

1

3,592,677

PRESSURE SENSITIVE RECORDING MATERIALS
Masayoshi Tsuboi, Yoshiaki Suzuki, and Fumiko Kato,
Kanagawa, Japan, assignors to Fuji Photo Film Co.,
Ltd., Kanagawa, Japan

No Drawing. Filed Feb. 7, 1968, Ser. No. 703,522

Claims priority, application Japan, Feb. 7, 1967,

42/7,829; Féb. 13, 1967, 42/9,156, 42/9,157;

Feb. 17, 1967, 42/10,229

Int. Cl. B41m 5/22

U.S. Cl. 117—36.2

15 Claims 10

ABSTRACT OF THE DISCLOSURE

A pressure sensitive recording system comprising two supported layers, one of which layers contains an organo-vanadium compound and the other of which layers contains an aromatic hydroxy compound capable of a color-forming reaction with the organo-vanadium compound, at least one of said compounds being present in the form of a solution encapsulated in pressure-rupturable microcapsules. The organo-vanadium compounds employed comprise the reaction product of an inorganic vanadium compound with particular nitrogen-containing compounds characterized by the presence of a hydrocarbon group having 6 to 21 carbon atoms.

BACKGROUND OF THE INVENTION

The present invention relates to a pressure sensitive recording material and more particularly to a pressure sensitive recording material for forming records or images utilizing the color forming reaction of two color forming components, namely, an organo-vanadium compound and an aromatic hydroxyl compound.

Hitherto, pressure sensitive recording materials or papers utilizing the coloring reaction of a leuco dye or a lactone of a dye and a solid acid such as a clay or a metal oxide have been suggested, but these pressure sensitive recording papers have fatal defects in that the recorded image obtained is temporarily faded by the action of water, or is faded or discolored by the action of sunlight, ultraviolet light or fluorescent light. Moreover, if the recorded sheets are manipulated with fingers wetted by a weak-alkaline wetting agent, the recorded image will be faded permanently. Furthermore, if the recorded image is formed by a blue dye such as Crystal Violet or Methylene Blue the reproduction of the recorded image by a diazo copying method or a thermal copying method is difficult.

BRIEF DESCRIPTION OF THE INVENTION

Therefore, an object of this invention is to provide a pressure sensitive recording material capable of forming stable colored images.

Another object of this invention is to provide a pressure sensitive recording material capable of forming a colored image which can be reproduced clearly, even by a diazo copying method or a thermal copying method.

Still another object of this invention is to provide a pressure sensitive recording material capable of forming colored images without using the so-called clay papers.

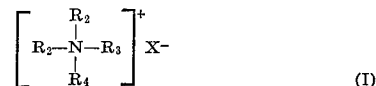
A further object of this invention is to provide a pressure sensitive recording paper having a layer of microcapsules containing an organo-vanadium compound dissolved in an oleophilic organic solvent having a boiling point higher than 100° C. at normal pressure.

Another object of this invention is to provide a pressure sensitive recording paper prepared by applying to a paper a coating composition comprising water as a solvent and oil-containing microcapsules containing an organo-vanadium compound.

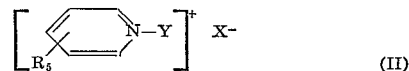
According to the present invention, there is provided a

2

pressure sensitive recording material comprising a sheet having a layer containing an organo-vanadium compound prepared by the reaction of a nitrogen compound represented by the following general Formulae I or II and a vanadium compound represented by general Formula III. Also, according to the present invention, the nitrogen compound and the organo-vanadium compound may be applied to one surface of a sheet or to separate surfaces of a sheet respectively:



wherein R₁ represents a mono-valent hydrocarbon group having 6–21 carbon atoms or a derivative thereof (having one or more side chains or one or more unsaturated bonds), R₂, R₃, and R₄, which may be the same or different, each represents a hydrogen atom, or a mono-valent hydrocarbon group (having one or more side chains or one or more unsaturated bonds), and X[–] represents an anion;



wherein R₅ represents an alkyl group having 1–3 carbon atoms, a methoxy group, an ethoxy group or a halogen atom and Y represents an alkyl group having 1–12 carbon atoms, a benzyl group, COOR₇, or —CH₂—NHCOR₇ (wherein R₇ represents an alkyl group having 1–6 carbon atoms); and



wherein M represents a mono-valent metal or ammonium, a and b each is an integer, and n is 0-18.

