye was used to make a thermal transfer ink ribbon, followed by a similar printing test. As a result, there was obtained an image which assumed a good yellow color and good gradation properties. Fig. 8 shows a so-called dynamic sensitivity (color-development) characteristic of the ink ribbons. As shown in the figure, the ink ribbon obtained in this example ensures gradation printing by the thermal transfer on the printing sheets.

#### Example 8 - Preparation of laurylsulfate of C.I. Basic Yellow 73

**[0060]** In the same manner as in Example 1, 1 g of C.I. Basic Yellow 73 (commercial name: Aizen Cathilon Yellow CD-RLH, made by Hodogaya Chem. Ind. Co., Ltd.) and 1 g of sodium laurylsulfate were reacted to obtain about 1.8

g of a tar-like captioned hydrophobic cationic dye. The hydrophobic cationic dye was placed in a water-toluene phase and shaken, whereupon the dye mostly remained in the toluene phase. This reveals that the substitution with the organic anion contributes to drastically improved miscibility with the organic solvent.

**[0061]** In the same manner as in Example 1, the resultant hydrophobic cationic dye was used to make a thermal transfer ink ribbon, followed by a similar printing test. As a result, there was obtained an image which assumed a good yellow color and good gradation properties. Fig. 9 shows a so-called dynamic sensitivity (color-development) characteristic of the ink ribbon. As shown in the figure, the ink ribbon obtained in this example ensures gradation printing by the thermal transfer on the printing sheets.

#### Example 9 - Preparation of dodecylbenzenesulfonate of C.I. Basic Red 14

**[0062]** In the same manner as in Example 1, 1 g of C.I. Basic Red 14 (commercial name: Aizen Cathilon Red 4GH, made by Hodogaya Chem. Ind., Co., Ltd.) and 1 g of sodium dodecylbenzenesulfonate were reacted to obtain about 1.6 g of a dark reddish purple tar-like captioned hydrophobic cationic dye. The hydrophobic cationic dye was placed in a water-toluene phase and shaken, whereupon the dye mostly remained in the toluene phase. This reveals that the substitution with the organic anion contributes to drastically improved miscibility with the organic solvent.

**[0063]** In the same manner as in Example 1, the resultant hydrophobic cationic dye was used to make a thermal transfer ink ribbon, following by a similar printing test. As a result, there was obtained an image which assumed a good red color and good gradation properties. Fig. 10 shows a so-called dynamic sensitivity (color-development) characteristic of the ink ribbon. As shown in the figure, the ink ribbon obtained in this example ensures gradation printing by the thermal transfer on the printing sheets.

#### Example 10 - Preparation of diethylhexylsulfosuccinate of C.I. Basic Red 13

**[0064]** In the same manner as in Example 1, 1 g of C.I. Basic Red 13 (commercial name: Aizen Cathilon Pink FGH, made by Hodogaya Chem. Ind., Co., Ltd.) and 1 g of sodium diethylhexylsuccinate were reacted to obtain about 1.8 g of a tar-like captioned hydrophobic cationic dye. The hydrophobic cationic dye was placed in a water-toluene phase and shaken, whereupon the dye mostly remained in the toluene phase. This reveals that the substitution with the organic anion contributes to drastically improved miscibility with the organic solvent.

**[0065]** In the same manner as in Example 1, the resultant hydrophobic cationic dye was used to make a thermal transfer ink ribbon, followed by a similar printing test. As a result, there was obtained an image which assumed a good magenta color and good gradation properties. Fig. 11 shows a so-called dynamic sensitivity (color-development) characteristic of the ink ribbon. As shown in the figure, the ink ribbon obtained in this example ensures gradation printing by the thermal transfer on the printing sheet.

#### Example 11 - Preparation of dodecylbenzenesulfonate of C.I. Basic Violet 7

**[0066]** In the same manner as in Example 1, 1 g of C.I. Basic Violet 7 (commercial name: Aizen Cathilon Red 6BH, made by Hodogaya Chem. Ind. Co., Ltd.) and 1 g of sodium dodecylbenzenesulfonate were reacted to obtain about 1.8 g of the captioned hydrophobic cationic dye. The hydrophobic cationic dye was placed in a water-toluene phase and shaken, whereupon the dye mostly remained in the toluene phase. This reveals that the substitution of the counter ion with the organic anion contributes to drastically improved miscibility with the organic solvent.

**[0067]** In the same manner as in Example 1, the resultant hydrophobic cationic dye was used to make a thermal transfer ink ribbon, followed by a similar printing test. As a result, there was obtained an image which assumed a good magenta color and good gradation properties. Fig. 12 shows a so-called dynamic sensitivity (color-development) characteristic of the ink ribbon. As shown in the figure, the ink ribbon obtained in this example ensures gradation printing by the thermal transfer on the printing sheets.

#### Example 12 - Preparation of diethylhexylsulfosuccinate of C.I. Basic Blue 75

**[0068]** In the same manner as in Example 1, 1 g of C.I. Basic Blue 75 (commercial name: Kayacryl Light Blue 4GSL, made by Nippon Kayaku K.K.) and 1 g of sodium diethylhexylsuccinate were reacted to obtain about 1.6 of a dark bluish green, tar-like captioned hydrophobic cationic dye. The hydrophobic cationic dye was placed in a water-toluene phase and shaken, whereupon the dye mostly remained in the toluene phase. This reveals that the substitution with the organic anion contributes to drastically improving miscibility with the organic solvent.

**[0069]** In the same manner as in Example 1, the resultant hydrophobic cationic dye was used to make a thermal transfer ink ribbon, followed by a similar printing test using a printing sheet (VMP-30STA) of Sony Co., Ltd. As a result, there was obtained an image which assumed a good cyan color and good gradation properties. Fig. 13 shows a so-

called dynamic sensitivity (color-development) characteristic of the ink ribbon. As shown in the figure, the ink ribbon obtained in this example ensures gradation printing by the thermal transfer on the printing sheets.

#### Example 13 - Preparation of dodecylbenzenesulfonate of C.I. Basic Blue 3

**[0070]** In the same manner as in Example 1, 1 g of C.I. Basic Blue 3 (commercial name: Aizen Cathilon Pure Blue 5GH, made by Hodogaya Chem. Ind. Co., Ltd.) and 1 g of sodium dodecylbenzenesulfonate were reacted to obtain about 1/8 g of crystals of the captioned hydrophobic cationic dye. the hydrophobic cationic dye was placed in a water-toluene phase and shaken, whereupon the dye mostly remained in the toluene phase. This reveals that the substitution of the counter ion with the organic anion contributes to drastically improved miscibility with the organic solvent.

**[0071]** In the same manner as in Example 12, the resultant hydrophobic cationic dye was used to make a thermal transfer ink ribbon, followed by a similar printing test. As a result, there was obtained an image which assumed a good cyan color and good gradation properties. Fig. 13 shows a so-called dynamic sensitivity (color-development) characteristic of the ink ribbon. As shown in the figure, the ink ribbon obtained in this example ensures gradation printing by the thermal transfer on the printing sheets.

#### Example 14 - Preparation of laurylsulfate of C.I. Basic Blue 3

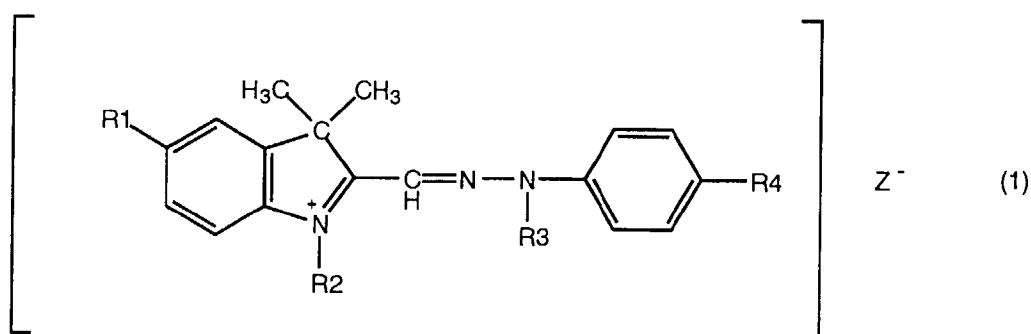
**[0072]** In the same manner as in Example 1, 1 g of C.I. Basic Blue 3 (commercial name: Aizen Cathilon Pure Blue 5GH, made by Hodogaya Chem. Ind. Co., Ltd.) and 1 g of sodium laurylsulfate were reacted to obtain about 1.8 g of crystals of the captioned hydrophobic cationic dye. The hydrophobic cationic dye was placed in a water-toluene phase and shaken, whereupon the dye mostly remained in the toluene phase. This reveals that the substitution of the counter ion contributes to drastically improved miscibility with the organic solvent.

**[0073]** In the same manner as in Example 12, the resultant hydrophobic cationic dye was used to make a thermal transfer ink ribbon, followed by a similar printing test using a printing sheet (UPC-3010) of Sony Co., Ltd. As a result, there was obtained an image which assumed a good cyan color and good gradation properties. Fig. 13 shows a so-called dynamic sensitivity (color-development) characteristic of the ink ribbon. As shown in the figure, the ink ribbon obtained in this example ensures gradation printing by the thermal transfer on the printing sheets.

**[0074]** Since the cationic dyes used according to the invention are hydrophobic in nature, they can be mixed with hydrophobic polymers satisfactorily and uniformly with good storage stability. Accordingly, when these hydrophobic cationic dyes and hydrophobic polymers are used to form an ink layer of a thermal transfer ink ribbon, the sensitivity at the time of the transfer and the color and light fastness of the resultant images can be improved.

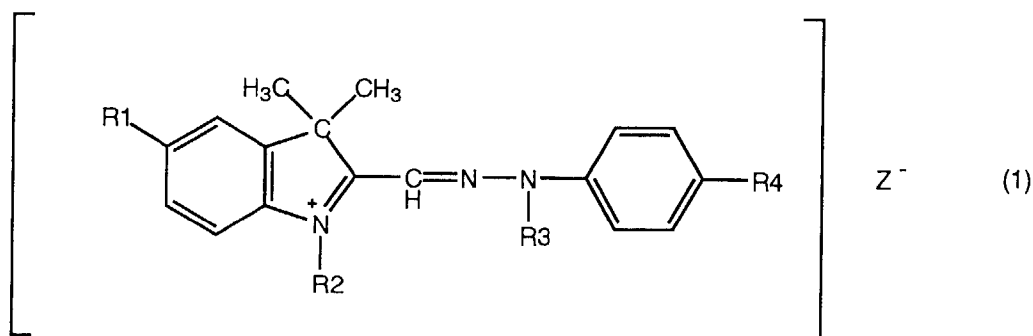
#### Claims

1. Use of a hydrophobic cationic dye in an ink layer of a thermal transfer ink ribbon, said ink layer containing a hydrophobic polymer and said dye being obtainable by substituting, with an organic anion, a counter ion of a diazacarbocyanine cationic dye of the formula (1)



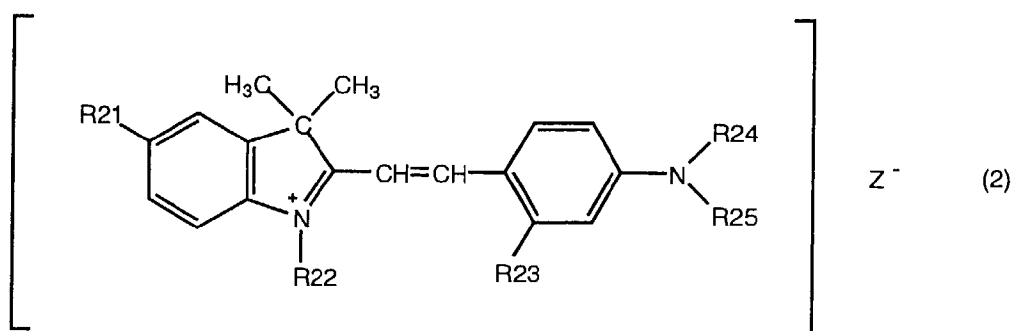
wherein R1, R2, R3 and R4 independently represent a hydrogen atom, a halogen atom, a cyano group, an alkyl group, a cycloalkyl group, an alkoxy group, an aryl group, an aryloxy group, an aralkyl group, an aralkoxy group, an alkenyl group, an alkenoxy group, an alkoxy carbonyl group, an acyloxy group, or an acyl group which may be substituted, and Z<sup>-</sup> represents a counter ion.

2. A thermal transfer ink ribbon comprising a support and an ink layer formed on said support, wherein said ink layer comprises a hydrophobic cationic dye which is obtained by substituting, with an organic anion, a counter ion of a diazacyanocyanine cationic dye of the formula (1)



wherein R1, R2, R3 and R4 independently represent a hydrogen atom, a halogen atom, a cyano group, an alkyl group, a cycloalkyl group, an alkoxy group, an aryl group, an aryloxy group, an aralkyl group, an aralkoxy group, an alkenyl group, an alkenoxy group, an alkoxycarbonyl group, an acyloxy group, or an acyl group which may be substituted, and Z- represents a counter ion.

