(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 123 224**
**A2**

# (12) EUROPEAN PATENT APPLICATION

(21) Application number: 84104136.1

(22) Date of filing: 12.04.84

(51) Int. Cl.$^3$: G 03 C 1/76
G 03 C 1/52

(30) Priority: 13.04.83 JP 65043/83
24.06.83 JP 114752/83
30.08.83 JP 158469/83
13.09.83 JP 169015/83

(43) Date of publication of application:
31.10.84 Bulletin 84/44

(84) Designated Contracting States:
DE FR GB

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## (54) Heat sensitive recording materials.

(57) A heat sensitive recording material comprising a support and a recording layer formed thereon, the recording layer containing (a) a diazo compound, (b) a coupling component and (c) a coloring activator, as the three main components, at least one of the three components (a) to (c) being present in microcapsules and the wall of the microcapsules being composed of a polymer formed around the material encapsulated by a polymerization of reactants. By incorporating a part of the main components in microcapsules, the shelf life of the heat sensitive recording material is greatly improved and when the wall of the microcapsules is formed by the polymerization of reactants around the material encapsulated, the reactive component in the microcapsules immediately passes through the capsule wall upon heating to cause coloration.

Croydon Printing Company Ltd

# HEAT SENSITIVE RECORDING MATERIALS

## FIELD OF THE INVENTION

This invention relates heat sensitive recording materials, and particularly to fixable diazo heat-sensitive recording materials. More particularly, the invention relates to heat sensitive recording materials which have excellent shelf life before heat recording, provide high coloring density as a result of heat recording, and can be fixed by light after heat recording.

## BACKGROUND OF THE INVENTION

A heat sensitive recording method has the advantages that (1) development is unnecessary, (2) when the support of the heat sensitive material is paper, the characteristics of the paper are similar to those of paper in general, (3) handling is easy, (4) a coloring density is high, (5) the recording device is simple and inexpensive, (6) noise is not generated on recording, etc., and hence the heat sensitive recording method is being widely used in facsimile and printer fields.

Heat sensitive recording materials for the recording method include predominantly a leuco coloring type heat sensitive recording material with excellent coloring density and coloring speed. However, a leuco coloring type heat sensitive recording material has the disadvantages that the recording material is colored on handling, heating, or solvent treatment although after recording to stain the recorded image and also the recorded color images disappear due to the action of plasticizers present in adhesive tape.

For preventing formation of color in a leuco coloring type heat sensitive recording material by careless handling, addition of a granular wax (Japanese Patent Publication No. 14,531/1975) has been proposed and also for preventing permeation of plasticizers, formation of a protective layer on the recording layer of the recording material (Japanese utility Model Publication (Unexamined) No. 125,354/1981) was proposed.

However, the foregoing techniques are still unsatisfactory. In particular, these techniques cannot be used for the purpose of preventing the falsification or alteration after recording. Hence an improvement in these techniques has been keenly desired.

A method of using a heat sensitive recording material composed of a diazo compound, a coupling component, and an alkali generating agent or a coloring assistant and irradiating the recording material with light after heat recording to decompose the unreacted diazo compound, whereby further coloring of the recording material is stopped is known as a method of stopping coloring of unnecessary areas of a heat sensitive recording material after heat recording.

However, in a heat sensitive recording material, sometimes during the storage of the recording material, a coupling reaction gradually proceeds to form undesirable coloring (fog). Therefore, prevention of contact of the coloring components with each other to eliminate the occurence of the coupling reaction by containing at least one of the coloring components in the form of discontinuous particles (solid dispersion) is attempted. Howerver, this attempt has the disadvantages that the shelf life of the recording material is still insufficient and also coloring on heating is reduced.

As an alternative approach, it is known to place the diazo compound and the coupler component in different layers to minimize the contact of the components. This technique may improve the shelf life of the recording material but since the heat coloring property is reduced and the recording material cannot respond to high-speed recording with short pulse width, the technique is unsuitable for practical use.

Furthermore, a method of satisfying both the shelf life and the heat coloring property cf heat sensitive recording materials involving isolating (soluting) one of the coupling component and the coloring assistant from the other components by encapsulating the component with a nonpolar waxy material (Japanese Patent Publication (Unexamined) Nos. 4414/1982 and 142,636/1982) or a hydrophobic polymer (Japanese Patent Publication (Unexamined) No. 192,944/1982) is known. In the foregoing encapsulation methods, a waxy material or a hydrophobic polymer is dissolved in a solvent, a coloring component is dissolved or dispersed in the solution, and then the solvent is evaporated off to form microcapsules containing the coloring component. However, in using the encapsulation method, the coloring component is incompletely encapsulated as the core material of the microcapsules and is uniformly mixed with the encapsulating material of the microcapsules. Thus, pre-coupling gradually proceeds at the interface of the walls of the microcapsules during storage of the recording material and hence the shelf life of the recording material is not satisfactory. Also, in the technique, the walls of the microcapsules must be fused by heating for performing the coloring reaction, which results in a reduction in the heat coloring property. Furthermore, in the foregoing method, there is the difficult problem that after forming the microcapsules, the solvent used for dissolving the waxy material or the hydrophobic polymer must be removed and hence the foregoing method is still unsatisfactory in this point.

## SUMMARY OF THE INVENTION

A first object of this invention is, therefore, to provide a heat sensitive recording material having excellent shelf life and high coloring speed and coloring density.

A second object of this invention is to provide a heat sensitive recording material capable of stopping the formation of coloring in unnecessary areas (hereinafter, referred to as "fixing") by photodecomposing unreacted diazo compound after heat recording.

A third object of this invention is to provide a heat sensitive recording material having excellent production aptitude.

As the result of various investigations, it has now been discovered that the foregoing objects of this invention are attained by microcapsulating at least one (with the exclusion of three components in a same microcapsule) of a diazo compound, a coupling component and a coloring assistant or activator(hereinafter, referred to as a "coloring activator"), the wall of the microcapsules being formed around the core material of the microcapsules by polymerization after emulsifying the core material.

That is, according to this invention, there is provided a heat sensitive recording material comprising a support having thereon a recording layer containing a diazo compound, a coupling component and a coloring activator, wherein at least one of the diazo compound, the coupling component and the coloring activator is contained in microcapsules with the exclusion of the case that the three components are present in the same microcapsule, the wall of the microcapsules being formed around the core material by the polymerization of a reactant or reactants after dispersing the core material.

According to a preferred embodiment of this invention, in the foregoing heat sensitive recording material, the wall of the microcapsules are composed of polyurethane, polyurea, polyamide or polyester.

According to another preferred embodiment of this invention, in the foregoing heat sensitive recording material, the core materials are present in the microcapsules together with an organic solvent.

According to still another preferred embodiment of this invention, in the foregoing heat sensitive recording material, the core material is the diazo compound and the wall of said microcapsules is composed of a polymer formed around the core material by the reaction of a polyhydric isocyanate and a polyol.

According to an ever further preferred embodiment of this invention, in the foregoing heat sensitive recording material, the diazo compound is one represented by the general formula

$$ArN_2^+X^-$$

wherein Ar represents a substituted or unsubstituted aromatic moiety and $X^-$ represents an acid anion containing a perfluoroalkyl group or an acid anion containing a perfluoroalkenyl group.

## DETAILED DESCRIPTION OF THE INVENTION

The microcapsules in this invention are not of the type that a coloring reaction occurs upon rupturing of microcapsules by heat or pressure to contact a reactive material present in the microcapsules as the core material and a reactive material present outside the microcapsules as used for conventional recording materials but of the type that the core material present in the microcapsules and a reactive material present outside the microcapsules react through the walls of the microcapsules upon heating.

It is known that when the wall of a microcapsule is formed by polymerization, the wall thus formed is not a completely impermeable film but is permeable to some extent. The permeability of the wall of the microcapsule in the above-described conventional case results in a low molecular material gradually permeating therethrough over a long period of time. However, the phenomenon that a reactive material permeates instantly through the wall of the microcapsule on heating as in the present invention is not yet known. Accordingly, in the case of the microcapsules in this invention it is unnecessary to fuse the wall of the microcapsules by heating and the wall may be formed using a polymer having a high melting point, which provides the heat sensitive recording material with excellent shelf life.