DETAILED DESCRIPTION OF THE INVENTION

The aforesaid organo-vanadium compound may be prepared by various methods.

In general, by mixing an aqueous solution of a compound shown by general Formula I or II with an aqueous solution of a compound shown by general Formula III at 0–50° C., preferably 0–35° C., and stirring the system for one hour at 10–30° C. or finishing the reaction by increasing the temperature of the system to 30–50° C., the organo-vanadium compound is obtained as a precipitate or a pasty product.

As the solvent for the reaction, there may be used, besides water, a water-alcohol mixed solvent, a water-ketone mixed solvent or a water-ester mixed solvent.

The concentration of each of the reactant solutions is preferably higher than about 1% by weight. If the concentrations of the solutions are lower, the reaction product becomes colloidal, which tends to reduce the yield of the product.

During the reaction, the pH of the system is maintained at 5.0–11.0, preferably 6.0–10.0. In particular, if the pH of the system is near 5.0, the reaction product tends to be yellow colored and if the pH is higher than 10.0, the yield of the product is frequently reduced. The optimum pH range is from about 6.5 to about 9.0.

The organo-vanadium compound prepared by the above-mentioned reaction is sufficiently washed with water to remove the unreacted materials and then dried. However, the product may be directly dissolved in an organic solvent after filtering. The drying procedure may be conducted by reduced pressure drying or by freeze drying. In some instances drying may be achieved by dissolving the product in an alcohol-water mixed solvent followed by spray drying. In the case of drying under a reduced pressure, the temperature and the time of drying are important factors for obtaining the organo-vanadium compound having a good quality. When the product is dried for longer

3

than 2 hours at a temperature higher than 70° C., the organo-vanadium compound tends to become a very viscous paste, which makes subsequent handling or treatment difficult. In a preferable drying procedure under a reduced pressure, the product is first dried under reduced pressure for about 1 hour at 65° C. ± 15° C. and thereafter dried for a long period of time at 45° C. ± 5° C.

As the solvent for the reaction water is preferred. However, there may also be employed a water immiscible organic solvent such as a mixed solvent of water and an alcohol, ketone, or ester. Further, the reactants may be reacted in a solvent system containing a considerable proportion of an organic solvent and then the reaction system poured into a large proportion of water, whereby uniform and fine organo-vanadium particles are obtained.

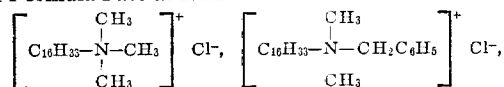
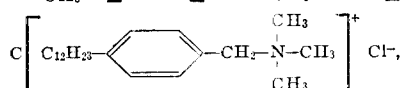
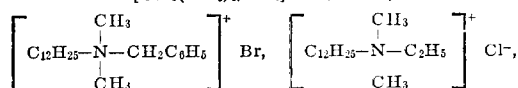
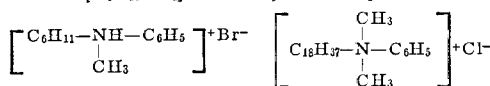
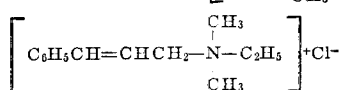
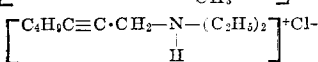
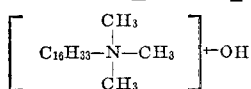
In the compound represented by general Formula I mentioned above, suitable examples of group R₁ are a straight chain or side chain alkyl group having 6-21 carbon atoms, a phenyl group, a cyclo-hexyl group, a benzyl group, a para-tolyl group, a para-methoxyphenyl group, para-methoxybenzyl group, a dodecylbenzyl group, a para-chloro-benzyl group, a phenethyl group, a para-methylphenethyl group, a 3-phenyl-propyl group, and a 4-phenylbutyl group.