3. Use of a hydrophobic cationic dye in an ink layer of a thermal transfer ink ribbon, said ink layer containing a hydrophobic polymer and said dye being obtainable by substituting a counter ion of a cationic dye of C.I. Basic Yellow 21, 36, 67 or 73 with an organic anion.
4. A thermal transfer ink ribbon comprising a support and an ink layer formed thereon, wherein said ink layer comprises a hydrophobic cationic dye which is obtained by substituting a counter ion of a cationic dye of C.I. Basic Yellow 21, 36, 67 or 73 with an organic anion.
5. Use of a hydrophobic cationic dye in an ink layer of a thermal transfer ink ribbon, said ink layer containing a hydrophobic polymer and said dye being obtainable by substituting, with an organic anion, a counter ion of a hemicyanine cationic dye of the formula (2)

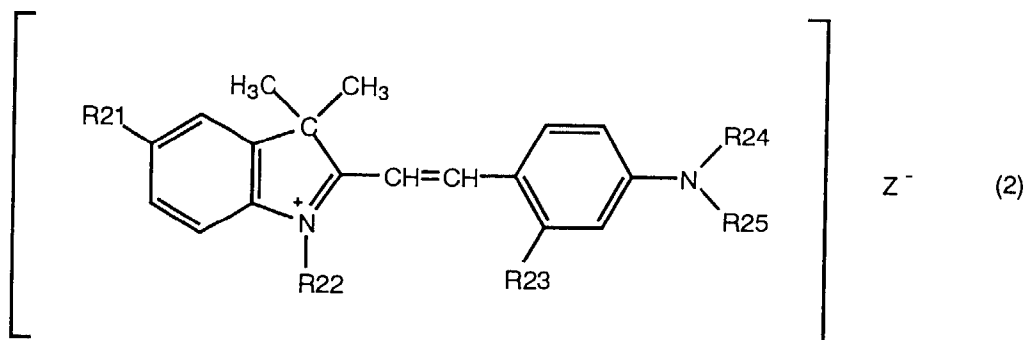


wherein R21, R22, R23, R24 and R25 independently represent a hydrogen atom, a halogen atom, a cyano group, an alkyl group, a cycloalkyl group, an alkoxy group, an aryl group, an aryloxy group, an aralkyl group, an aralkoxy group, an alkenyl group, an alkenoxy group, an alkoxycarbonyl group, an acyloxy group, or an acyl group which may be substituted, provided that R24 and R25 may join together to form a ring, and Z- represents a counter ion.

6. A thermal transfer ink ribbon comprising a support and an ink layer formed on said support, wherein said ink layer comprises a hydrophobic cationic dye obtained by substituting, with an organic anion, a counter ion of a hemicyanine cationic dye of the formula (2)

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wherein R21, R22, R23, R24 and R25 independently represent a hydrogen atom, a halogen atom, a cyano group, an alkyl group, a cycloalkyl group, an alkoxy group, an aryl group, an aryloxy group, an aralkyl group, an aralkoxy group, an alkenyl group, an alkenoxy group, an alkoxy carbonyl group, an acyloxy group, or an acyl group which may be substituted, provided that R24 and R25 may join together to form a ring, and Z<sup>-</sup> represents a counter ion.

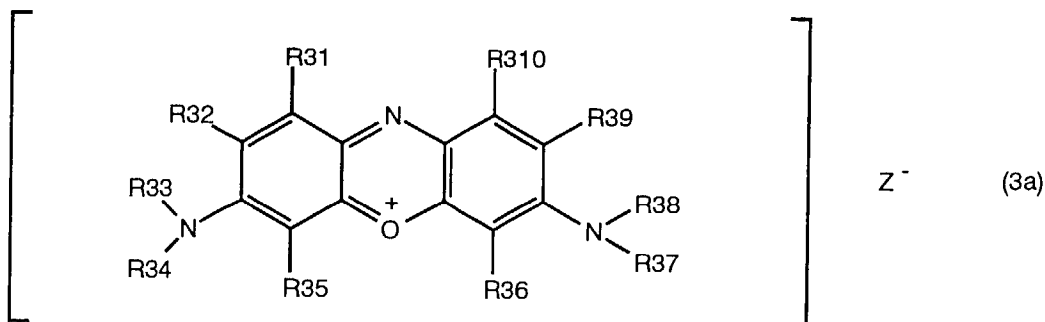
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7. Use of a hydrophobic cationic dye in an ink layer of a thermal transfer ink ribbon, said ink layer containing a hydrophobic polymer and said dye being obtainable by substituting, with an organic anion, a counter ion of an oxazine cationic dye of the formula (3a) or (3b)

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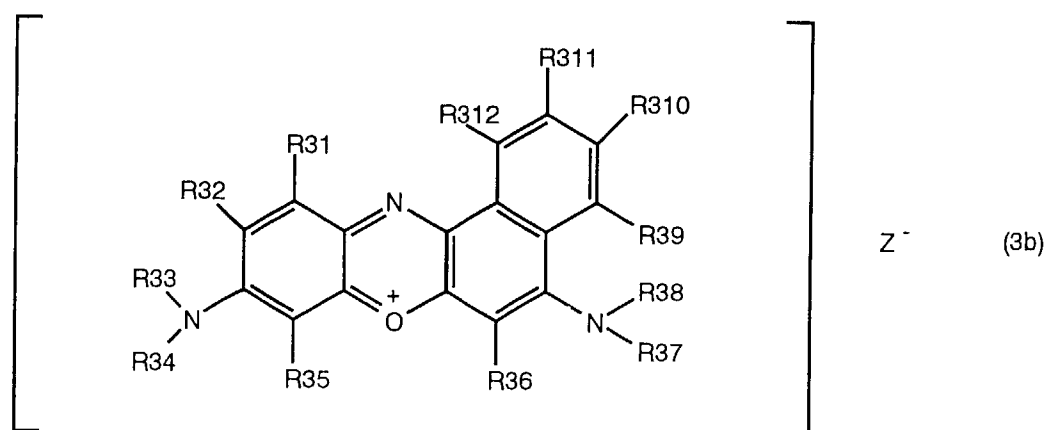
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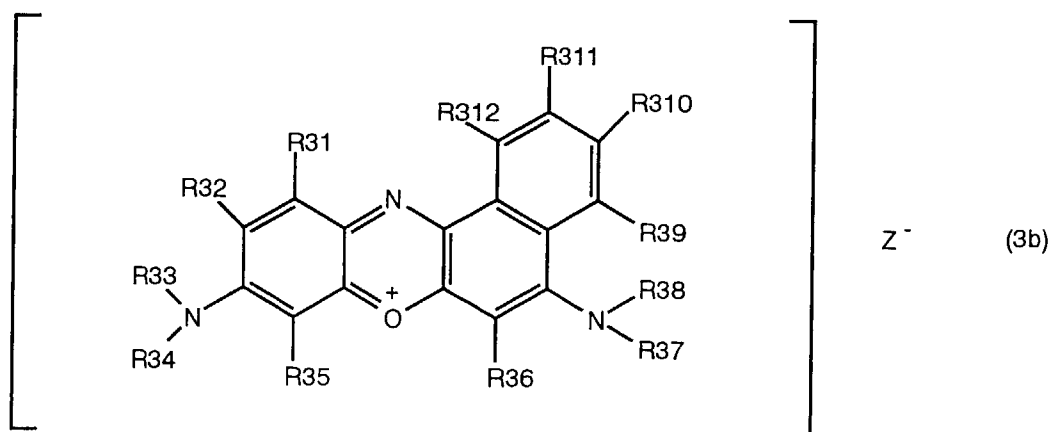
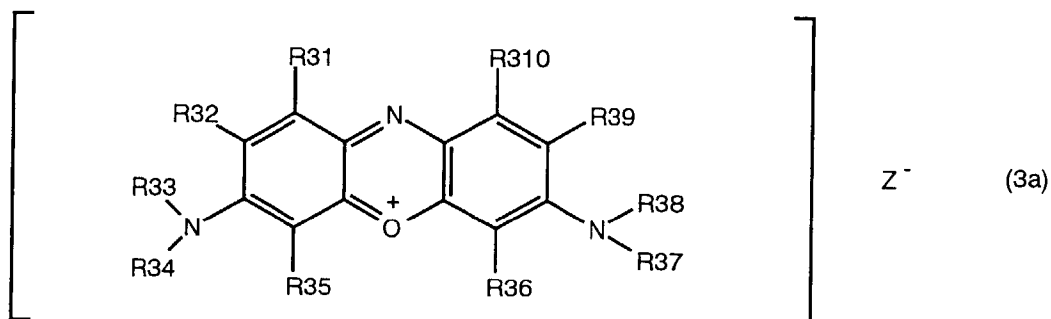


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wherein R31, R32, R33, R34, R35, R36, R37, R38, R39, R310, R311 and R312 independently represent a hydrogen atom, a halogen atom, a cyano group, an alkyl group, a cycloalkyl group, an alkoxy group, an aryl group, an aryloxy group, an aralkyl group, an aralkoxy group, an alkenyl group, an alkenoxy group, an alkoxy carbonyl group, an acyloxy group, or an acyl group which may be substituted, provided that R31 and R32, R33 and R34, R37 and R38, R39 and R310, R310 and R311, and R311 and R312 may, respectively, join together to form a ring, and Z<sup>-</sup>

represents a counter ion.

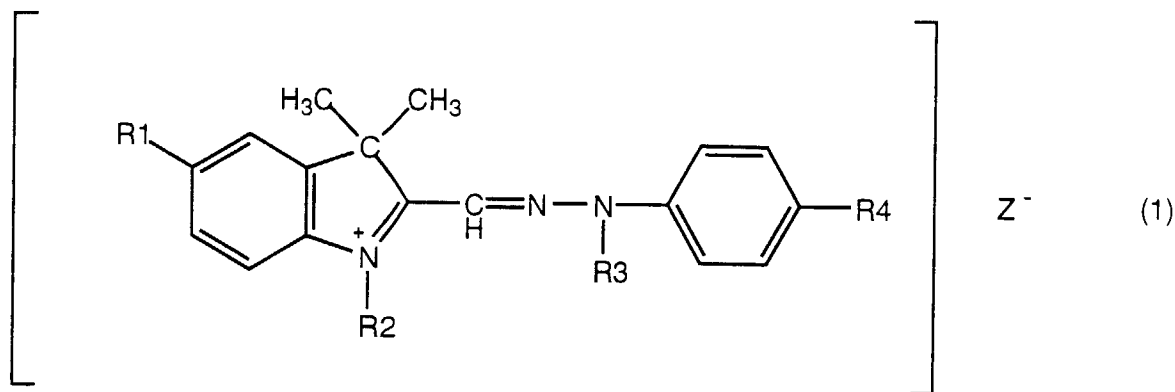
8. A thermal transfer ink ribbon comprising a support and an ink layer formed on said support, wherein said ink layer comprises a hydrophobic cationic dye obtained by substituting, with an organic anion, a counter ion of an oxazine cationic dye of the formula (3a) or (3b)



wherein R31, R32, R33, R34, R35, R36, R37, R38, R39, R310, R311 and R312 independently represent a hydrogen atom, a halogen atom, a cyano group, an alkyl group, a cycloalkyl group, an alkoxy group, an aryl group, an aryloxy group, an aralkyl group, an aralkoxy group, an alkenyl group, an alkenoxy group, an alkoxy carbonyl group, an acyloxy group, or an acyl group which may be substituted, provided that R31 and R32, R33 and R34, R37 and R38, R39 and R310, R310 and R311, and R311 and R312 may, respectively, join together to form a ring, and Z- represents a counter ion.