In fact, when the core material is removed from the microcapsules in this invention and the residue is heated, the wall of the microcapsules is scarecely fused.

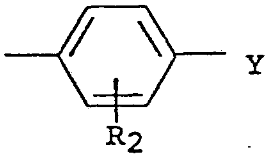
The heat sensitive recording material contains (a) a diazo compound, (b) a coupling component and (c) a coloring activator in the recording layer in a form that one or two of these three components are present in microcapsules (when two components are encapsulated, the components may be present in the same microcapsules or in different microcapsules), the wall of the microcapsules being composed of a high molecular weight compound formed around the core material by polymerization after emulsifying the core material in a reactant for the high molecular material.

The diazo compound used in this invention is a diazonium salt represented by general formula (I)

$$ArN_2^+X^- \qquad (I)$$

wherein Ar represents a substituted or unsubstituted aromatic moiety; $N_2^+$ represents a diazonium group and $X^-$ represents an acid anion, preferably an acid anion containing a perfluoroalkyl group or an acid anion containing perfluoroalkenyl group, which can be colored by undergoing a coupling reaction with the coupling component and can be decomposed by light.

The substituted aromatic moiety represented by Ar are, preferably, represented by general formula

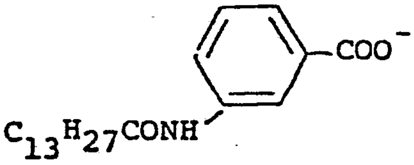


wherein Y represents a substituted amino group, an alkoxy group having 1 to 18 carbon atoms, an alkylthio group having

1 to 18 carbon atoms, an arylamino group having 6 to 18 carbon atoms, or an acylamino group having 1 to 18 carbon atoms; said substituted amino group preferably including a dialkylamino group having 1 to 36 carbon atoms, an arylamino group having 6 to 18 carbon atoms, a morpholino group, a piperidino group, a pyrrolidino group, etc., and R represents hydrogen an alkyl group having 1 to 5 carbon atoms, a halogen atom (e.g., I, Br, Cl, F), an alkoxy group having 1 to 18 carbon atoms, or an arylamino group having 1 to 18 carbon atoms.

Special examples of the diazonium compounds forming salts are 4-diazo-1-dimethylaminobenzene, 4-diazo-1-diethylaminobenzene, 4-diazo-1-dipropylaminobenzene, 4-diazo-1-dibenzylaminobenzene, 4-diazo-1-dibenzylaminobenzene, 4-diazo-1-ethylhydroxyethylaminobenzene, 4-diazo-1-diethylamino-3-methoxybenzene, 4-diazo-1-dimethylamino-2-methylbenzene, 4-diazo-1-benzylamino-2,5-diethoxybenzene, 4-diazo-1-morpholinobenzene, 4-diazo-1-morpholino-2,5-diethoxybenzene, 4-diazo-1-morpholino-2,5-dibutoxybenzene, 4-diazo-1-anilinobenzene, 4-diazo-1-toluylmercapto-2,5-diethoxybenzene, 4-diazo-1,4-methoxybenzoylamino-2,5-diethoxybenzene, etc.

Special examples of suitable acid anions are $C_nF_{2n+1}COO^-$ (wherein n is 3 to 9), $C_mF_{2m+1}SO_3^-$ (wherein m is 2 to 8), $(ClF_{2\ell+1}SO_2)_2CH^-$ (wherein $\ell$ is 1 to 18),



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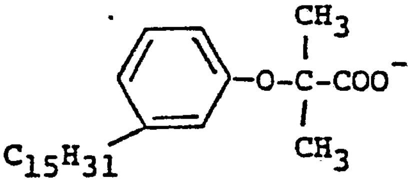

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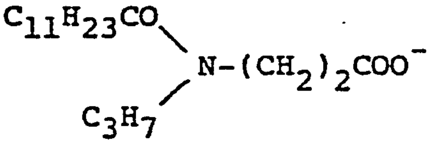

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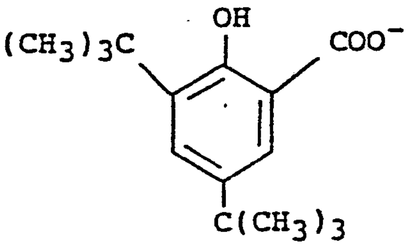

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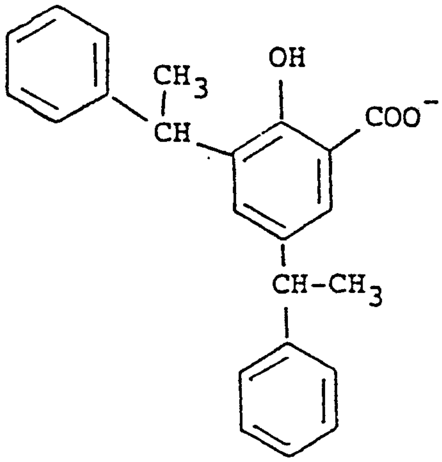

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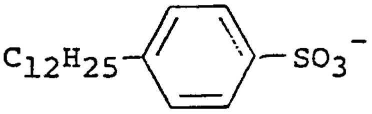

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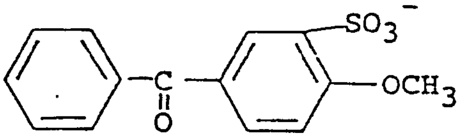

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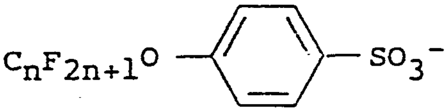

(n is 3 to 9)

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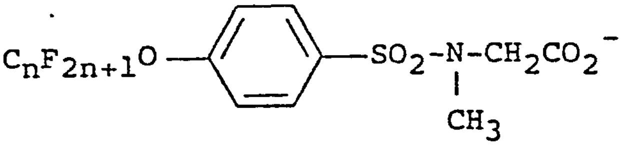


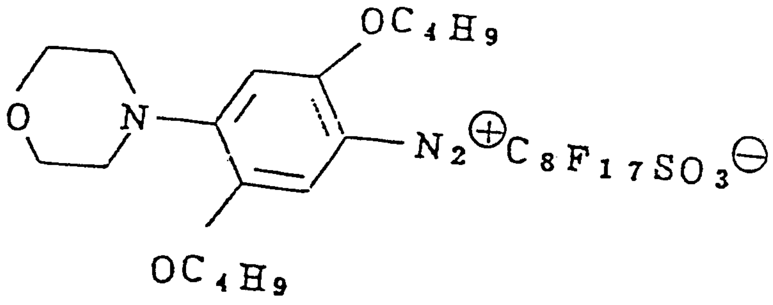
(n is 3 to 9)

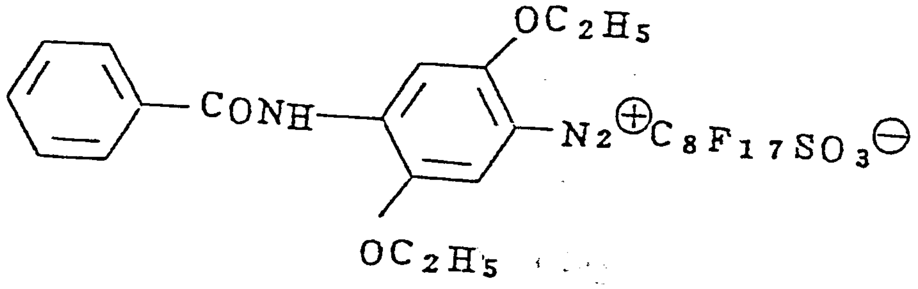
,

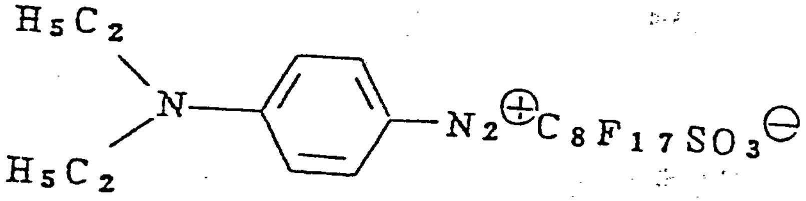
$BF_4^-$, $PF_6^-$, etc.