Preferred as R₂, R₃, and R₄ are hydrogen, an alkyl group having 1-4 carbon atoms, a phenyl group, a benzyl group, a dodecylbenzyl group, and a 2-hydroxyethyl group.

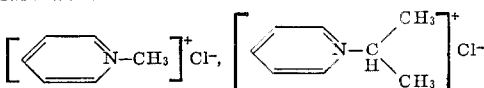
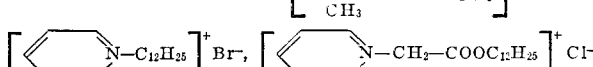
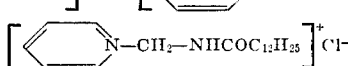
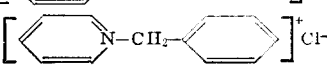
As X in the general formula, there may be mentioned a chlorine atom, a bromine atom, an iodine atom, a hydroxyl group, and an acetoxy group.

R₇ is an alkyl group having 1-6 carbon atoms as stated above.

Typical examples of the compound represented by general Formula I are as follows:

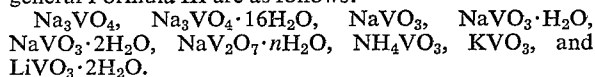


Typical examples of compounds represented by general Formula II are as follows:



4

Typical examples of the compounds represented by general Formula III are as follows:

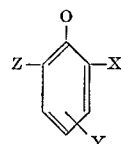


The vanadium in the compound shown in general Formula III is pentavalent; however, the compound may contain a small amount of vanadium having a lower valency.

In the case of preparing the organo-vanadium compound using as the compound represented by general Formula III, for example, an aqueous sodium orthovanadate solution for reaction with the compound of Formula I or II, the desired reaction product is scarcely obtained since the pH of the aqueous solution of the ortho-vanadate is higher than 11. Therefore, the reaction is conducted after adding an acid to the aqueous solution of sodium ortho-vanadate to adjust the pH to about 8-9, preferably about 8.5. The yield of the product is markedly increased. In this case, there are present in the aqueous solution of sodium ortho-vanadate adjusted to a pH of about 8.5, polyvanadate ions, such as, $[\text{V}_2\text{O}_7]^{4-}$, $[\text{V}_4\text{O}_{13}]^{9-}$, $[\text{V}_5\text{O}_{16}]^{3-}$ and the like. By reaction of these ions and the compound shown by general Formula I or II, the organo-vanadium compound is produced.

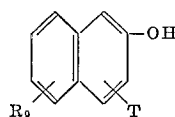
Furthermore, when two or more of the compounds represented by general Formula I or II are caused to react with two or more of the compounds represented by general Formula III, a mixture of organo-vanadium compounds is obtained.

As the aromatic hydroxy compound used in this invention for forming color images upon reaction with the aforesaid organo-vanadium compound, there may be employed the compounds shown by general Formulas IV or V, metha-di-gallic acid and tannic acid:



(IV)

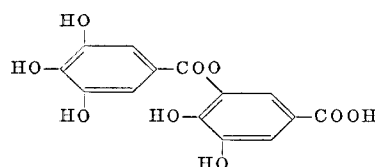
wherein X represents H, OH, COOM, M being an alkali metal, or COOR₈, R₈ being H, an alkali metal, ammonium, or a mono-valent hydrocarbon group having 1-12 carbon atoms; Y represents H, CHO, SO₃H, a halogen atom, a nitro group, or COOR₈, R₈ being the same as above; and Z represents H or OH;



(V)

wherein T represents H or OH or COOR₆, R₆ being the same as above, said group T being present at the 1- or 3-position of the compound, and R₉ represents H or SO₃H.

Metha-di-gallic acid has the following structure



Tannic acid is a glucose wherein the hydroxy group has been esterified with at least one member selected from the group consisting of gallic acid or di-gallic acid although the accurate structure of tannic acid has not yet been determined definitely.