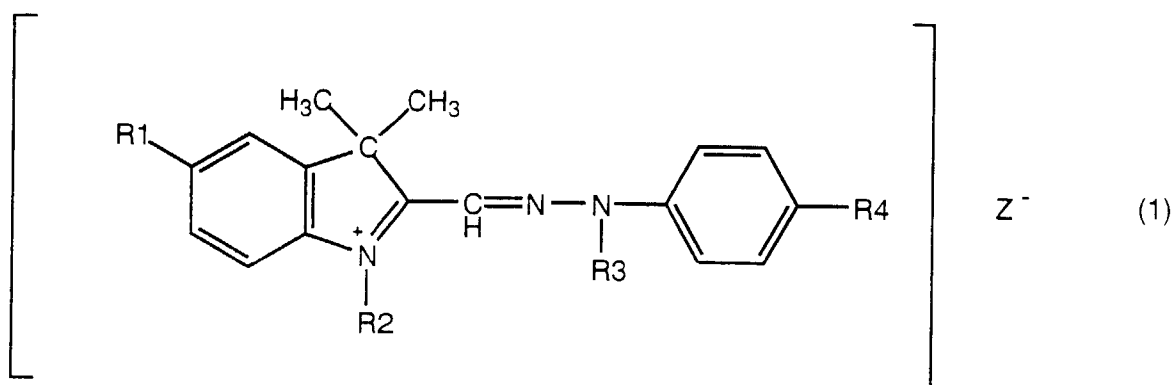
## Patentansprüche

1. Verwendung eines hydrophoben kationischen Farbstoffs in einer Farbschicht eines Thermotransferfarbbands, wobei die Farbschicht ein hydrophobes Polymer enthält und der Farbstoff erhältlich ist indem das Gegenion eines kationischen Diazacarbocyaninfarbstoffs der Formel (1)



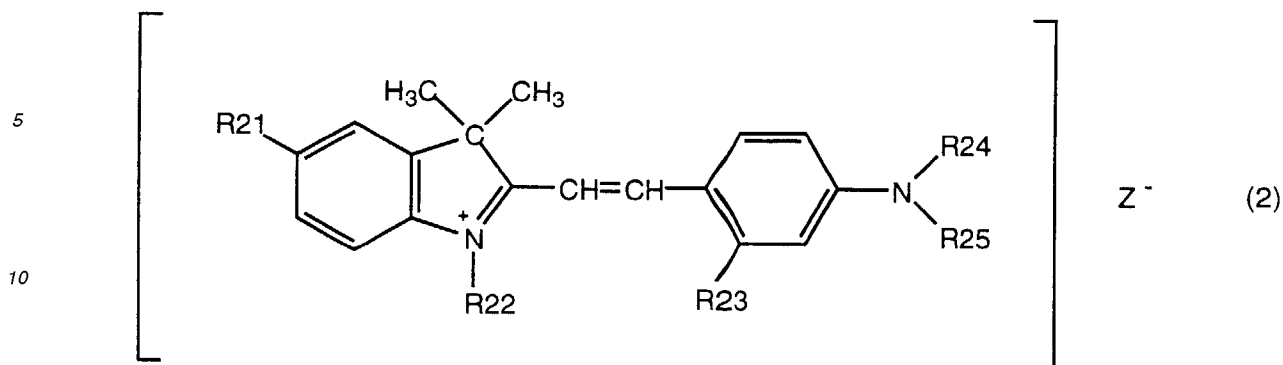
in der R1, R2, R3 und R4 unabhängig voneinander ein Wasserstoffatom, ein Halogenatom, eine Cyangruppe, eine Alkylgruppe, eine Cycloalkylgruppe, eine Alkoxygruppe, eine Arylgruppe, eine Aryloxygruppe, eine Aralkylgruppe, eine Aralkoxygruppe, eine Alkenylgruppe, eine Alkenoxygruppe, eine Alkoxy-carbonylgruppe, eine Acyloxygruppe oder eine Acylgruppe, welche auch substituiert sein können, bedeuten und Z<sup>-</sup> ein Gegenion bedeutet, durch ein organisches Anion ersetzt wird.

2. Thermotransferfarbband, mindestens umfassend einen Träger und eine auf dem Träger ausgebildete Farbschicht, die einen hydrophoben kationischen Farbstoff enthält, der erhältlich ist indem das Gegenion eines kationischen Diazocarbocyaninfarbstoffs der Formel (1)



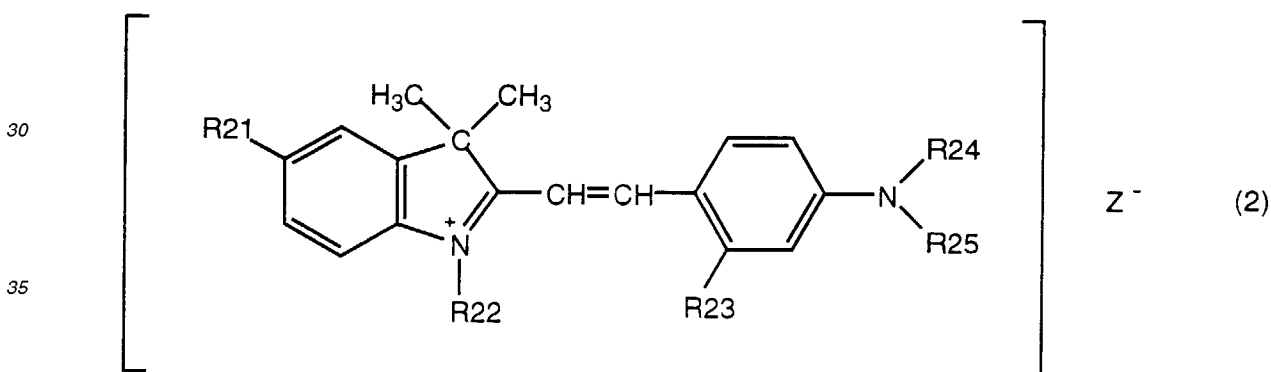
in der R1, R2, R3 und R4 unabhängig voneinander ein Wasserstoffatom, ein Halogenatom, eine Cyangruppe, eine Alkylgruppe, eine Cycloalkylgruppe, eine Alkoxygruppe, eine Arylgruppe, eine Aryloxygruppe, eine Aralkylgruppe, eine Aralkoxygruppe, eine Alkenylgruppe, eine Alkenoxygruppe, eine Alkoxy-carbonylgruppe, eine Acyloxygruppe oder eine Acylgruppe, welche auch substituiert sein können, bedeuten und Z<sup>-</sup> ein Gegenion bedeutet, durch ein organisches Anion ersetzt wird.

3. Verwendung eines hydrophoben kationischen Farbstoffs in einer Farbschicht eines Thermotransferfarbbands, wobei die Farbschicht ein hydrophobes Polymer enthält und der Farbstoff erhältlich ist indem das Gegenion des kationischen Farbstoffs C.I. Basic Yellow 21, 36, 67 oder 73 durch ein organisches Anion ersetzt wird.
4. Thermotransferfarbband, mindestens umfassend einen Träger und eine auf dem Träger ausgebildete Farbschicht, die einen hydrophoben kationischen Farbstoff enthält, der erhältlich ist indem das Gegenion des kationischen Farbstoffs C.I. Basic Yellow 21, 36, 67 oder 73 durch ein organisches Anion ersetzt wird.
5. Verwendung eines hydrophoben kationischen Farbstoffs in einer Farbschicht eines Thermotransferfarbbands, wobei die Farbschicht ein hydrophobes Polymer enthält und der Farbstoff erhältlich ist indem das Gegenion eines kationischen Hemicyaninfarbstoffs der Formel (2)



15 in der R21, R22, R23, R24 und R25 unabhängig voneinander ein Wasserstoffatom, ein Halogenatom, eine Cyan-  
gruppe, eine Alkylgruppe, eine Cycloalkylgruppe, eine Alkoxygruppe, eine Arylgruppe, eine Aryloxygruppe, eine  
Aralkylgruppe, eine Aralkoxygruppe, eine Alkenylgruppe, eine Alkenoxygruppe, eine Alkoxycarbonylgruppe, eine  
Acyloxygruppe oder eine Acylgruppe, welche auch substituiert sein können, bedeuten, unter der Voraussetzung,  
daß R24 und R25 zusammen einen Ring bilden können, und in der Z<sup>-</sup> ein Gegenion bedeutet, durch ein organisches  
20 Anion ersetzt wird.

- 25 6. Thermotransferfarbband, mindestens umfassend einen Träger und eine auf dem Träger ausgebildete Farbschicht,  
die einen hydrophoben kationischen Farbstoff enthält, der erhältlich ist indem das Gegenion eines kationischen  
Hemicyaninfarbstoffs der Formel (2)



40 in der R21, R22, R23, R24 und R25 unabhängig voneinander ein Wasserstoffatom, ein Halogenatom, eine Cyan-  
gruppe, eine Alkylgruppe, eine Cycloalkylgruppe, eine Alkoxygruppe, eine Arylgruppe, eine Aryloxygruppe, eine  
Aralkylgruppe, eine Aralkoxygruppe, eine Alkenylgruppe, eine Alkenoxygruppe, eine Alkoxycarbonylgruppe, eine  
Acyloxygruppe oder eine Acylgruppe, welche auch substituiert sein können, bedeuten, unter der Voraussetzung,  
daß R24 und R25 zusammen einen Ring bilden können, und in der Z<sup>-</sup> ein Gegenion bedeutet, durch ein organisches  
45 Anion ersetzt wird.

- 50 7. Verwendung eines hydrophoben kationischen Farbstoffs in einer Farbschicht eines Thermotransferfarbbands, wo-  
bei die Farbschicht ein hydrophobes Polymer enthält und der Farbstoff erhältlich ist indem das Gegenion eines  
kationischen Oxazinfarbstoffs der Formel (3a) oder (3b)

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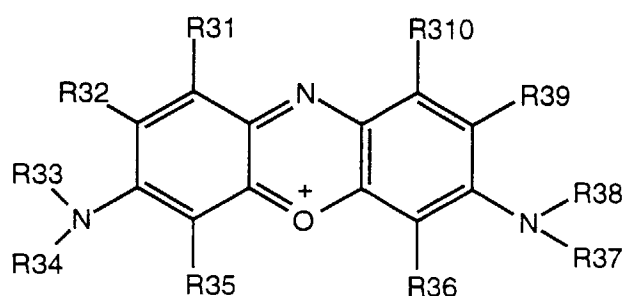
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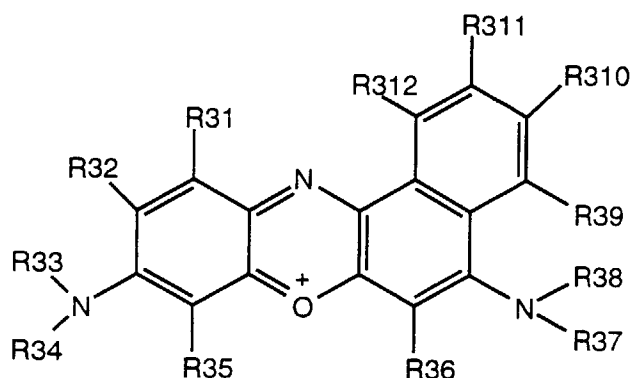
 $Z^-$  (3a)

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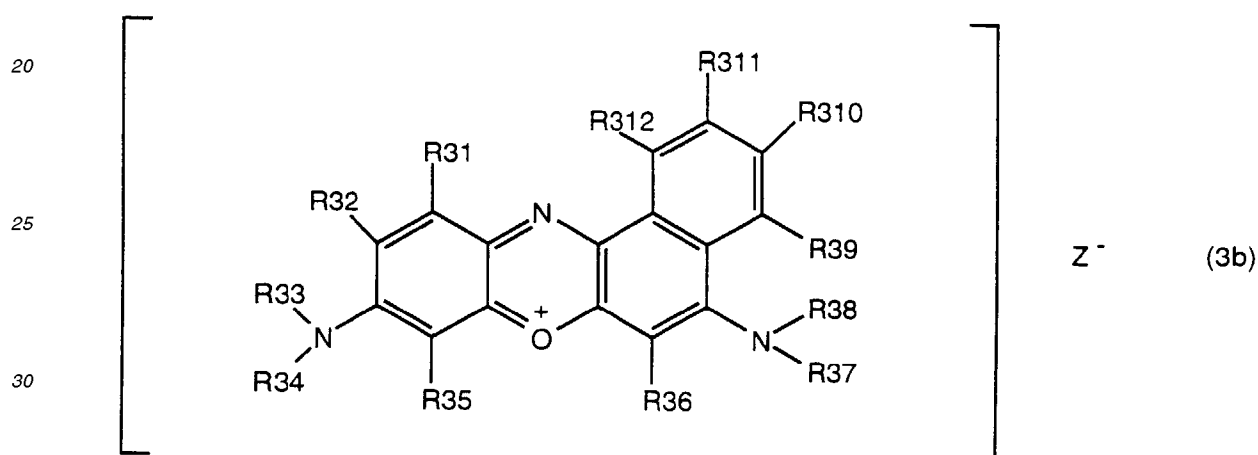
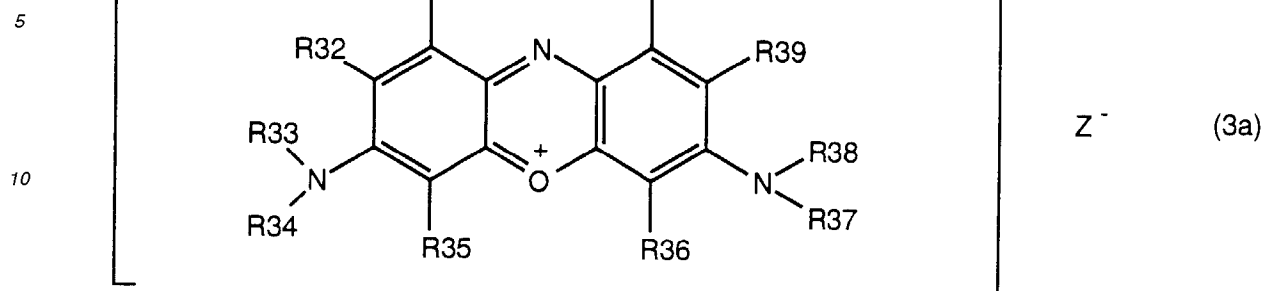
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 $Z^-$  (3b)

in der R31, R32, R33, R34, R35, R36, R37, R38, R39, R310, R311 und R312 unabhängig voneinander ein Wasserstoffatom, ein Halogenatom, eine Cyangruppe, eine Alkylgruppe, eine Cycloalkylgruppe, eine Alkoxygruppe, eine Arylgruppe, eine Aryloxygruppe, eine Aralkylgruppe, eine Aralkoxygruppe, eine Alkenylgruppe, eine Alkenoxygruppe, eine Alkoxy-carbonylgruppe, eine Acyloxygruppe oder eine Acylgruppe, welche auch substituiert sein können, bedeuten, unter der Voraussetzung, daß R31 und R32, R33 und R34, R37 und R38, R39 und R310, R310 und R311 sowie R311 und R312 jeweils zusammen einen Ring bilden können, und in der  $Z^-$  ein Gegenion bedeutet, durch ein organisches Anion ersetzt wird.