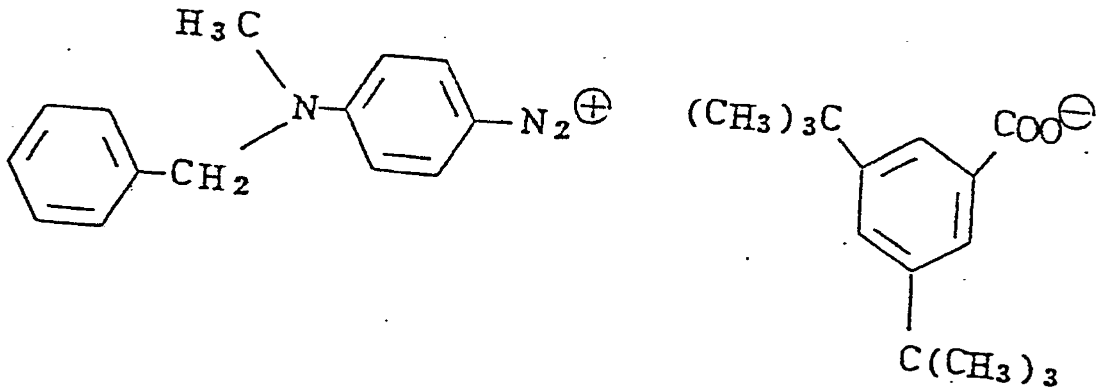
Of the foregoing acid anions, acid anions having a perfluoroalkyl group or a perfluoroalkenyl group each having less than 20 carbon atoms are preferred since the increase of fog at shelf life of the heat sensitive recording material is less.

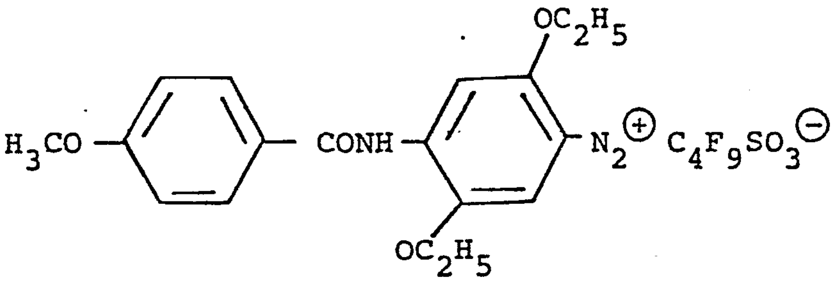
Special examples of diazo compounds (diazonium salts) which can be used in this invention are as follows:

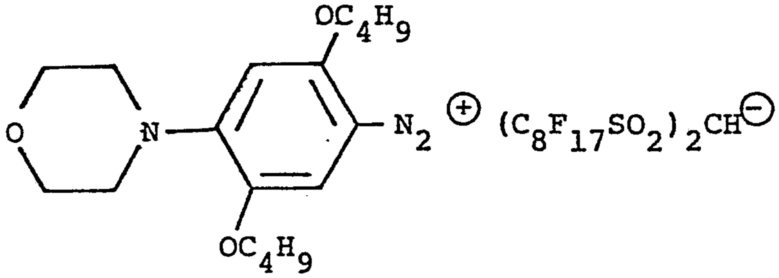


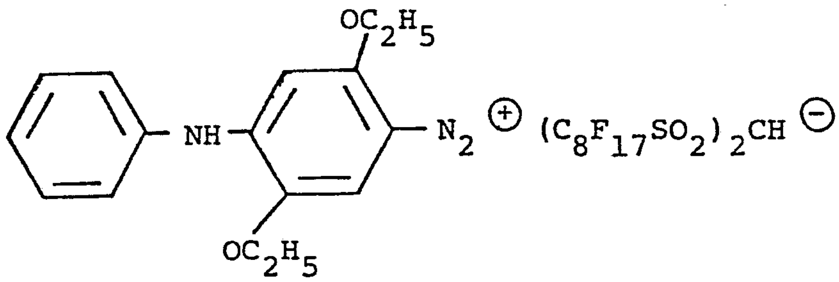


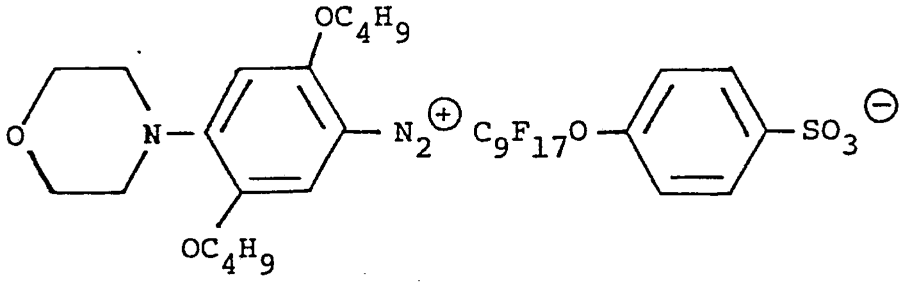


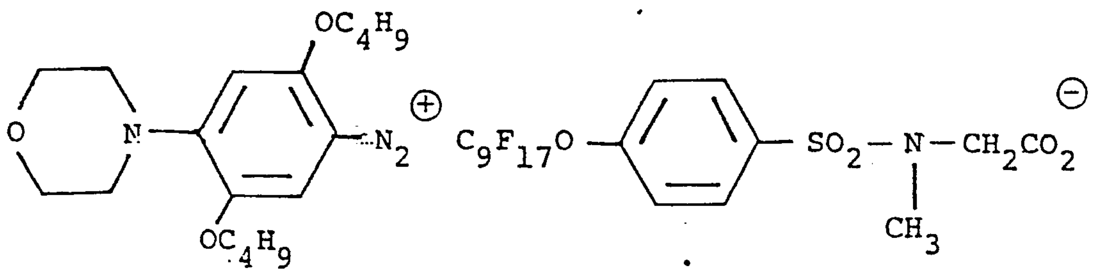


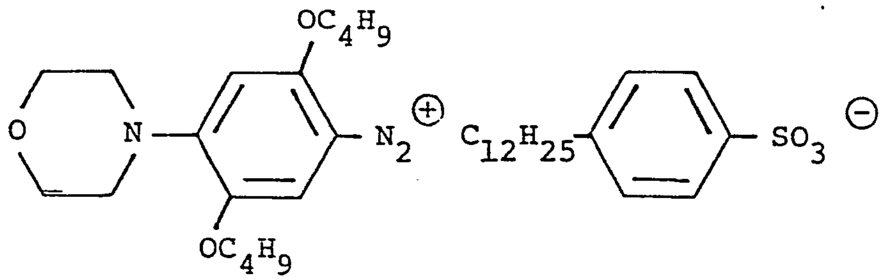

$H_3CO$
CONH
$OC_2H_5$
$OC_2H_5$
$N_2^{\oplus}$ $C_4F_9SO_3^{\ominus}$

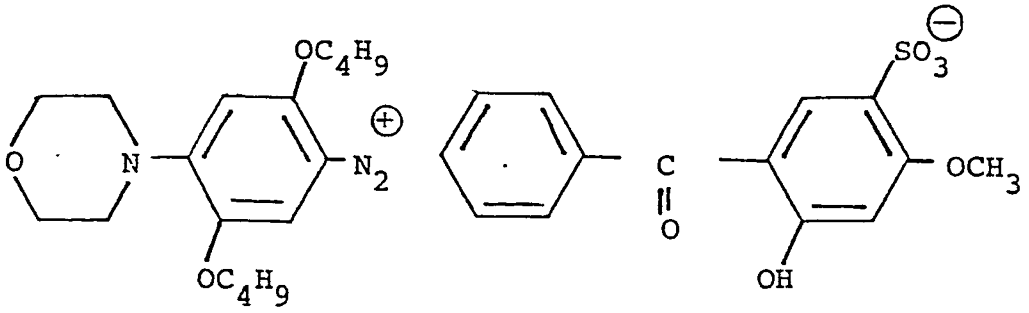

O
N
$OC_4H_9$
$OC_4H_9$
$N_2^{\oplus}$ $(C_8F_{17}SO_2)_2CH^{\ominus}$

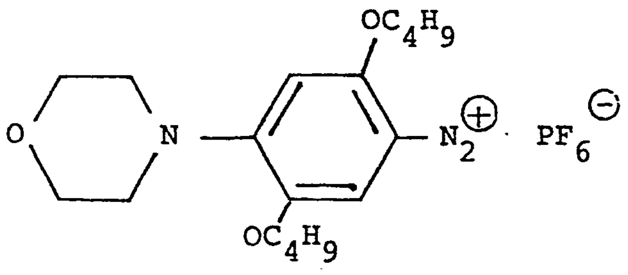

NH
$OC_2H_5$
$OC_2H_5$
$N_2^{\oplus}$ $(C_8F_{17}SO_2)_2CH^{\ominus}$


O
N
$OC_4H_9$
$OC_4H_9$
$N_2^{\oplus}$ $C_9F_{17}O$
$SO_3^{\ominus}$


OC4H9
O
N
N2 ⊕
C9F17O
SO2 — N — CH2CO2 ⊖
CH3
OC4H9


OC4H9
O
N
N2 ⊕
C12H25
SO3 ⊖
OC4H9


OC4H9
SO3 ⊖
O
N
⊕
N2
C
O
OCH3
OC4H9
OH


OC4H9
O
N
N2 ⊕
PF6 ⊖
OC4H9

The coupling component used in this invention is a compound which forms a dye upon coupling with the diazo compound (diazonium salt) under basic conditions. Specific examples of suitable coupling components are resorcin, fluoroglucin, sodium 2,3-dihydroxynaphthalene-6-sulfonate, 1-hydroxy-2-naphthoic acid morpholinopropylamide, 1,5-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,3-dihydroxy-6-sulfanilnaphthalene, 2-hydroxy-3-naphthoic acid morpholinopropylamide, 2-hydroxy-3-naphthoic acid anilide, 2-hydroxy-3-naphthoic acid-2'-methylanilide, 2-hydroxy-3-naphthoic acid ethanolamide, 2-hydroxy-3-naphthoic acid octylamide, 2-hydroxy-3-naphthoic acid-N-dodecyl-oxypropylamide, 2-hydroxy-3-naphthoic acid tetradecylamide, acetanilide, acetoacetanilide, benzylacetanilide, 1-phenyl-3-methyl-5-pyrazolone, 1-(2',4',6'-trichlorophenyl)-3-benzamido-5-pyrazolone, 1-(2',4',6'-trichlorophenyl)-3-anilino-5-pyrazolone, 1-phenyl-3-phenylacetamido-5-pyrazolone, etc.

Furthermore, by using two or more of these coupling components, images having a desired hue can be obtained.

A sparingly water-soluble or water insoluble basic material or a material generating an alkali upon heating is used as the coloring activator.

Examples of coloring activators which can be used in this invention include nitrogen-containing compounds such as inorganic and organic ammonium salts, organic amines, amides, urea and derivatives thereof, thiourea and derivatives thereof, thiazoles, pyrroles, pyrimidines, piprazines, guanidines, indoles, imidazoles, imidazolines, triazoles, morpholines, piperidines, amidines, formazines, pyridines, etc.

Specific examples of coloring activators are ammonium acetate, tricyclohexylamine, tribenzylamine, octadecylbenzylamine, stearylamine, allylurea, thiourea, methylthiourea, allylthiourea, ethylenethiourea, 2-benzylimidazole, 4-phenylimidazole, 2-phenyl-4-methylimidazole, 2-undecyl-imidazoline, 2,4,5-trifuryl-2-imidazoline, 1,2-diphenyl-4,4-dimethyl-2-imidazoline, 2-phenyl-2-imidazoline, 1,2,3,-triphenylguanidine, 1,2-ditolylguanidine, 1,2-dichlorohexylguanidine, 1,2,3-tricyclohexylguanidine, guanidine trichloroacetate, N,N'-dibenzylpiperazine, 4,4'-dithiomorpholine, morpholium trichloroacetate, 2-amino-benzothiazole, 2-benzoylhydrazinobenzothiazole, etc. These coloring activators may be used individually or as a combination thereof.

In this invention, by appropriately selecting the material for and the thickness of the wall of the microcapsules, the core material in the microcapsules may be a solution, a semi-solid, or a solid but a solution is preferred since in this case, the core material immediately permeates or reacts to form color at heat recording. Accordingly, it is preferred to use a high-boiling solvent which is a liquid at normal temperature as the core material in this invention.

In this invention, it is effective for improving the shelf life of the heat sensitive recording material and increasing the coloring speed and coloring density of the recording material to dissolve or disperse the core material in a water-insoluble organic solvent, emulsify the solution or dispersion, and form a microcapsule wall around the core material by polymerization. Organic solvents having a boiling point of higher than about 180°C, such as phosphoric acid esters, phthalic acid esters, other carboxylic acid esters, fatty acid amides, alkylated biphenyls, alkylated terphenyls, chlorinated paraffins, alkylated naphthalenes, diarylethanes, etc., are preferred as suitable organic solvents.

Special examples of suitable organic solvents which can be used in this invention are tricresyl phosphate, trioctyl phosphate, octyldiphenyl phosphate, tricylohexyl phosphate, dibutyl phthalate, dioctyl phthalate, dilauryl phthalate,dicyclohexyl phthalate, butyl oleate, diethylene glycol dibenzoate, dioctyl sebacate, dibutyl sebacate, diocyl adipate, trioctyl trimellitate, acetyltriethyl citrate, octyl maleate, dibutyl maleate, isoprophlbiphenyl, isoamylbiphenyl, chlorinated paraffin, diisopropylnaphthalene, 1,1'-ditolylethane, 2,4-di-t-aminophenol, N,N-dibutyl-2-butoxy-5-t-octylaniline, etc. Of these solvents, ester solvents such as dibutyl phthalate, diethyl phthalate, dibutyl maleate, etc., are preferred.

The microcapsules used in this invention are prepared by emulsifying a core material containing a reactive material and then forming a wall of a high molecular weight compound around the oil drops of the core material. In this invention, one or two of the foregoing diazo compound, the coupling component and the coloring activator are present in the microcapsules. When the two components are present in the microcapsules, both components may be present in same microcapsules or may be present in different microcapsules. Furthermore, in this invention, the foregoing three components may be present in different microcapsules or two components are present in the same microcapsules and another component may be present in other microcapsule. However, where the three components are present in the same microcapsules are excluded in this invention. Thus, the term "encapsulating at least one of the three components" in this invention means the embodiments described above.

In forming a high-molecular weight material around the droplets of the core material thus formed by emulsification as the wall of the microcapsules, the reactant or reactants forming the high molecular weight material are added to the interior and/or the exterior of the oil droplets.

Special examples of high molecular weight compounds thus formed are polyurethane,polyurea, polyamide, polyester, polycarbonate, a urea-formaldehyde resin, a melamine resin, polystyrene, a styrene-methacrylate copolymer, a styrene-acrylate copolymer, gelatin, polyvinyl pyrrolidone, polyvinyl alcohol, etc.

Two or more of the foregoing high molecular weight materials may be employed as the wall materials in this invention. Preferred high molecular weight materials are polyurethane, polyurea, polyamide, polyester, polycarbonate, etc., and polyurethane and polyurea are more preferred.

The high molecular weight material used in this invention has preferably a melting point higher than about 150°C so that the wall is not melted at the temperature of heat recording.

As described above, in this invention, at least one of the diazo compound, the coupling component and the coloring activator which are the main components used in this invention is employed as the core material of the microcapsules. That is, the diazo compound, the coupling component or the coloring activator may be used as the core material; or the diazo compound and the coupling component, the diazo compound and the coloring activator, or the coupling component and the coloring activator may be used as the core material, and in the latter case, another component may be incorporated in the recording layer without being encapsulated. When two components are used as the core material, both components may be present in the same microcapsules or different microcapsules. In this invention, each of the three components may be present in different microcapsule or two components may be present in the same microcapsules and another component is present in other microcapsules.

For forming the wall of the microcapsules in this invention, a microcapsulation method involving polymerization of a reactant from the inside of the droplets of the core material can be effectively used. That is, in this case, microcapsules having a uniform particle size can be obtained in a short period of time and such microcapsules are preferred for a heat sensitive recording material having excellent shelf life.