As the aromatic hydroxy compounds shown by general Formula IV there may be mentioned o-dihydroxy aromatic compounds such as catechol, 3,4-di-hydroxybenzoic

acid, 3,4-dihydroxybenzoic acid ethyl ester, 2,3-dihydroxybenzoic acid, 3,4-dihydroxybenzaldehyde, 4,5-dichlorocatechol, p-tert-butylcatechol, 4-octylcatechol, and sodium catechol - 5 - sulfonate; and (b) polyhydroxy aromatic compounds such as pyrogallol, gallic acid, propyl gallate, dodecyl gallate, and pyrogallol-4-carboxylic acid.

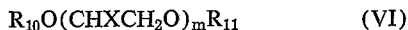
As the aromatic hydroxy compounds shown by general Formula V, there may be mentioned 1,2 - dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 1,2-dihydroxynaphthalene - 3,6 - disulfonic acid, the sodium salt of the disulfonic acid, 2-hydroxy - 3 - naphthoic acid, and 2-hydroxy-3-naphthoic acid ethyl ester.

When these aromatic hydroxy compounds are mixed with an organo-vanadium compound in, for example, ethanol, they are colored blue to black, however, some are colored violet, green-blue, or red-purple.

The aromatic hydroxy compounds may be used alone or as a mixture thereof.

The organo-vanadium compounds and the aromatic hydroxy compounds used in this invention are soluble in various organic solvents, such as, aromatic solvents, e.g., benzene, toluene, or chlorinated diphenyl; ester solvents, e.g., ethyl acetate, dibutyl phthalate, or tributyl phosphate; amide solvents, e.g., dimethylformamide, dimethylacetamide, dimethyldodecylamide, or hexamethylphosphoramide; polyol compounds or derivatives thereof, e.g., ethylene glycol, polyethylene glycol, glycerine, glycerine monoacetate, glycerine diacetate, or glycerine triacetate; alcohols, e.g., ethanol, phenylethanol, or hexadecyl alcohol; and ethers such as diethylene glycol dimethyl ether, or ethylene glycol monobenzyl ether.

It has further been found that the organo-vanadium and the aromatic hydroxyl compound of this invention have a very high solubility in benzyl ether or the amides shown above among the aforesaid solvents as well as the solvents represented by the following general Formula VI and VII:



wherein X represents H or OH; R_{10} represents H, an alkyl group having 1-6 carbon atoms (straight or branched), or an acetyl group, R_{11} represented a phenyl group, a halogen-introduced phenyl group, a benzyl group, an alkyl group (branched or straight) having 1-6 carbon atoms, or a hydrogen atom; m is 1-3; R_{12} represents H, a phenyl group, a hydrogen-introduced phenyl group, or CH_2OH ; R_{13} represents H, CH_3 , or CH_2OH ; R_{14} represents an alkyl group (branched or straight) having 1-16 carbon atoms or $C_6H_7CH(OH)CH(C_2H_5)$, said R_{14} is an alkyl group having more than 5 carbon atoms, however, when R_{12} and R_{13} are H.

Examples of the compound represented by general Formula VI are ethylene glycol, ethylene glycol monohexyl ether, ethylene glycol monophenyl ether, ethylene glycol monobenzyl ether, ethylene glycol dibutyl ether, diethylene glycol dibutyl ether, triethylene glycol dimethyl ether, ethylene glycol monohexyl ether acetate, and propylene glycol monophenyl ether. Examples of the compound represented by general Formula VII are amyl alcohol, secondary hexyl alcohol, n-decanol, tridecyl alcohol, benzyl alcohol, 1-phenylethyl alcohol, 2-phenylethyl alcohol, and glycerine, and a solvent which is weakly soluble in water, for example a glycol which is dissolved in 100 g. of water at 20° C. in an amount less than 6 g., such as, 2-ethyl-1,3-hexanediol.