8. Thermotransferfarbband, mindestens umfassend einen Träger und eine auf dem Träger ausgebildete Farbschicht, die einen hydrophoben kationischen Farbstoff enthält, der erhältlich ist indem das Gegenion eines kationischen Oxazinfarbstoffs der Formel (3a) oder (3b)

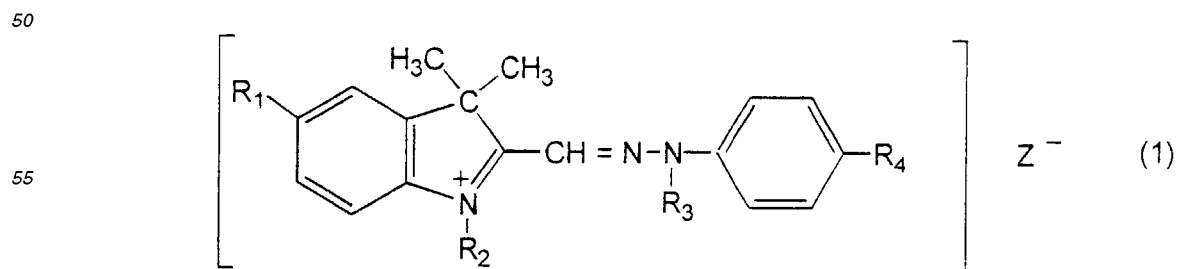


35 in der R31, R32, R33, R34, R35, R36, R37, R38, R39, R310, R311 und R312 unabhängig voneinander ein Wasserstoffatom, ein Halogenatom, eine Cyangruppe, eine Alkylgruppe, eine Cycloalkylgruppe, eine Alkoxygruppe, eine Arylgruppe, eine Aryloxygruppe, eine Aralkylgruppe, eine Aralkoxygruppe, eine Alkenylgruppe, eine Alkenoxygruppe, eine Alkoxycarbonylgruppe, eine Acyloxygruppe oder eine Acylgruppe, welche auch substituiert sein können, bedeuten, unter der Voraussetzung, daß R31 und R32, R33 und R34, R37 und R38, R39 und R310, R310 und R311 sowie R311 und R312 jeweils zusammen einen Ring bilden können, und in der Z<sup>-</sup> ein Gegenion bedeutet, durch ein organisches Anion ersetzt wird.

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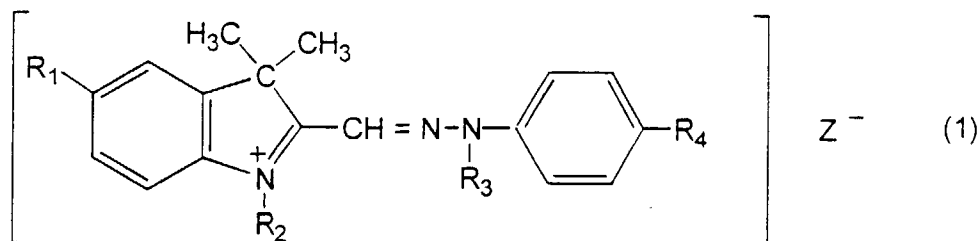
# Revendications

- 45
1. Utilisation d'un colorant cationique hydrophobe dans une couche d'encre d'un ruban d'encre pour transfert thermique, ladite couche d'encre contenant un polymère hydrophobe et ledit colorant pouvant être obtenu par substitution, par un anion organique, d'un contre-ion d'un colorant cationique diazocarbocyanine de formule (1)



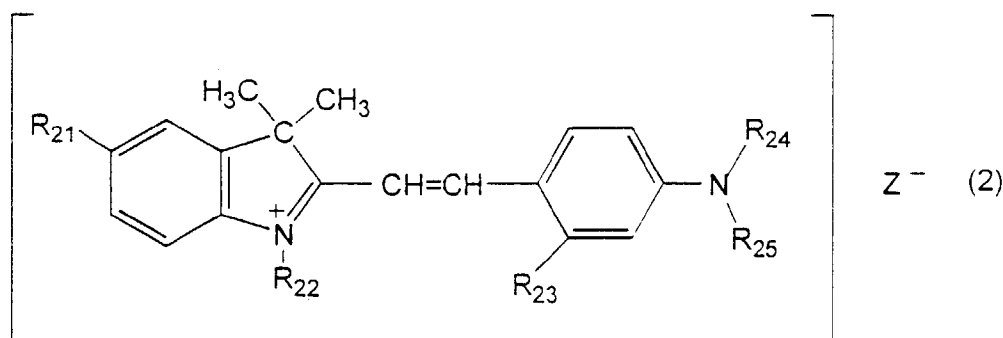
dans laquelle  $R_1$ ,  $R_2$ ,  $R_3$  et  $R_4$  représentent indépendamment un atome d'hydrogène, un atome d'halogène, un groupe cyano, un groupe alkyle, un groupe cycloalkyle, un groupe alcoxy, un groupe aryle, un groupe aryloxy, un groupe aralkyle, un groupe aralcoxy, un groupe alcényle, un groupe alcénoxy, un groupe alcoxycarbonyle, un groupe acyloxy, ou un groupe acyle qui peut être substitué, et  $Z^-$  représente un contre-ion.

2. Ruban d'encre pour transfert thermique comprenant un support et une couche d'encre formée sur ledit support, caractérisé en ce que ladite couche d'encre comprend un colorant cationique hydrophobe qui est obtenu par la substitution, par un anion organique, d'un contre-ion d'un colorant diazacarbocyanine de formule (1)



dans laquelle  $R_1$ ,  $R_2$ ,  $R_3$  et  $R_4$  représentent indépendamment un atome d'hydrogène, un atome d'halogène, un groupe cyano, un groupe alkyle, un groupe cycloalkyle, un groupe alcoxy, un groupe aryle, un groupe aryloxy, un groupe aralkyle, un groupe aralcoxy, un groupe alcényle, un groupe alcénoxy, un groupe alcoxycarbonyle, un groupe acyloxy, ou un groupe acyle qui peut être substitué, et  $Z^-$  représente un contre-ion.

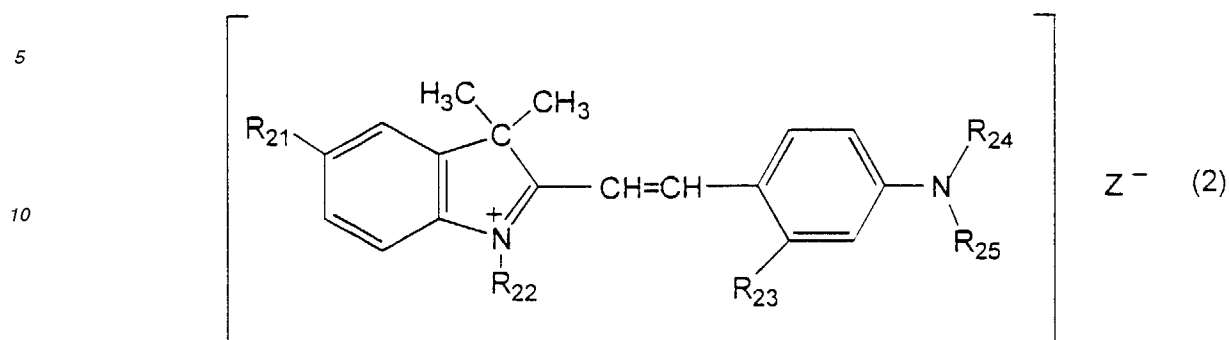
3. Utilisation d'un colorant cationique hydrophobe dans une couche d'encre d'un ruban d'encre pour transfert thermique, ladite couche d'encre contenant un polymère hydrophobe et ledit colorant pouvant être obtenu par substitution, par un anion organique, d'un contre-ion d'un colorant cationique jaune basique C. I. 21, 36, 67 ou 73.
4. Ruban d'encre pour transfert thermique comprenant un support et une couche d'encre formée sur celui-ci, caractérisé en ce que ladite couche d'encre comprend un colorant cationique hydrophobe qui est obtenu par la substitution, par un anion organique, d'un contre-ion d'un colorant cationique jaune basique C. I. 21, 36, 67 ou 73.
5. Utilisation d'un colorant cationique hydrophobe dans une couche d'encre d'un ruban d'encre pour transfert thermique, ladite couche d'encre contenant un polymère hydrophobe et ledit colorant pouvant être obtenu par substitution, par un anion organique, d'un contre-ion d'un colorant cationique hémicyanine de formule (2)



dans laquelle  $R_{21}$ ,  $R_{22}$ ,  $R_{23}$ ,  $R_{24}$  et  $R_{25}$  représentent indépendamment un atome d'hydrogène, un atome d'halogène, un groupe cyano, un groupe alkyle, un groupe cycloalkyle, un groupe alcoxy, un groupe aryle, un groupe aryloxy, un groupe aralkyle, un groupe aralcoxy, un groupe alcényle, un groupe alcénoxy, un groupe alcoxycarbonyle, un groupe acyloxy, ou un groupe acyle qui peut être substitué, à condition que  $R_{24}$  et  $R_{25}$  puissent se lier ensemble pour former un cycle, et  $Z^-$  représente un contre-ion.

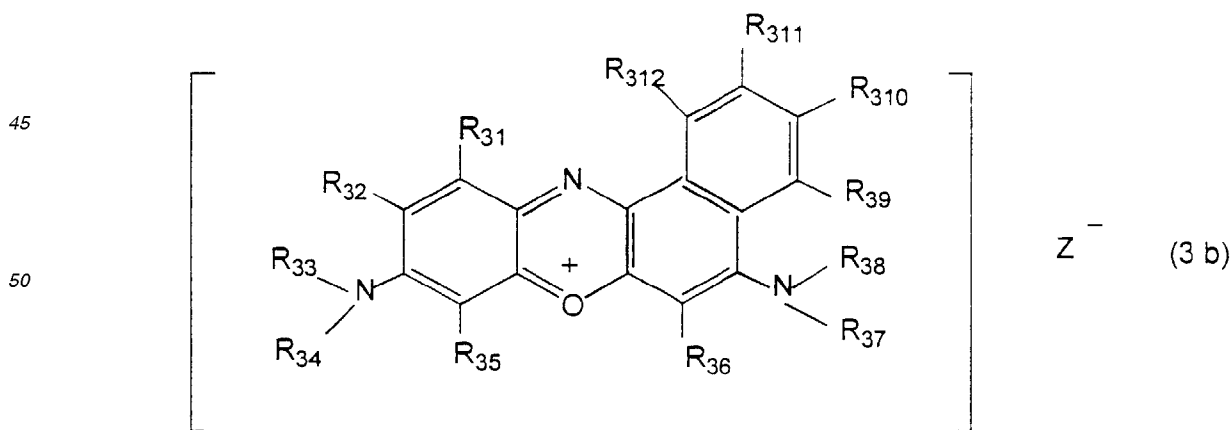
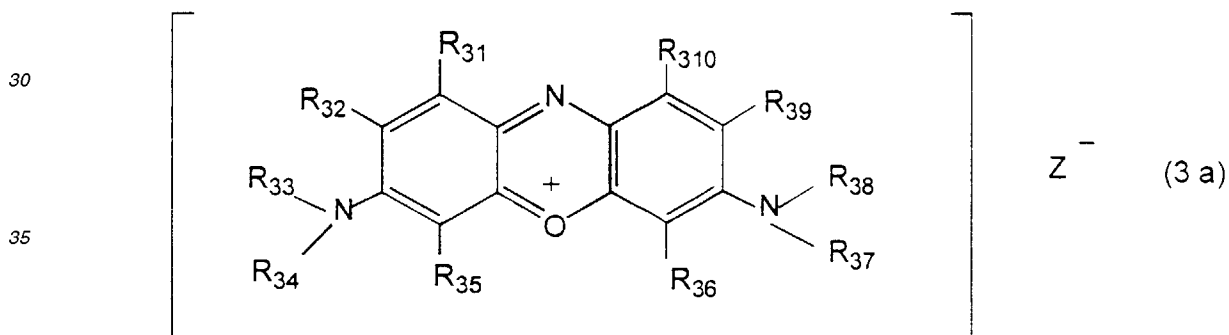
6. Ruban d'encre pour transfert thermique comprenant un support et une couche d'encre formée sur ledit support, caractérisé en ce que ladite couche d'encre comprend un colorant cationique hydrophobe qui est obtenu par la