Specific examples of compounds which can be used in the foregoing microcapsulation method are described in, for example, U.S. Patent Nos. 3,726,804 and 3,796,669.

For example, in using polyurethane as the wall of the microcapsules, a polyvalent isocyanate and a material (e.g., a polyol) forming the microcapsule wall by a reaction with the isocyanate are mixed with an oily solution of the core material, the mixture is dispersed by emulsification in water, and the temperature is increased to cause a polymer-forming reaction at the interface of the oil droplets in the emulsion, whereby the wall of the microcapsules is formed. In this case, a low-boiling auxiliary solvent having a high dissolving power can be used in the oily solution.

The polyisocyanates and polyols used in the above case are described in, for example, U.S. Patent Nos. 3,135,716; 3,281,383; 3,468,922; 3,773,695; 3,793,268; Japanese Patent Publication Nos. 40,347/'73; 24,159/'74; and Japanese Patent Publication (Unexamined) Nos. 80,191/'73 and 84,086/'73.

Also, in this case, a tin salt, etc., may be used for promoting the urethane forming reaction.

In forming the microcapsules used in this invention, it is effective for obtaining a heat sensitive recording material having a good shelf life and high coloring speed and high heat coloring property to use a polyhydric isocyanate as a first wall-forming material and a polyol as a second wall-forming material as described above.

Examples of polyhydric isocyanates used as the first wall-forming material are diisocyanates such as m-phenylene diisocyante, p-phenylene diisocyanate, 2,6-trichlene diisocyanate, 2,4-tolylene diisocyanate, naphthalene-1,4-diisocyanate, diphenylmethane-4,4'-diisocyanate, 3,3'-dimethoxy-4,4'-biphenyl-diisocyanate, 3,3'-dimethyldiphenylmethane-4,4'-diisocyanate, xylylene-1,4-diisocyanate, 4,4'-diphenylpropane diisocyanate, trimethylene diisocyanate, hexamethylene diisocyanate, propylene-1,2-diisocyanate, butylene-1,2-diisocyanate, cyclohexylene-1,2-diisocyanate, cyclohexylene-1,4-diisocyanate, etc.; triisocyanates such as 4,4'4"-triphenylmethane triisocyanate, toluene-2,4,6-triisocyanate, etc.; tetraisocyanates such as 4,4'-dimethyldiphenylmethane-2,2',5,5'-tetraisocyanate, etc.; and isocyanate prepolymers such as an addition product of hexamethylene diisocyanate and trimethylolpropane, an addition product of 2,4-tolylene diisocyanate and trimethylolpropane, an addition product of xylylene diisocyanate and trimethylolpropane, and an addition product of tolylene diisocyanate and hexanetriol.

The polyol used as the second wall-forming material includes aliphatic and aromatic polyhydric alcohols, hydroxy polyesters, hydroxy polyalkylene ethers, etc.

Preferred polyols are polyols having a molecular weight lower than 5,000 and having the following group (I), (II), (III) or (IV) between the two hydroxy groups in the molecular structure;

(I) aliphatic hydrocarbon group having 2 to 8 carbon atoms,

(II) $-\overset{|}{\underset{|}{C}}-O-Ar'-O-\overset{|}{\underset{|}{C}}-$

(III) $-\overset{|}{\underset{|}{C}}-Ar'-\overset{|}{\underset{|}{C}}-$

(IV) $-O-Ar'-\overset{|}{\underset{|}{C}}-Ar'-O-$

In groups (II), (III) and (IV), Ar′ represents an unsubstituted or substituted aromatic moiety and the aliphatic hydrocarbon group of (I) has the moiety $-C_nH_{2n}-$ wherein n is 2 to 8 as the fundamental skelton and the hydrogen atom may be replaced by another element.

Specific examples of polyols of group (I) are ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, propylene glycol, 2,3-dihydroxybutane, 1,2-dihydroxybutane, 1,3-dihydroxybutane, 2,2-dimethyl-1,3-propanediol, 2,4-pentanediol, 2,5-hexanediol, 3-methyl-1,5-pentanediol, 1,4-cyclohexanedimethanol, dihydroxycyclohexane, diethylene glycol, 1,2,6-trihydroxyhexane, phenylethylene glycol, 1,1,1-trimethylolpropane, hexanetriol, pentaerythritol, glycerol, etc.

Specific examples of polyols of group (II) are the condensation products of aromatic polyhydric alcohols such as 1,4-di(2-hydroxyethoxy)benzene, resorcinol dihydroxyethyl ether, etc., and alkylene oxides.

Specific examples of polyols of group (III) are p-xylylene glycol, m-xylylene glycol, α,α'-dihydroxy-p-diisopropylbenzene, etc.

Specific examples of polyols of group (IV) are 4,4'-dihydroxydiphenylmethane, 2-(p,p'-dihydroxydiphenylmethyl)benzyl alcohol, an addition product of bisphenol A and ethylene oxide, an addition product of bisphenol A and propylene oxide, etc. It is preferred to use the polyol at 0.02 to 2 moles of the hydroxy group per mole of isocyanate group.

In forming microcapsules in this invention, a water-soluble polymer can be used and examples of water-soluble polymer used in this invention include a water-soluble anionic polymer, a water-soluble nonionic polymer and a water-soluble amphoteric polymer.

A natural anionic polymer and a synthetic anionic polymer can be used as the water-soluble anionic polymer. For example, anionic polymers having $-COO^-$ group, $-SO_3^-$ group, etc. can be used. Specific examples of anionic natural polymers are gum arabic, alginic acid, etc., and examples of the semisynthetic products are carboxy methyl cellulose, phthalated gelatin, sulfated starch, sulfated cellulose, ligninsulfonic acid, etc. Also, examples of the synthetic products are maleic anhydride (including hydrolyzed derivatives) copolymers, acrylic acid (including methacrylic acid) polymers and copolymers, vinylbenzenesulfonic acid polymers and copolymers, carboxy-denatured polyvinyl alcohol, etc. Examples of nonionic polymers are polyvinyl alcohol, hydroxyethyl cellulose, methyl cellulose, etc. Examples of the amphoteric anionic polymer are gelatin, etc.

Such a water-soluble polymer is used as an aqueous solution in an amount of 0.01 to 10% by weight of the polymer. The particle size of the microcapsules is controlled to below about 20 μm. If the particle size of the microcapsules is over 20 μm, the quality of print images tends to be reduced. In particular, when the recording material is heated from the coated layer side by a thermal head, the particle size of the microcapsules is preferably less than 8 μm.

The microcapsules can be prepared from an emulsion containing the component or components to be encapsulated in an amount of higher than 0.2% by weight. It is also preferred for the component to permeate more smoothly through the wall of the microcapsules to encapsulate the component together with a high-boiling organic solvent as described hereinbefore.

When one or two of the diazo compound, the coupling component and the coloring activator are present in microcapsules or present in the recording layer without being encapsulated, it is preferred for the coupling component to be used in an amount of about 0.1 to about 10 parts by weight to 1 part by weight of the diazo compound and the coloring activator is used in an amount of about 0.1 to about 20 parts by weight to 1 part by weight of the diazo compound. Also, it is preferred that the diazo compound be coated in an amount of about 0.05 to about 2.0 g/m$^2$.

When the diazo compound, the coupling component and the coloring activator used in this invention are not encapsulated, it is preferred for each component to be in the form of a solid dispersion. In this case, each component is each dispersed in a different water-soluble polymer solution. As the water-soluble polymer used in this case, it is preferred to use the water-soluble polymer used for forming microcapsules. In this case, the concentration of the water-soluble polymer is about 2 to about 30% by weight and each of the diazo compound, the coupling component and the coloring activator is added to each solution of the water-soluble polymer at a concentration of about 5 to about 40% by weight. It is preferred that the partcicle size of each component thus dispersed in the solution be less than about 10 μm.

For the heat sensitive recording material of this invention, a pigment such as silica, barium sulfate, titanium oxide, aluminum hydroxide, zinc oxide, calcium carbonate, etc., and a fine powder such as styrene beads, a urea-melamine resin powder, etc., may be used for the purposes of preventing adhesion of the recording paper to a thermal head and improving the writability. Also, for preventing adhesion of the recording material, metal soaps, etc., can be used. The amount of the foregoing material is about 0.2 to about 7 $g/m^2$.