The organo-vanadium compound can be dissolved easily in the solvent shown by general Formula VI or VII of this invention and, in particular, the organo-vanadium compound having a benzyl group can be dissolved in 100 g. of the oxygen-containing compound in an amount larger than 100 g.

Therefore, the pressure sensitive recording material of this invention may be prepared by dissolving one of the aforesaid organo-vanadium compound or the aromatic hydroxyl compound in the aforesaid solvent, making microcapsules of the solution, applying the microcapsules containing the solution to a support such as a paper using a proper binder while applying the other of the color-forming compounds to another support such as paper using a proper binder. Alternatively, the microcapsules of one of the color-forming compounds and the other of the color-forming compounds may be applied to the same surface of one support using a proper binder.

In the case of applying the color-forming components to one support, they may be applied thereto in a single layer or in two layers each of which contains each of the color-forming components. Moreover, if necessary, both the organo-vanadium compound and the aromatic hydroxy compound and the aromatic hydroxy compound must be in a state such that the one is not brought into contact with the other before recording. In order to form color images by the contact of the one with the other, it is necessary that they be brought into contact with each other in the presence of the aforesaid solvent, and hence at least one of the color-forming components must be in a state of solution thereof in the solvent contained in microcapsules.

The microcapsules containing the color-forming component may be prepared as follows:

In the case of using a hydrophobic solvent or a material which is dissolved in 100 g. of water at 20° C. in an amount less than 7 g. as the medium of this invention, the microcapsules may be prepared by a phase separation method from an aqueous solution (c.f., U.S. Pats. 2,800,457 and 2,800,458), a phase separation method from an organic solvent solution (c.f., U.S. Pat. 3,173,878), an interfacial polymerization method (c.f., British Pat. 989,264), a melting, dispersion, and cooling method (c.f., British Pat. 952,805), and a spray drying method (c.f., French Pats. 1,362,933 and 1,362,934). In the case of using a material which is solid at normal temperatures as the oxygen-containing compound, it is desirable to use an oxygen-containing compound having less carbon atoms as a subsidiary solvent or to use a hydrophobic solvent capable of dissolving oxygen-containing solvent such as tridecyl alcohol, tributyl phosphate or chlorinated diphenyl supplementally.

In general, a solvent which is weakly soluble in water and has a high boiling point is most preferable inasmuch as the pressure sensitive recording material prepared by using such a solvent has a good preservability. That is, the most preferable medium is a solvent weakly soluble in water, having a boiling point of higher than 180° C. at normal pressure and being a liquid at normal temperatures.

The oxygen-containing compounds may be used alone or as a mixture of two or more of them, and may be used together with each other subsidiary solvents miscible therewith. Also, microcapsules containing different kinds of oxygen-containing compounds as nuclei may be mixed.

Further, in the case of employing a water-soluble solvent as the medium, such as, glycerine or ethylene glycol, the microcapsulation may be conducted by an interfacial polymerization method in, for example, toluene or ligroin (c.f., British Pats. 950,443 and 1,046,409).

In the case of dissolving the organo-vanadium compound in the medium and forming therefrom oil-containing microcapsules, the weight ratio of the medium to the organo-vanadium compound is generally 100:1-80, preferably 100:8-65 or most preferably, 100:15-50. However, the weight ratio may be determined in any particular case by the solubility of the medium and the molecular weight of the organo-vanadium compound.

When a sheet having a layer of microcapsules containing the solution of the organo-vanadium compound in the aforesaid solvent or a layer of the organo-vanadium compound is superimposed over a sheet having a layer of the

aromatic hydroxy compound and the assembly is partially pressed by, e.g., hand writing or type writing, the layer of the pressed portions are immediately colored black, dark blue or blue-purple. The color image thus formed is very stable and has a quite high light fastness as well as a high resistance to air and water. Thus, the organo-vanadium compound of this invention is a very excellent color former for pressure sensitive recording materials.

Moreover, when a sheet having a layer of microcapsules containing a solution of the aromatic hydroxy compound in a known proper solvent is superimposed over a sheet having a layer of the organo-vanadium compound and the assembly is pressed partially by, e.g., hand writing or type writing, the locally pressed portions of the layer are colored black, dark blue or blue-purple. However, in this case, the color image thus formed may sometimes gradually become discolored brown.