substitution, par un anion organique, d'un contre-ion d'un colorant cationique hémicyanine de formule (2)



dans laquelle R<sub>21</sub>, R<sub>22</sub>, R<sub>23</sub>, R<sub>24</sub> et R<sub>25</sub> représentent indépendamment un atome d'hydrogène, un atome d'halogène, un groupe cyano, un groupe alkyle, un groupe cycloalkyle, un groupe alcoxy, un groupe aryle, un groupe aryloxy, un groupe aralkyle, un groupe aralcoxy, un groupe alcényle, un groupe alcénoxy, un groupe alcoxycarbonyl, un groupe acyloxy, ou un groupe acyle qui peut être substitué, à condition que R<sub>24</sub> et R<sub>25</sub> puissent se lier ensemble pour former un cycle, et Z<sup>-</sup> représente un contre-ion.

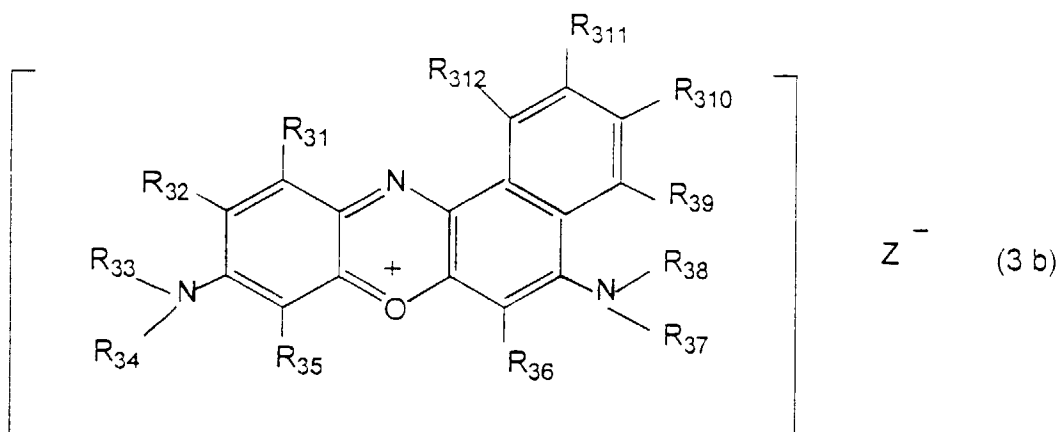
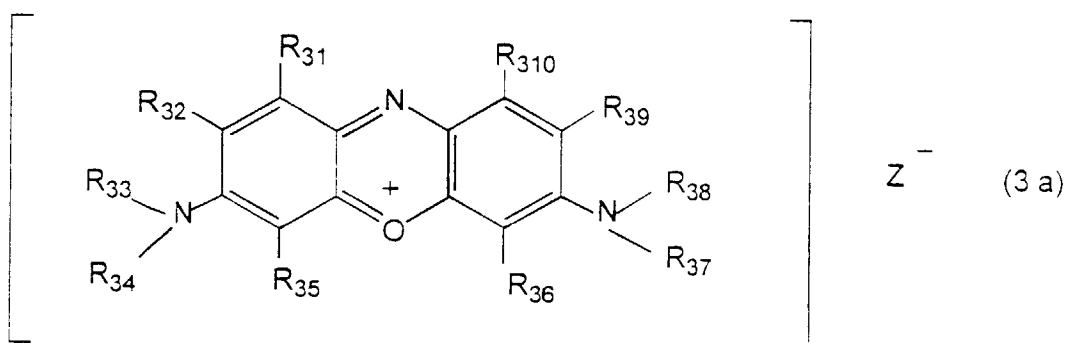
7. Utilisation d'un colorant cationique hydrophobe dans une couche d'encre d'un ruban d'encre pour transfert thermique, ladite couche d'encre contenant un polymère hydrophobe et ledit colorant pouvant être obtenu par substitution, par un anion organique, d'un contre-ion d'un colorant cationique oxazine de formule (3a) ou (3b) :



dans laquelle R<sub>31</sub>, R<sub>32</sub>, R<sub>33</sub>, R<sub>34</sub>, R<sub>35</sub>, R<sub>36</sub>, R<sub>37</sub>, R<sub>38</sub>, R<sub>39</sub>, R<sub>310</sub>, R<sub>311</sub> et R<sub>312</sub> représentent indépendamment un atome d'hydrogène, un atome d'halogène, un groupe cyano, un groupe alkyle, un groupe cycloalkyle, un groupe

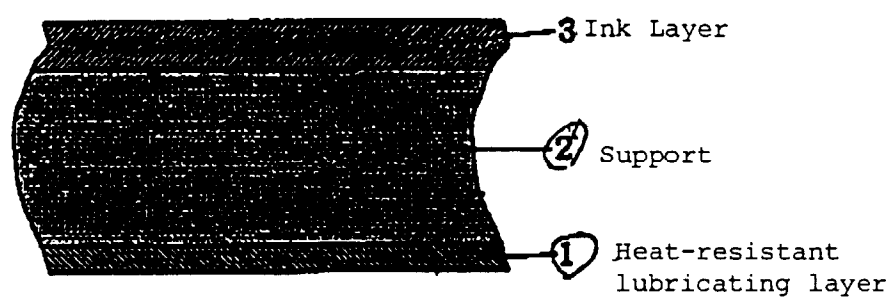
alcoxy, un groupe aryle, un groupe aryloxy, un groupe aralkyle, un groupe aralcoxy, un groupe alcényle, un groupe alcénoxy, un groupe alcoxycarbonyle, un groupe acyloxy, ou un groupe acyle qui peut être substitué à condition que  $R_{31}$  et  $R_{32}$ ,  $R_{33}$  et  $R_{34}$ ,  $R_{37}$  et  $R_{38}$ ,  $R_{39}$  et  $R_{310}$ ,  $R_{310}$  et  $R_{311}$ , et  $R_{311}$  et  $R_{312}$  puissent, respectivement, se lier ensemble pour former un cycle, et  $Z^-$  représente un contre-ion.

8. Ruban d'encre pour transfert thermique comprenant un support et une couche d'encre formée sur ledit support, caractérisé en ce que ladite couche d'encre comprend un colorant cationique hydrophobe qui est obtenu par la substitution, par un anion organique, d'un contre-ion d'un colorant cationique oxazine de formule (3a) ou (3b) :



dans laquelle  $R_{31}$ ,  $R_{32}$ ,  $R_{33}$ ,  $R_{34}$ ,  $R_{35}$ ,  $R_{36}$ ,  $R_{37}$ ,  $R_{38}$ ,  $R_{39}$ ,  $R_{310}$ ,  $R_{311}$  et  $R_{312}$  représentent indépendamment un atome d'hydrogène, un atome d'halogène, un groupe cyano, un groupe alkyle, un groupe cycloalkyle, un groupe alcoxy, un groupe aryle, un groupe aryloxy, un groupe aralkyle, un groupe aralcoxy, un groupe alcényle, un groupe alcénoxy, un groupe alcoxycarbonyle, un groupe acyloxy, ou un groupe acyle qui peut être substitué à condition que  $R_{31}$  et  $R_{32}$ ,  $R_{33}$  et  $R_{34}$ ,  $R_{37}$  et  $R_{38}$ ,  $R_{39}$  et  $R_{310}$ ,  $R_{310}$  et  $R_{311}$ , et  $R_{311}$  et  $R_{312}$  puissent, respectivement, se lier ensemble pour former un cycle, et  $Z^-$  représente un contre-ion.