Furthermore, for the heat sensitive recording material of this invention, a heat melting material can be used to increase the heat recording density. The heat melting material is a material having a melting point of about 50 to about 150°C, which is in a solid state at normal temperature but is melted by heating due to the thermal heat at heat recording and thus dissolves the diazo compound, the coupling component or the coloring activator. The heat melting material is dispersed as particle of a size of about 0.1 to about 10 μm and the amount used is about 0.2 to about 7 $g/m^2$ as solid. Specific examples of suitable heat melting material are fatty acid amides, N-substituted fatty acid amides, ketone compounds, N-substituted carbamate compounds, urea compounds, esters, etc.

For making the heat sensitive recording material of this invention, the coating composition may be coated using an appropriate binder. Various emulsions of polyvinyl alcohol, methyl cellulose, carboxymethyl cellulose, hydroxypropyl cellulose, gum arabic, gelatin, polyvinylpyrrolidone, casein, styrene-butadiene latex, acrylonitrile-butadiene latex, polyvinyl acetate, polyacrylic acid ester, ethylene-vinyl acetate copolymer, etc., can be used as the binder. The amount of the binder used is about 0.5 to 5 $g/m^2$.

The heat sensitive recording material of this invention may further contain citric acid, tartaric acid, oxalic acid, boric acid, phosphoric acid, pyrophosphoric acid, etc., as an acid stabilizer in addition to the foregoing compounds.

For preparing the heat sensitive recording material of this invention, a coating composition containing the diazo compound, the coupling component and the coloring activator together with, if desired, other additives as the core material of the microcapsules, a simple solid dispersion, or a solution thereof is prepared and coated on a support such as a paper, a synthetic resin film, etc., using coating method such as a bar coating method, a blade coating method, an air knife coating method, a gravure coating method, a roll coating method, a spray coating method, a dip coating method, etc., followed by drying to form a heat sensitive recording layer having a solid content of about 2.5 to about 15 $g/m^2$.

In other method of preparing the heat sensitive recording material of this invention, a coating composition containing the coupling component and the coloring activator as the main components together with, if desired, other components as the core Material of the microcapsules, a simple solid dispersion, or a solution thereof is prepared and coated on a support as above described followed by drying to form a pre-coated layer having a solid content of about 2 to about 10 $g/m^2$, and further a coating composition containing the diazo compound as the main component together with other additives, if any, as the main core material of the microcapsules, a simple solid dispersion, or a solution thereof is prepared and coated on the pre-coated layer followed by drying to form a diazo compound layer having a solid content of about 1 to about 10 g/m$^2$. Thus, a double layer type heat sensitive recording material is prepared. In this case, at least one of the diazo compound, the coupling component, and the color activator as the main components of the heat sensitive recording material is coated as a microencapsulated form. In a double layer type recording material, the order of the layers may be opposite to the above described embodiment. The double layers may be formed by successive coating or by simultaneous coating. The double layer type heat sensitive recording material has particularly excellent long shelf life.

In addition, in the case of using a paper as the support, it is advantageous from the standpoint of improving the shelf life of the recording material to use a neutral paper having a heat extraction pH of 6 to 9 sized with a neutral size such as an alkylketene dimer, etc., (e.g., as described in Japanese Patent Publication (Unexamined) No. 14,281/'80).

Also, for preventing the permeation of a coating liquid in a paper support and improving the contact of the heat sensitive recording layer with the thermal head, a paper having a Beck flatness of above 90 sec. and the following Stöckigt sizing degree

$$\frac{\text{Stöckigt sizing degree}}{(\text{basis weight})^2} \geqq 3 \times 10^{-3}$$

as described in Japanese Patent Publication (Unexamined) No. 116,687/'82 can be advantageously used.

Moreover, a paper having an optical surface roughness of less than 8 μm and a thickness of 40 to 75 μm described in Japanese Patent Application No. 20,047/'82; a paper having a density of less than 0.9 g/cm$^3$ and an optical contact ratio of higher than 15% as described in Japanese Patent Publication (Unexamined) No. 69,091/'83; a paper capable of preventing the permeation of a coating liquid manufactured using a pulp beated above 400 cc. as Canadian standard freeness (JIS P8121) as described in Japanese Patent Publication (Unexamined) No. 69,097/'83; a paper for improving the coloring density and the resolving power using the luster surface of a base paper manufactured on a Yankee paper machine as a coating surface as described in Japanese Patent Publication (Unexamined) No. 65,695/'83; a paper having improved coatability by applying a corona discharging treatment to a base paper as described in Japanese Patent Application No. 145,872/'82, etc., can be used in this invention with good results. Thus, these supports used in general in the field of ordinary heat sensitive recording papers can be used as support in this invention.

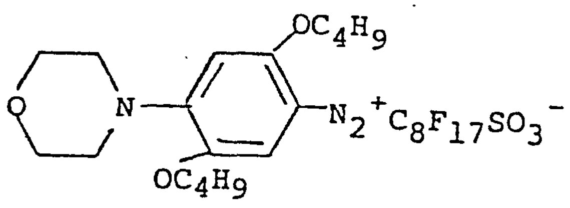
The heat sensitive recording material of this invention can be used as printer papers for facsimile and computers requiring high-speed recording and can be fixed by exposing the recording material to light, after heat printing, to decompose the unreacted diazo compound. Furthermore, the heat sensitive recording material can be used as a heat developable copying paper.

The invention is explained below in greater detail by reference to the following examples but the invention is not to be construed limited to these examples. In addition, the "part" for the addition amount is "by part by weight".

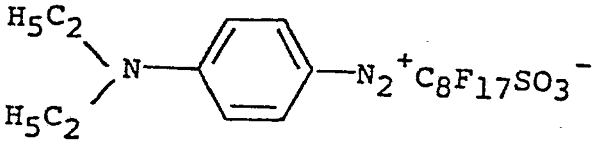
## Examples 1 to 5 and Comparison Examples 6 to 8

Using following Diazo Compounds (1) to (3) each of the diazo compound in an amount shown in Table 1 below and 10 parts of the addition product of xylylene diisocyanate and trimethylolpropane (3 : 1 by weight) were dissolved in a mixture of 20 parts of dibutyl phthalate and 5 parts of ethyl acetate. The solution of the diazo compound was mixed with an aqueous solution of 3.5 parts of polyvinyl alcohol, 1.7 parts of gelatin, and 3.6 parts of 1,5-dihydroxypentane dissolved in 58 parts of water and the mixture was an emulsion dispersion at 20°C to provide an emulsion having a mean particle size of 3 μm. To the emulsion was added 100 parts of water and the mixture was heated to 40 to 70°C with stirring. Thus, after 2 hours, three kinds of capsule-containing solutions containing the diazo compound as the core material of the microcapsules were obtained.

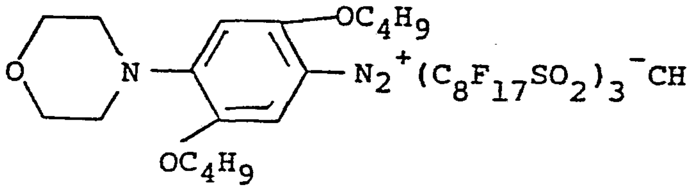
Diazo Compound (1)



Diazo Compound (2)



Diazo Compound (3)



Each of the dispersions of coupling components (1) to (3) shown below having a mean particle size of about 3 µm was obtained by dispersing 20 parts of each coupling component and 5 parts of polyvinyl alcohol in 100 parts of water for about 24 hours using a sand mill.

Coupling Component (1):

2-hydroxy-3-naphthoeic acid morpholinopropylamide

Coupling Component (2):

2-hydroxynaphthoeic acid anilide

Coupling Component (3):

2-Hydroxy-3-naphthoeic acid-2'-methylanilde

Then, 20 parts of triphenyl guanidine and 5 parts of polyvinyl alcohol were dispersed in 100 parts of water for about 24 hours using a sand mill to provide a dispersion of triphenyl guanidine having a mean particle size of about 3 µm.