The organo-vanadium compound of this invention may be applied to a so-called colorless carbon paper and reproduction recording system. The paper containing microcapsules may be prepared by well-known methods as, for example, that disclosed in, U.S. Pats. 2,548,366 and 2,712,507.

The organo-vanadium compound used in this invention, owing to its very excellent stability and solubility, may be stored in the open air and is stably used in the recording papers shown in U.S. Pats. 2,548,366 and 2,712,507.

Any binder may be used in this invention but it is profitable to use an aqueous solution of a hydrophilic binder such as gelatin, gum arabic or dextrine or an emulsified dispersion of a binder soluble in organic solvent, such as, a synthetic rubber latex or a polyvinyl acetate latex.

Furthermore, solutions of polyvinyl acetate, ethylcellulose, a polystyrene-butadiene copolymer, polyacrylic acid and the like may be used as the binder.

As the support sheet of the pressure sensitive recording material of this invention, there may be used papers, triacetylcellulose, polyethylene terephthalate, polycarbonate or polyvinyl chloride; however, paper is preferable.

Since the organo-vanadium compound used in this invention can be dissolved in a hydrophobic organic solvent, the organo-vanadium compound can be microcapsulated from an oil-in-water type dispersion system and hence a coating composition for the pressure sensitive recording material may be prepared using water as the solvent. Thus, in this case, the pressure sensitive recording material may be prepared easily without taking care to avoid the occurrence of explosion caused by employing a volatile organic solvent and generation of poisonous vapors of an organic solvent.

The present invention will now be explained in greater detail by the following examples.

Example 1

Into 350 ml. of distilled water was dissolved 2.5 g. of ammonium meta-vanadate while heating and the solution thus prepared was, after cooling sufficiently with ice-cooled water, placed in a separate flask equipped with a dropping funnel and a stirrer. When 6.4 g. of hexadecyltrimethyl ammonium chloride was dissolved in 50 g. of distilled water and, after cooling, added dropwise very gradually to the afore-prepared solution through the dropping funnel with stirring, a precipitate was formed immediately. After stirring the system for 15 minutes, the precipitate was recovered by filtration under suction, washed sufficiently with water and dried under reduced pressure to provide 6.0 g. of a light yellow solid having a melting point of 210–214° C., (decomp.) and colored brown.

Infrared absorption spectrum: 930 (cm.⁻¹) (strong absorption), 809 (strong "), 713 (weak "), and 636 (strong ").

A solution of 2.0 g. of the solid thus obtained in 4.0 g. of ethylene glycol monophenyl ether was mixed with 4.0 g. of dioctyl phthalate. 0.1 g. of Turkey red oil was dissolved

in a solution of 4 g. of gum arabic in 36 g. of distilled water and in the solution thus prepared was dispersed by emulsifying the above-prepared solution for 1–2 minutes by means of an ultrasonic emulsifier of 25 kc. so that the size of the oil drops in the dispersion became 1–5 microns. The dispersion was mixed with a solution of 4 g. of gelatin in 36 g. of distilled water and then 150 g. of warm water, and thereafter the pH of the system was reduced by adding thereto 4.2 ml. of 10% acetic acid, whereby microcapsules of 10–20 microns in diameter were formed around the oil drops in the system.

On the other hand a mixture of 2.0 g. of gallic acid dodecyl ester and 50 g. of ethanol was added with stirring in a mixture of 200 g. of water and 60 g. of a polystyrene-butadiene copolymer resin latex, and the resulting mixture was kneaded in a ball mill for 7 hours and then applied to a paper having a thickness of 50 g./sq. m. in a thickness of about 6 microns.

When the layer thus formed was brought into contact with the layer of microcapsules prepared above and the paper was pressed by means of a stylus or a ball pen, a dark-blue-black image was obtained.

The recorded image had very good water resistance and light fastness.