FIG. 1



10 Thermal transfer ink ribbon

FIG. 2

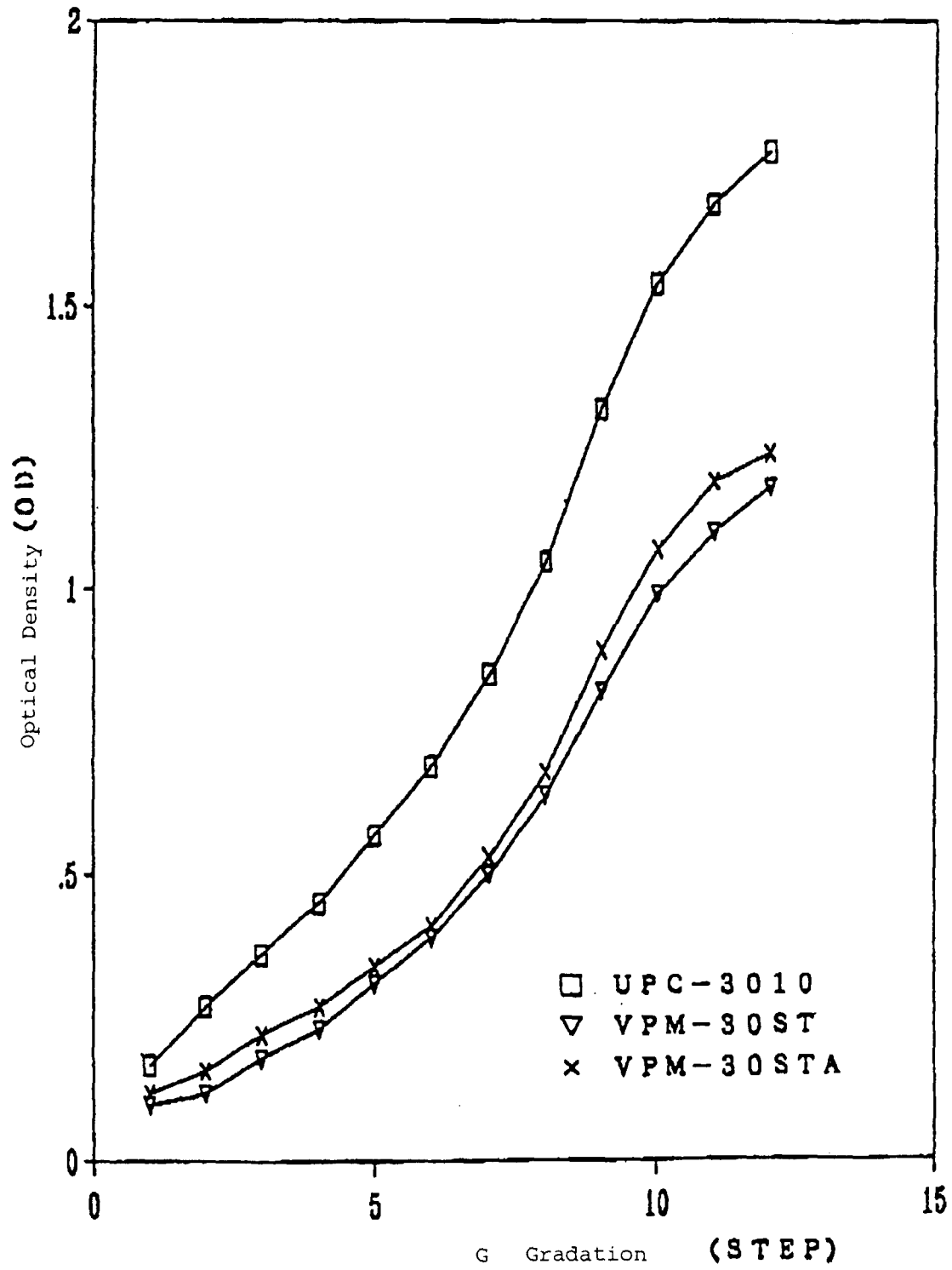


FIG. 3

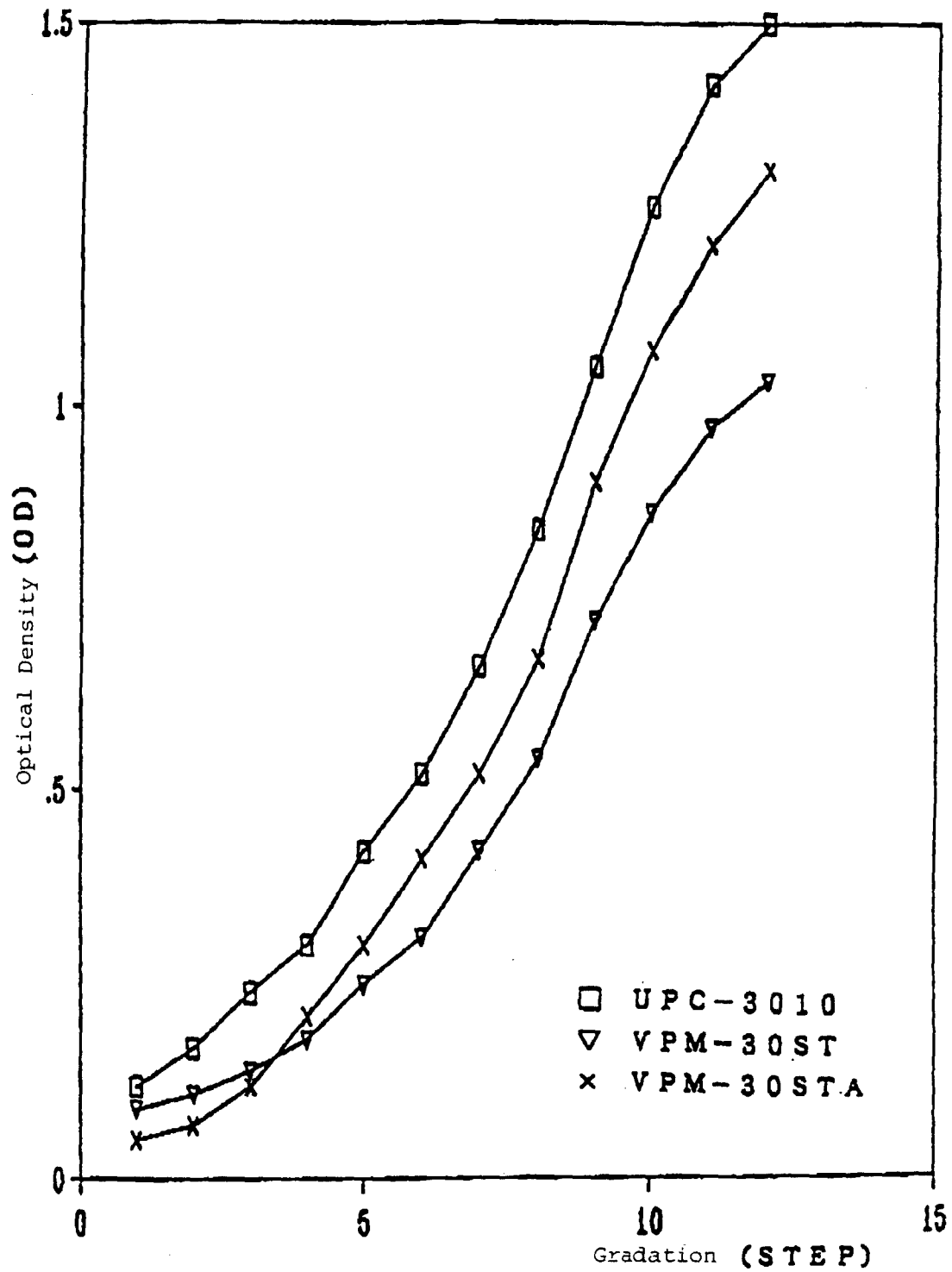


FIG. 4

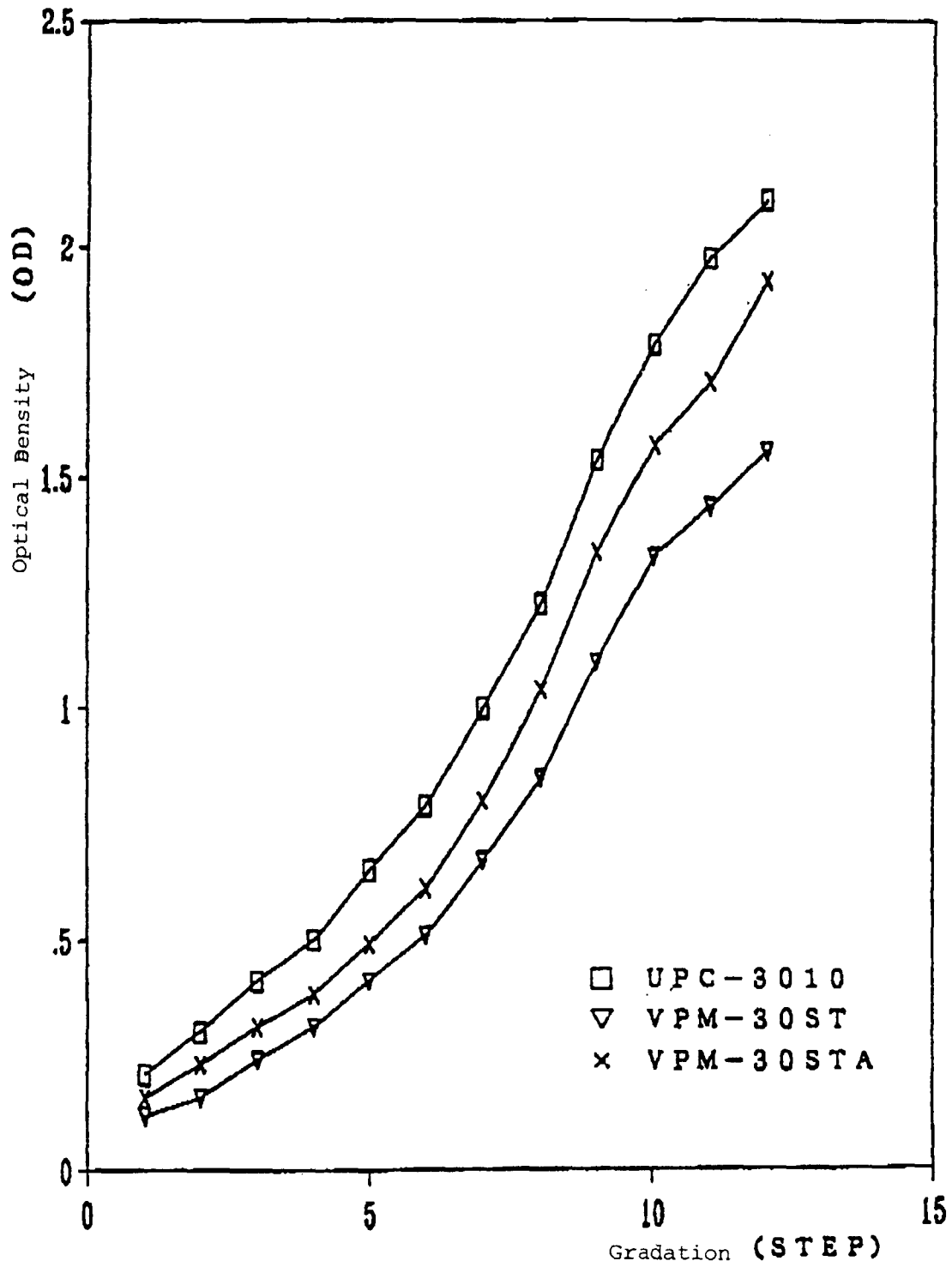


FIG. 5