Then, 50 parts of the liquid of the capsules of the diazo compound thus obtained, 15 parts of the dispersion of the coupling component, and 15 parts of the dispersion of triphenyl guanidine were added to 20 parts of an aqueous solution of 5% zinc stearate to provide a coating liquid. Each of the coating liquids was coated on a smooth a wood free paper (50 $g/m^2$) at a dry coverage of 14 $g/m^2$ using coating rod and dried for 30 minutes at 45°C to provide Heat Sensitive Recording Materials (1) to (5). The kind and addition amount of the diazo compound used and the kind of the coupling component are shown in Table 1 below.

On the other hand, for the sake of comparison, Heat Sensitive Recording Materials (6) to (8) were prepared as comparison samples. That is, a dispersion of a diazo compound having a mean particle size of 3 µm was prepared by adding an appropriate amount of the diazo compound and 5.2 parts of polyvinyl alcohol to 93.8 parts of water and dispersing the diazo compound for about 24 hours using a sand mill. Then, 25 parts of the dispersion of the diazo compound thus prepared, 15 parts of the dispersion of a coupling component prepared in the same manner as above described, and 15 parts of the dispersion of triphenyl guanidine prepared in the same manner as above described were added to 20 parts of a solution of 5% zinc stearate to provide a coating liquid. Each of the coating liquids thus prepared was coated on a smooth wood free paper as above described to provide comparison Heat Sensitive Recording Materials (6) to (8).

Furthermore, for comparison, Heat Sensitive Recording Materials (9) to (11) were prepared as comparison samples by following the same procedure as described above for preparing Heat Sensitive Recording Materials (1) to (5) except that each diazo compound was microencapsulated by the method shown in Example 1 of Japanese Patent Publication (Unexamined) No. 192,944/'82.

The kinds and the amounts of the diazo compounds and the coupling components used in the above comparison examples are shown in Table 1 below.

Heat Sensitive Recording Materials (1) to (11) thus prepared were employed in heat recording using a recording machine, G II Mode (Panafax 7200) made by Matsushita Denso K.K. and then each sample was fixed by an overall light exposure to the sample using a copying machine, Ricopy High Start Type 4, made by Ricoh Company, Ltd. The blue density of the recorded images thus obtained was measured using a Macbeth reflection densitometer. The results obtained are shown in Table 1 below.

On the other hand, when heat recording was employed again in the fixed area of each sample, no image was recorded and hence it was confirmed that each sample was completely fixed.

Then, to determine the shelf life of each sample, the back ground density (fog) of each of Heat Sensitive Recording Materials (1) to (11) and the fog of each sample after storing each sample in the dark under the conditions of 50°C and 90% relative humidity for forced deterioration testing were measured to evaluate change of fog. The results obtained are also shown in Table 1 below.

## Table 1

| Sample No. | Diazo Compound |  | Coupling Component | Image Density | Test Results |  |
|---|---|---|---|---|---|---|
|  | Kind | Amount (parts) |  |  | Fog Before Deterioration | Fog After Deterioration |
| (1)* | (1) | 2.00 | (1) | 1.1 | 0.08 | 0.13 |
| (2)* | (2) | 1.56 | (1) | 1.0 | 0.09 | 0.13 |
| (3)* | (3) | 3.16 | (1) | 1.1 | 0.08 | 0.12 |
| (4)* | (1) | 2.00 | (2) | 1.1 | 0.07 | 0.11 |
| (5)* | (1) | 2.00 | (3) | 1.2 | 0.09 | 0.12 |
| (6)** | (1) | 2.00 | (1) | 1.1 | 0.08 | 0.88 |
| (7)** | (2) | 1.56 | (1) | 1.2 | 0.08 | 0.81 |
| (8)** | (1) | 2.00 | (2) | 1.2 | 0.09 | 0.82 |
| (9)** | (1) | 2.00 | (1) | 0.9 | 0.08 | 0.68 |
| (10)** | (2) | 1.56 | (1) | 0.9 | 0.08 | 0.65 |
| (11)** | (1) | 2.00 | (2) | 0.9 | 0.09 | 0.65 |

(*): Sample of the invention (**): Comparison sample

As is clear from the results shown in Table 1 above, it can be seen that the image density of the samples of this invention is high as that of the comparison samples in which the diazo compound was not encapsulated and is higher than that of the comparison samples in which the diazo compound encapsulated according to the method of Japanese Patent Publication (unexamined) No. 192,944/'82. Also, the increase of fog after the forced deterioration test is less in the samples of this invention, which shows the samples of this invention have a very excellent shelf life as compared with the comparison examples.

Examples (12) to (16) and Comparison Examples (17) to (19)

By following the same procedures described previously for Heat Sensitive Recording Materials (1) to (5), a capsule liquid of a coupling component was prepared by adding 5 parts of the coupling component in place of adding the diazo compound and also a dispersion of a diazo compound was prepared by adding an appropriate amount of a diazo compound in place of adding 20 parts of the coupling component.

Then, a coating liquid composed of 50 parts of the capsule liquid of the coupling component, 15 parts of the dispersion of the diazo compound, 15 parts of a dispersion of triphenyl guanidine prepared in the same manner as in the foregoing examples, and 20 parts of a 5% zinc stearate aqueous solution was coated as in Examples (1) to (5) to provide Heat Sensitive

Recording Materials (12) to (16) as samples of this invention. The kind and addition amount of the diazo compound and the kind of the coupling component used in each example are shown in Table 2 below.

On the other hand, for comparison, Heat Sensitive Recording Materials (17) to (19) were prepared as comparison samples by employing the capsule wall-forming method described in Example 1 of Japanese Patent Publication (Unexamined) No. 192,244/'82, i.e., a method using a polymer for forming capsule walls in place of forming the wall by the polymerization of reactants as in this invention. That is, in 50 parts of cyclohexane were dissolved 10 parts of a copolymer of vinyl acetate, butyl methacrylate, and styrene and then 5 parts of a coupling component, and a solution composed of 5.2 parts of polyvinyl alcohol and 8.4 parts of water was added to the solution. The mixture was stirred at high speed and at room temperature (about 20 to 30°C) to form an emulsified dispersion and then cyclohexane was distilled off from the dispersion at reduced pressure with stirring to provide a capsule liquid of the coupling component. Then, the capsule liquid was filtered, washed with water, and dried in vacuum to provide a capsule powder. A coating liquid was prepared by adding 5 parts of the capsule powder thus obtained in place 50 parts of the capsule liquid of the coupling component for the coating liquid used in the case of preparing Heat

Sensitive Recording Materials (12) to (16) and the coating liquid was coated as in the case of Examples (1) to (5). Thus, comparison Heat Sensitive Recording Materials (17) to (19) were prepared. The kind and amounts of the diazo compound and the kind of the coupling component used in the above comparison examples are shown in Table 2 below.

About the Heat Sensitive Recording Materials (12) to (19) thus prepared, the measurement of the recorded image density and the measurement of fog before the forced deterioration test and fog after the forced deterioration test were performed as in Examples (1) to (5) and Comparison Examples (6) to (11). The results thus obtained are shown in Table 2 below.

Also, when heat recording was applied again to the fixed area of each of Heat Sensitive Recording Materials (12) to (19), no image was recorded, which showed the samples were completely fixed.

Table 2

| | Diazo Compound | | | | Test Results | |
|---|---|---|---|---|---|---|
| Sample No. | Kind | Amount (parts) | Coupling Component | .Image Density | Fog Before Deterioration | Fog After Deterioration |
| (12)* | (1) | 10 | (1) | 1.2 | 0.08 | 0.13 |
| (13)* | (2) | 7.8 | (1) | 1.1 | 0.09 | 0.14 |
| (14)* | (3) | 15.8 | (1) | 1.2 | 0.08 | 0.13 |
| (15)* | (1) | 10 | (2) | 1.2 | 0.08 | 0.12 |
| (16)* | (1) | 10 | (3) | 1.2 | 0.09 | 0.13 |
| (17)** | (1) | 10 | (1) | 1.0 | 0.08 | 0.62 |
| (18)** | (2) | 7.8 | (1) | 1.0 | 0.08 | 0.67 |
| (19)** | (1) | 10 | (2) | 1.0 | 0.09 | 0.67 |

(*): Sample of the invention (**): Comparison example

As is clear from the results shown in Table 2 above, the samples of this invention wherein the coupling component was emulsified as the core material and then the capsule wall composed of a polymer was formed by polymerizing the reactants around the core material gave high image density as compared to the comparison samples wherein the microcapsules were prepared by dissolving a previously polymerized polymer and the increase of fog after the forced deterioration testing is less in the samples of this invention as compared to the comparison samples, which shows the excellent shelf life of the samples of this invention.