Example 2

The coating composition containing the microcapsules prepared in Example 1 was applied to a paper having a thickness of 50 g./sq. m. 60 g. of an emulsified dispersion (40% aqueous solution) of gallic acid and a polyvinyl chloride-polyvinyl acetate copolymer resin latex was mixed with 200 g. of water and the mixture was kneaded in a ball mill for 5 hours and applied to a paper having a thickness of 60 g./sq. m. in a thickness of 5 microns. When the both layers thus coated were brought into contact with each other and the papers were partially pressed by type writing, a black image having a good water resistance and light fastness was obtained.

Example 3

Into 200 ml. of distilled water was dissolved 12.6 g. of sodium meta-vanadate and the solution sufficiently cooled with ice water. On the other hand, 3.3 g. of 2-ethylhexylammonium chloride was dissolved into 100 ml. of distilled water in a separate flask equipped with a dropping funnel and a stirrer and the solution thus prepared was sufficiently cooled. When the aqueous sodium meta-vanadate solution prepared above was added very slowly to the solution in the flask with stirring through the dropping funnel, white turbidity was initially formed and a precipitate was formed gradually. After stirring the system for one hour, the precipitate was recovered by filtration under suction, washed with water and dried under reduced pressure at 50° C. to provide 6.7 g. of a light yellow solid having a melting point of 146° C. (decomp.). The infrared absorption spectrum: 2,900 (cm.⁻¹) (strong absorption); 1582 (middle absorption); 1450 (middle absorption); 900 (strong absorption); 828 (strong absorption); 770 (strong absorption); and 720 (middle absorption).

Into 10 g. of ethylene glycol monohexyl ether was dissolved 2 g. of the solid thus obtained and the solution thus prepared was dispersed by emulsifying in 30 g. of an aqueous 10% gum arabic solution by means of a high-power agitator.

When the emulsified dispersion was added to a solution of 3 g. of gelatin in 200 g. of distilled water and 3.8 g. of 10% acetic acid was added into the system with stirring at 50° C., a coacervation occurred between the two kinds of colloids and microcapsules having 5–15 microns in diameter were produced.

After gelling the microcapsules by cooling, they were mixed with 2 ml. of 10% chrouim alum and the system was stirred for 30 minutes. Then the pH of the system was increased to 5–6 by adding an aqueous 2% sodium bicarbonate solution and after 4 hours the pH thereof was

adjusted to 9.5 with the addition of an alkali. After allowing the system to stand for 3 days, the white coating composition was applied to a paper having a thickness of 40 g./sq. m.

The paper thus prepared was placed on a paper having a layer of ethyl protocatechuate such that the layers were brought into contact with each other and they were pressed partially to provide a dark blue image. The color of the image was not discolored when it was exposed to sunlight for 42 hours.

Example 4

Into 9 g. of benzyl alcohol was dissolved 3 g. of the organo-vanadium compound prepared in Example 3 under heating and after microcapsulating the solution, the microcapsules were applied to a paper. When the paper thus prepared was placed on a paper having a layer of protocatechuic acid and they were partially pressed by type writing, a dark-blue image was obtained.

Example 5

Into 35 g. of distilled water was dissolved 3.7 g. of ethylhexadecyldimethylammonium bromide under heating and after cooling by ice water, the solution was placed in a separate flask equipped with a dropping funnel and a stirrer. On the other hand, 1.9 g. of a mixture of sodium meta-vanadate and sodium ortho-vanadate was dissolved into 25 g. of distilled water while heating and after cooling sufficiently, the solution was added dropwise slowly to the solution of ethylhexadecyldimethylammonium bromide through the dropping funnel. After stirring for 10 minutes, the precipitate thus formed was recovered by filtration under suction, washed with water and dried under reduced pressure at 40° C. to provide 3 g. of white solid.