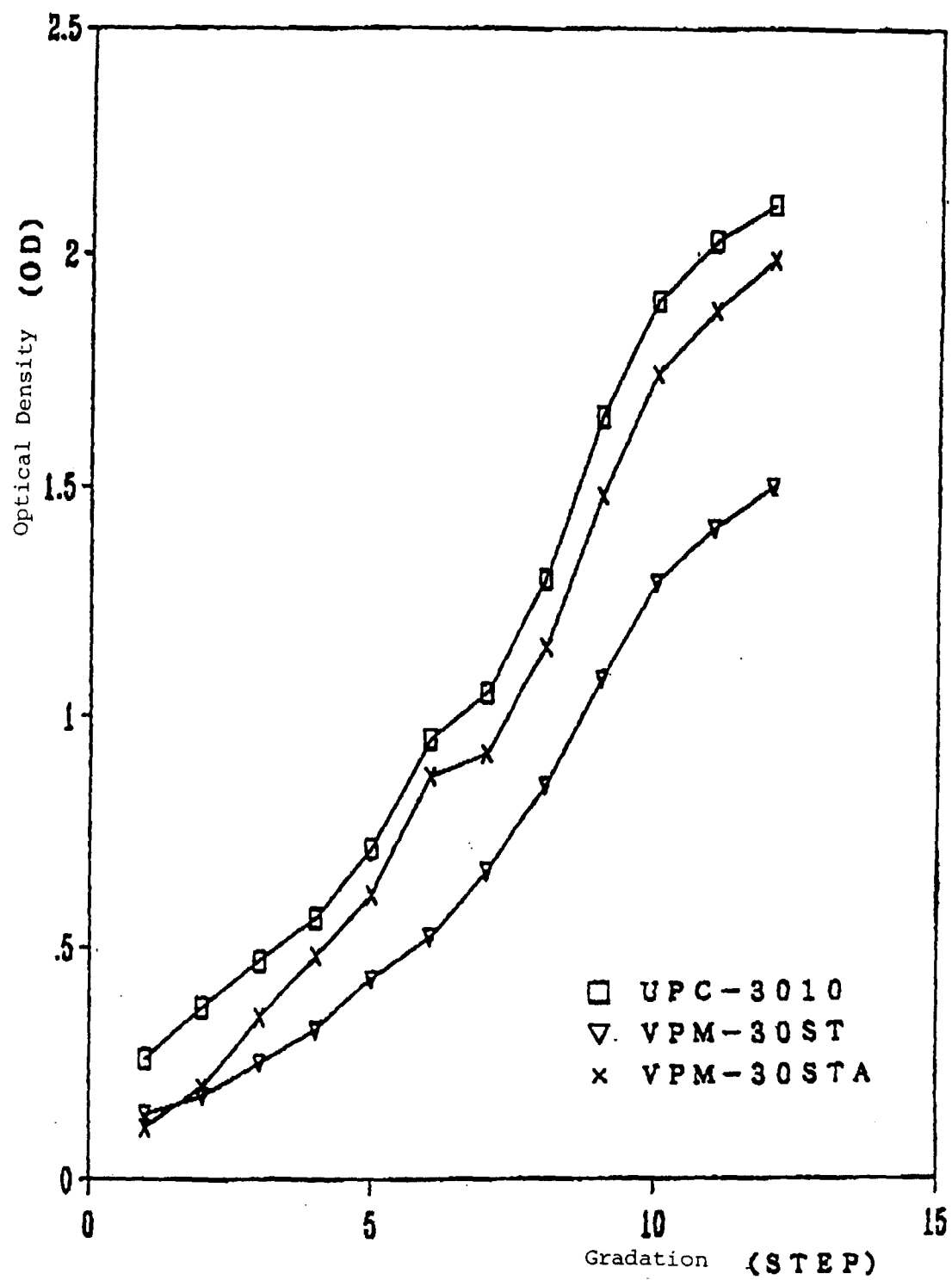


FIG. 6

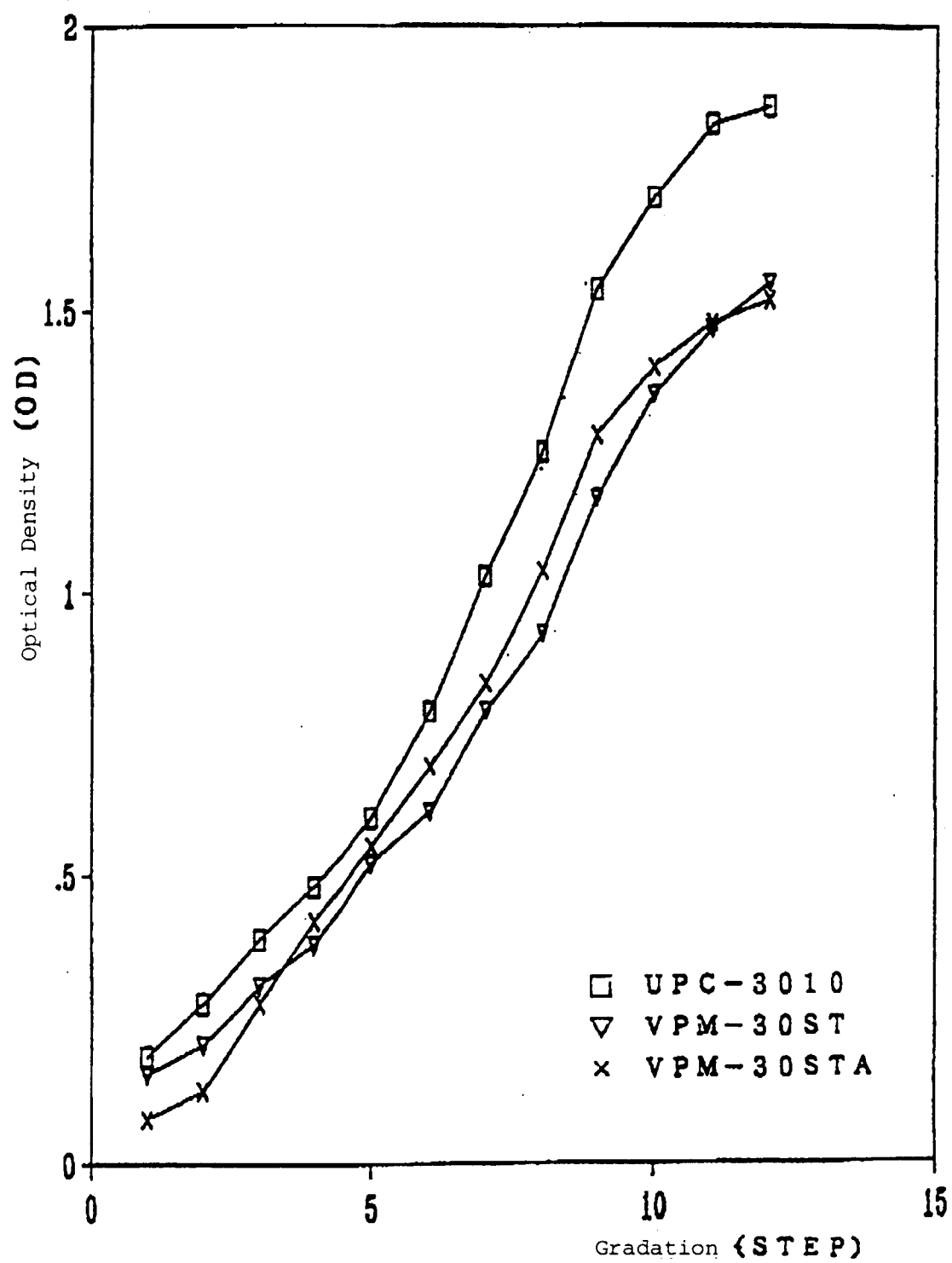


FIG. 7

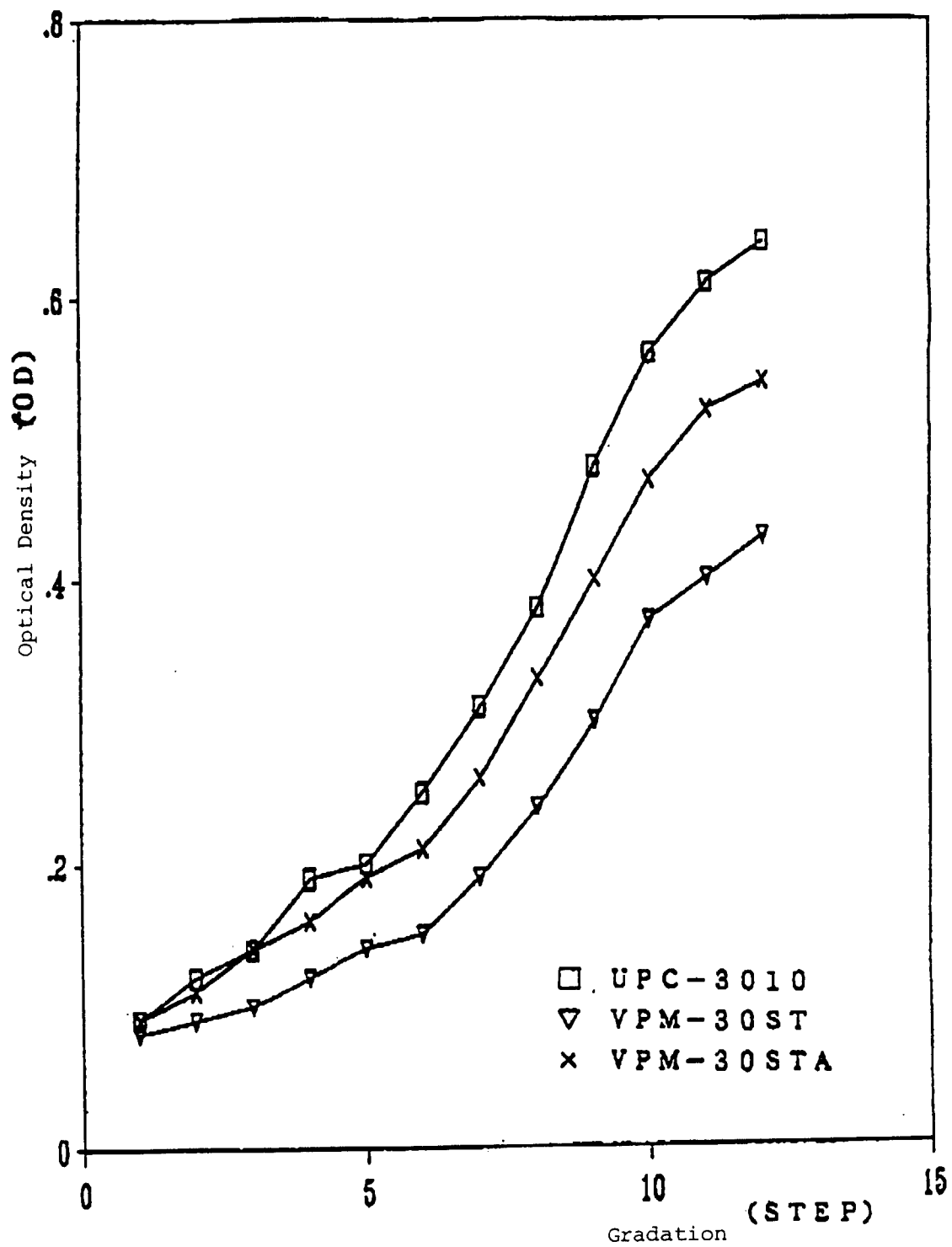


FIG. 8

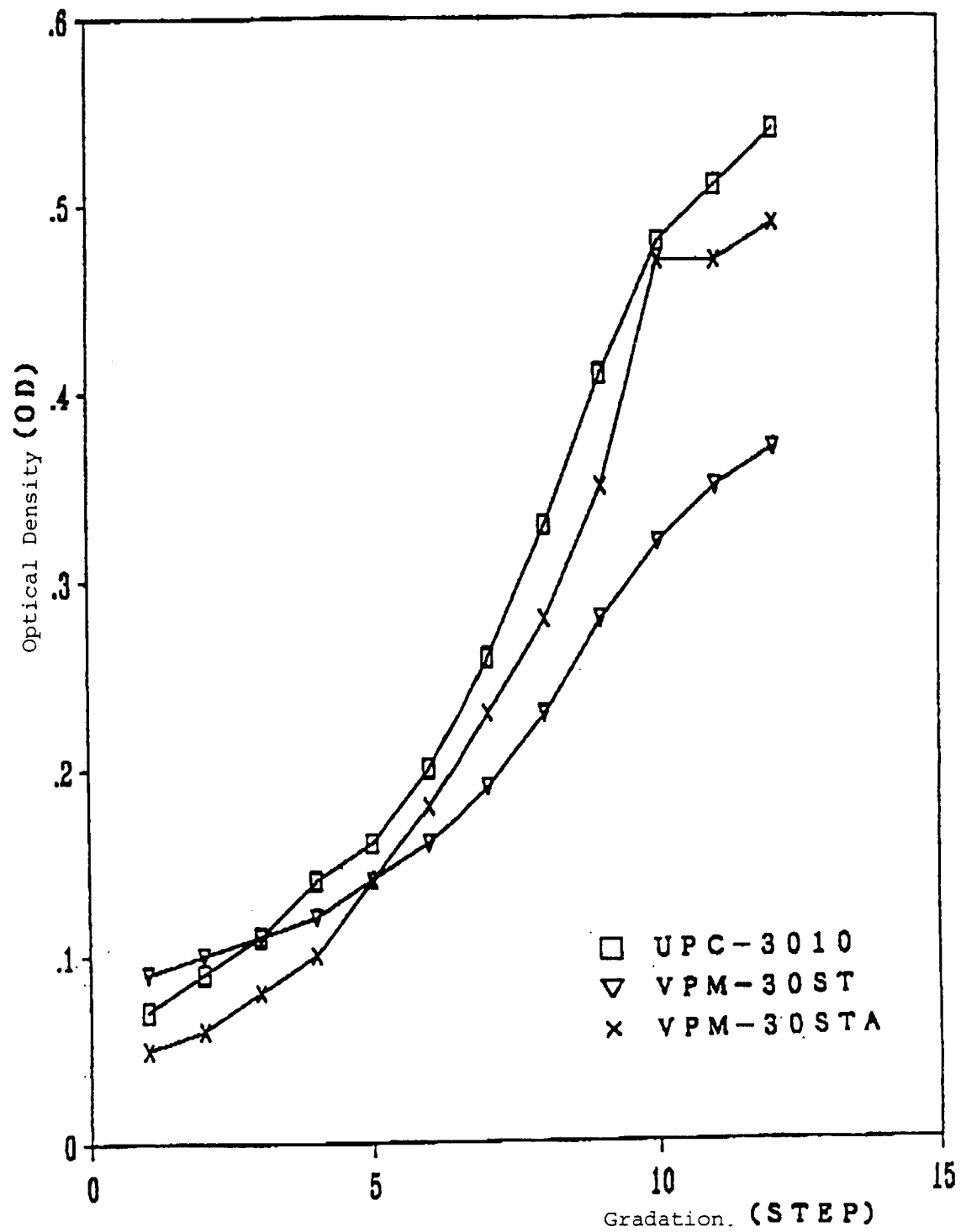


FIG. 9