Example 20

By following the same procedure of preparing the capsule liquid in Examples (1) to (5) except that 5 parts of 2-phenyl-4-methylimidazole was added in place of the diazo compound used in these examples, a capsule liquid was prepared. Then, a coating liquid was prepared by adding 50 parts of the capsule liquid thus obtained, 15 parts of the dispersion of coupling component (1) prepared in the same manner as in Examples (1) to (5), and 15 parts of the dispersion of diazo compound (1) prepared in the same manner as in Examples (1) to (5) to 20 parts of a 5% zinc stearate aqueous solution. By coating the coating solution as in Examples (1) to (5), Heat Sensitive Recording Material (20) was prepared and tested as in the foregoing examples. The results obtained are shown in Table 3 below.

## Example 21

By following the method of preparing the capsule liquid as in Examples (1) to (5) except that 1 part of diazo compound (1) and 1 part of coupling component (2) were added in place of the diazo compound used in the foregoing examples, a capsule liquid was prepared. A coating liquid was prepared by adding 65 parts of the capsule liquid thus obtained and 20 parts of the dispersion of triphenyl guanidine prepared by the same manner as in Examples (1) to (5) to 15 parts of a 5% zinc stearate aqueous solution and coated as in the foregoing examples to provide Heat Sensitive Recording Material (21). The sample was also tested as in the foregoing examples. The results thus obtained are shown in Table 3 below.

Table 3

| Sample No. | Test Results<br>Image Density | Fog Before Deterioration | Fog After Deterioration |
|---|---|---|---|
| (20) | 1.1 | 0.09 | 0.13 |
| (21) | 1.2 | 0.09 | 0.13 |

As is clear from the results shown in Table 3 above, Heat Sensitive Recording Materials (20) and (21) of this invention each containing a part of the main components in the microcapsules show high image density and less increase of fog after the forced deterioration testing, which shows the excellent shelf life of the samples.

## Example 22

By following the same method of preparing the capsule liquid of the diazo compound as in Examples (1) to (5) except that 5 parts of the addition product of xylylene diisocyanate and trimethylol propane (3 : 1 by weight) and 5 parts of an addition product of tolylene diisocyanate and trimethylolpropane (3 : 1 by weight) were used in place of 10 parts of the addition product of xylylene diisocyanate and trimethylolpropane, a capsule liquid of diazo compound (1) as the core material was prepared. Then, a coating liquid was prepared by adding 50 parts of the capsule liquid thus prepared, 15 parts of the dispersion of coupling component (1) prepared in the same manner as in Examples (1) to (5), and 15 parts of the dispersion of triphenyl guanidine prepared in the foregoing examples to 20 parts of a 5% zinc stearate aqueous solution and coated as in the foregoing examples to provide Heat Sensitive Recording Material (22). When the sample was tested as in Examples (1) to (5), the image density was 1.3 and the fog before and after the forced deterioration testing was 0.08 and 0.13, respectively. That is, the sample showed a high image density and excellent shelf life.

## Example 23

The same method as used in preparing the capsule liquid in Examples 1 to 5 was followed except that a solution of 5.2

parts of polyvinyl alcohol and 2.5 parts of hexamethylenediamine dissolved in 58 parts of water was used in place of the aqueous polyvinyl alcohol solution for emulsifying the solution of the diazo compound. A coating liquid was prepared by adding 50 parts of the capsule liquid of diazo compound (1) thus prepared, 15 parts of the dispersion of coupling component (1), and 15 parts of the dispersion of triphenyl guanidine to 20 parts of a 5% zinc stearate aqueous solution and coated as in Examples 1 to 5 to provide Heat Sensitive Recording Material (22). When the sample was tested as in the foregoing examples, the image density was 1.1 and the fog before and after the forced deterioration testing was 0.08 and 0.13, respectively. Thus, the sample showed a high image density and excellent shelf life.

## Example 24

By following the same procedure as in Example 23 except that 0.2 part of terephthalic acid chloride was further added to the solution containing the diazo compound as the core material in the method of preparing the capsule liquid in Example 23, Heat Sensitive Recording Material (24) was prepared. The capsule wall in this case was composed of polyurea and polyamide. When the sample was tested as in Examples 1 to 5, the image density was 1.1 and the fog before and after the forced deterioration testing was 0.08 to 0.1, respectively, which showed the excellent shelf life of the sample.

What is claimed is:

1. A heat sensitive recording material comprising a support having thereon a recording layer containing (a) a diazo compound, (b) a coupling component and (c) a coloring activator, wherein at least one of said diazo compound, said coupling component and said coloring activator is present in microcapsules as the core material with the proviso that all three components (a) to (c) are not present in the same microcapsules, the wall of said microcapsules being formed around the material encapsulated by polymerization of a reactant or reactants after dispersing the core material therein.

2. The heat sensitive recording material as claimed in claim 1, wherein the wall of the microcapsules is composed of polyurethane, polyurea, polyamide or polyester.

3. The heat sensitive recording material as claimed in claim 1, wherein one of the three components (a) to (c) is present in microcapsules and the component present in the microcapsules is the diazo compound (a) and the wall of the microcapsules is composed of a polymer formed around the material encapsulated by polymerization of at least one polyhydric isocyanate as a first wall-forming material and at least one polyol as a second wall-forming material capable of forming a polymer by reaction with the polyhydric isocyanate.

4. The heat sensitive recording material as claimed in claim 1, wherein two of the three components (a) to (c) are present in microcapsules.

5. The heat sensitive recording material as claimed in claim 5, wherein said two components are present in the same microcapsules.

6. The heat sensitive recording material as claimed in claim 5, wherein said two components are present in different microcapsules.

7. The heat sensitive recording material as claimed in claim 1, wherein each of said three components (a) to (c) is present in different microcapsules.

8. The heat sensitive recording material as claimed in claim 1, wherein said three components (a) to (c) are present in microcapsules, two components being present in the same microcapsules and the other component being present in other microcapsules.

9. The heat sensitive recording material as claimed in claim 1, wherein the material encapsulated is present in microcapsules together with an organic solvent.

10. The heat sensitive recording material as claimed in claim 9, wherein said organic solvent is a water-insoluble high-boiling solvent having a boiling point higher than 180°C.

11. The heat sensitive recording material as claimed in claim 10, wherein said organic solvent is a phosphoric

acid ester, a phthalic acid ester, a carboxylic acid ester, a fatty acid amide, an alkylated biphenyl, an alkylated terphenyl, a chlorinated paraffin, or a diarylethane.

12. The heat sensitive recording material as claimed in claim 1, wherein the diazo compound is represented by the general formula

$$ArN_2^+X^-$$

wherein Ar represents a substituted aromatic moiety and $X^-$ represents an acid anion containing a perfluoroalkyl group or an acid anion containing a perfluoroalkenyl group.

13. The heat sensitive recording material as claimed in claim 3, wherein the polyol is selected from the polyols having the following groups (I),(II),(III) or (IV) between the two hydroxy groups in the molecular structure;

(I) aliphatic hydrocarbon group having 2 to 8 carbon atoms

(II) $-\overset{|}{\underset{|}{C}}-O-Ar'-O-\overset{|}{\underset{|}{C}}-$

(III) $-\overset{|}{\underset{|}{C}}-Ar'-\overset{|}{\underset{|}{C}}-$

(IV) $-O-Ar'-\overset{|}{\underset{|}{C}}-Ar'-O-$

wherein Ar' in groups (II),(III) and (IV) represents an unsubstituted or substituted aromatic moiety and the aliphatic hydrocarbon group of (I) has the moiety $-C_nH_{2n}-$ (wherein n is 2 to 8) as the fundamental skeleton and the hydrogen atom may be replaced by another element.