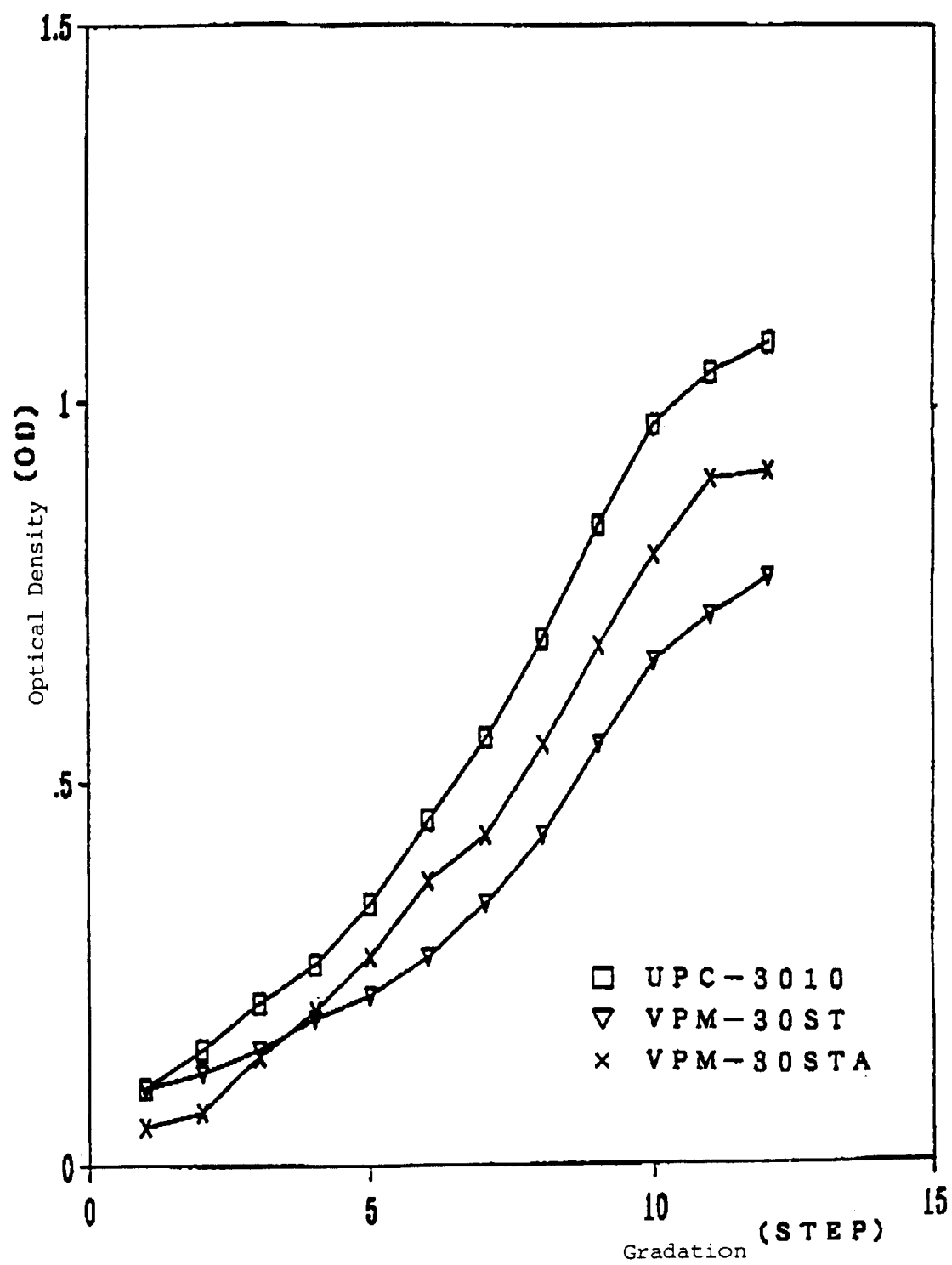


FIG. 10

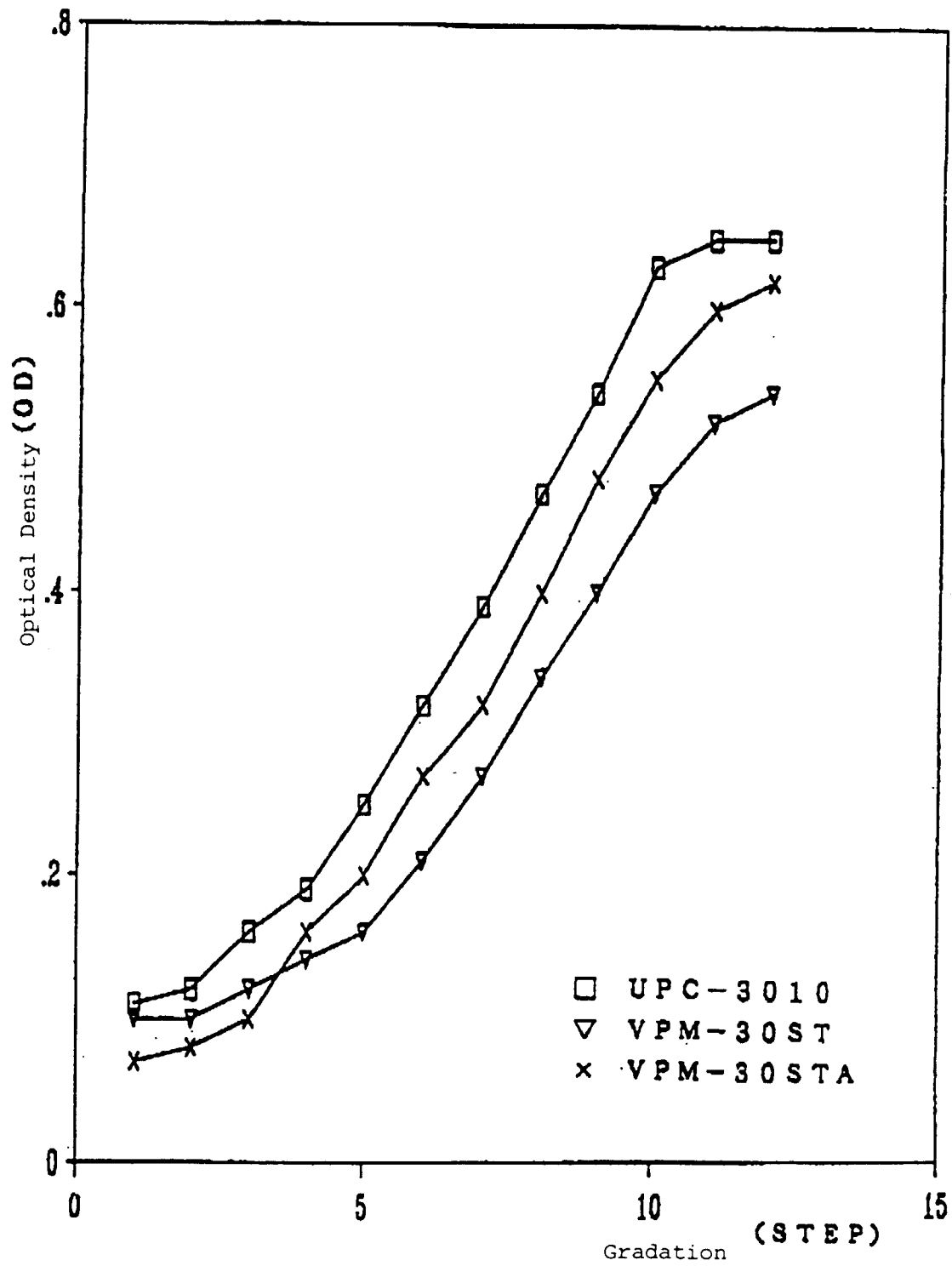


FIG. 11

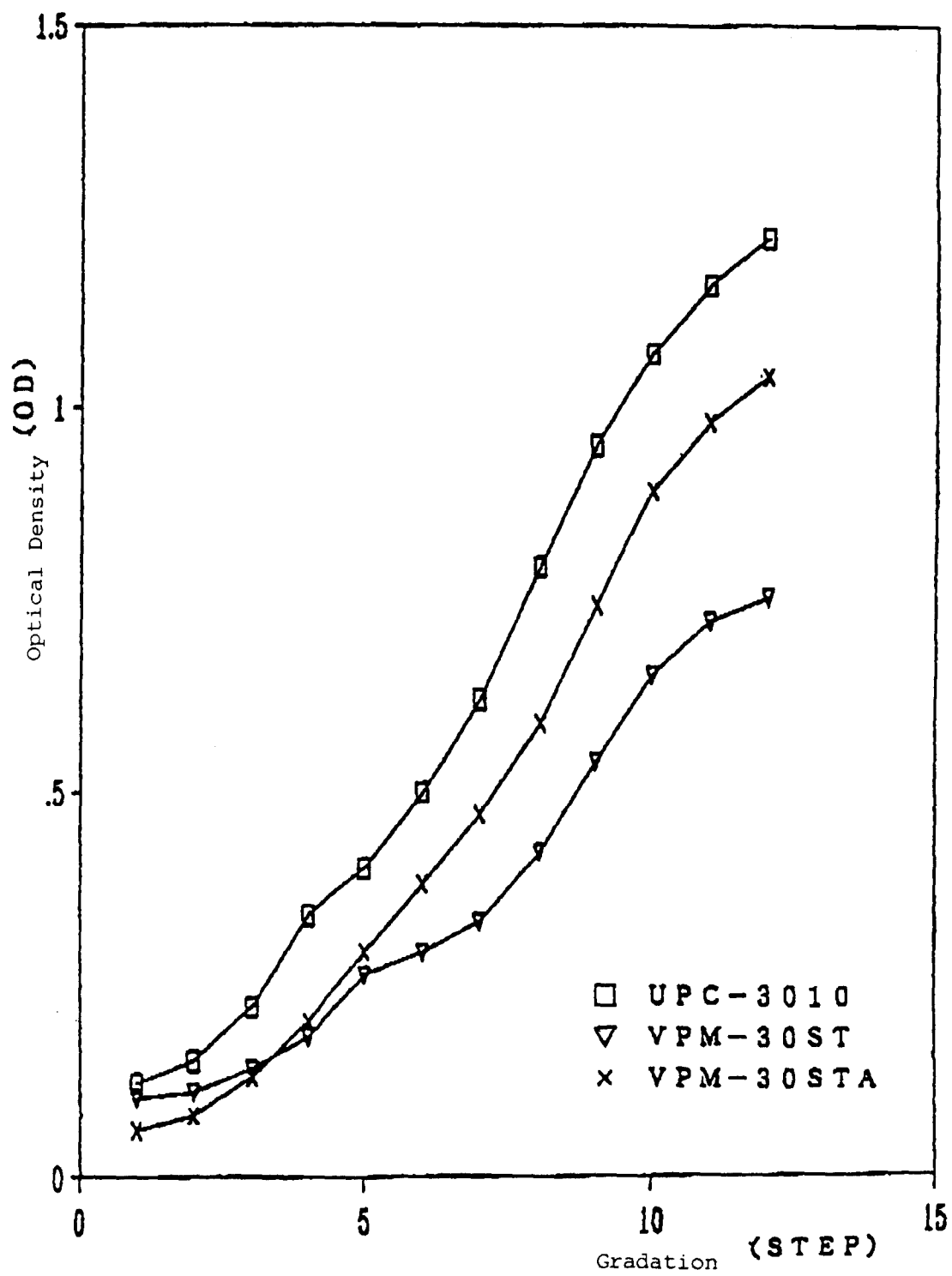


FIG. 12

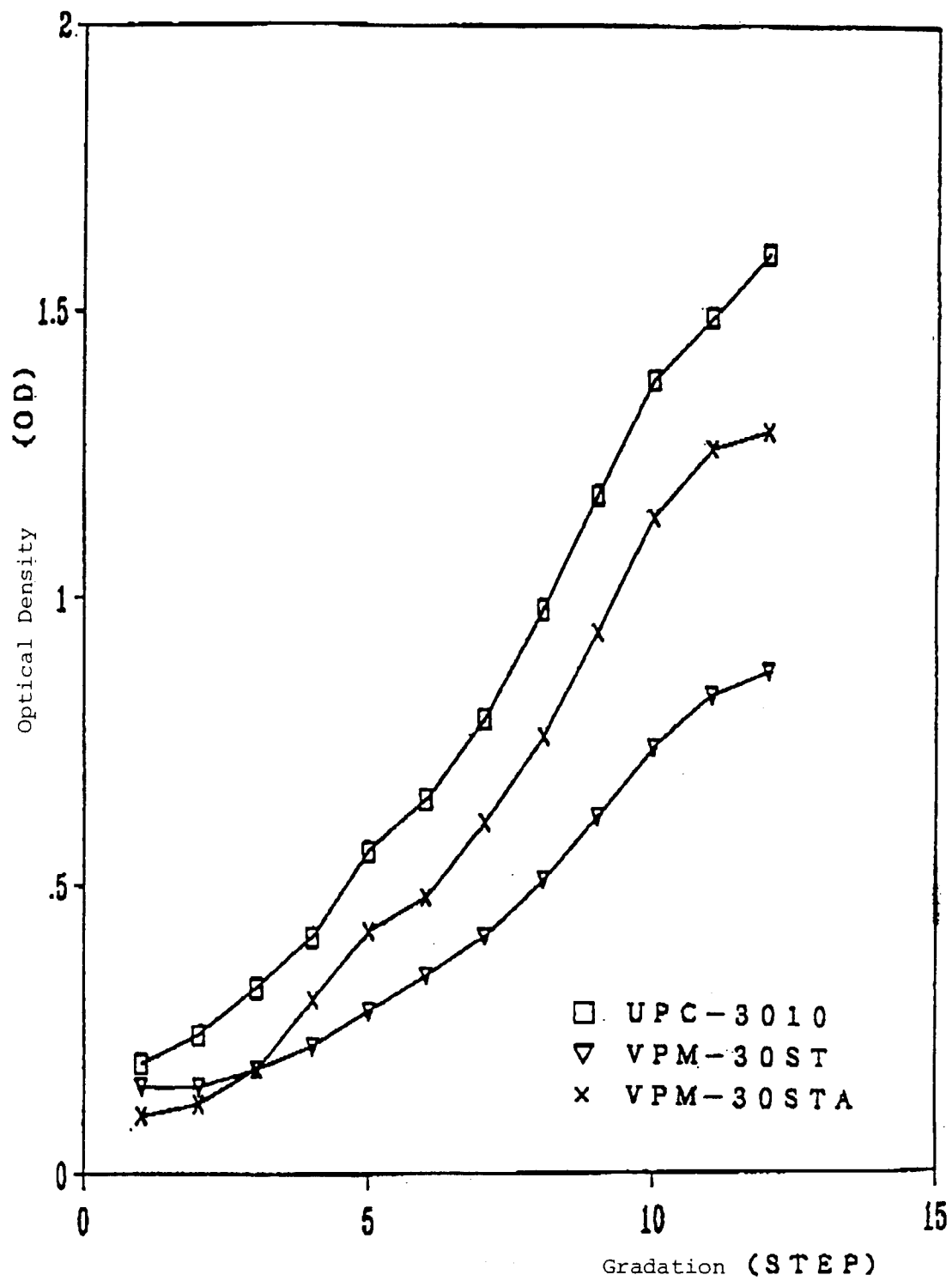


FIG. 13