Into 8 g. of tridecyl alcohol was dissolved 2 g. of the solid. The solution thus obtained was mixed with 30 g. of an aqueous 15% gum arabic solution and the system was emulsified in a homogenizer emulsifier to form oil drops of 0.5-4 microns in diameter. When the dispersion was mixed with 30 g. of a 15% gelatin solution and 150 g. of warm water and the pH of the system was adjusted to about 4.6 by adding a 10% tartaric acid, microcapsules of 10-15 microns in diameter were formed around the oil drops. After cooling, the system containing the microcapsules was mixed with 1.5 g. of a 37% formalin solution and after one hour, the pH thereof was adjusted to 9.5 with an aqueous 10% sodium bicarbonate solution and the temperature of the system was gradually increased to 60° C. over one hour. Thereafter, the system was heated for one hour at 75° C. and applied to a paper in a thickness of about 7 microns.

On the other hand, 10 g. of tannic acid and 15 g. of gallic acid were mixed with 50 g. of a butadiene-methacrylate copolymer resin latex (solid content: about 47.5%), the mixture was kneaded for 30 minutes in a ball mill and applied to a paper in a thickness of about 5 microns.

When the both layers were brought into contact with each other and they were partially pressed by means of a ball pen, a black image was obtained. The image had a high water resistance and was not discolored when exposed to a xenone lamp of 1500 watts for 20 hours. Further, from the image diazo copies were obtained by a diazo copying method.

Example 6

Into 8 g. of 1-phenylethyl alcohol was dissolved 2.5 g. of the organo-vanadium compound prepared in Example 5 and after mixing with 7 g. of chlorinated diphenyl (B.P. about 325° C.), the resulting solution was encapsulated to form oil-containing microcapsules which was applied to a paper in a thickness of about 6 microns.

On the other hand, a mixture of 6 g. of gallic acid, 10 g. of zinc oxide, 10 g. of an aqueous emulsion (solid

47% by weight) of polyvinyl acetate and 20 g. of distilled water was kneaded for 4 hours in a ball mill. The pH of the liquid was 4.3. The liquid was applied to a paper in a thickness of about 5.5 microns.

The both layers were brought into contact and pressed partially by an electric type writer to provide a clear black image with a white background.

Example 7

To 100 g. of distilled water was added 100 g. of an aqueous solution of about 20% by weight hexadecyldimethylbenzylammonium chloride. Into 120 g. of distilled water was dissolved under heating 10 g. of sodium methavanadate and the solution was gradually added to the above-prepared solution with stirring to immediately form a precipitate. Then, after stirring the system for 30 minutes, the precipitate was recovered by filtration under suction, washed with water thoroughly, and dried under reduced pressure at 45° C. to provide 20.4 g. of a viscous mass.

Into 21 g. of ethylene glycol diethyl ether was dissolved 3.0 g. of the mass thus prepared and 10 g. of the oil was encapsulated as in Example 5 and applied to a paper in a thickness of about 7 microns.

On the other hand, 5 g. of clay and 10 g. of ethyl gallate were added to a mixture of 12 g. of an aqueous emulsion of polyvinyl acetate (solid 47% by weight) and 8 g. of distilled water and the solution was applied to a paper in a thickness of about 4.5 microns.

Both layers were brought into contact and a pattern was written on the papers by means of a press pen to provide a black copy of the pattern.

Example 8

Microcapsules containing a solution of 2 g. of the solid in Example 7 in 8 g. of proylene glycol monophenyl ether were applied to a paper in a thickness of about 5 microns. To the layer was applied a coating composition of a polyacrylate resin in a thickness of about one or two microns and to the layer was further applied a mixture of 4 g. of gallic acid, 2 g. of catechol, and 15 g. of an aqueous emulsion (solid content 40% by weight) of polyacrylate in a thickness of about 2 microns.

When the coated layer was pressed partially by a stylus, the pressed portions were colored in light black.

Example 9

In a separate flask equipped with a dropping funnel and an agitator, 30 g. of sodium meta-vanadate was completely dissolved in 450 ml. of distilled water under heating and the resulting solution was cooled sufficiently by ice water. To the system in the flask was added dropwise very slowly 180 g. of dimethylhexadecylbenzylammonium hydroxide (25% methanol solution) through the dropping funnel, whereby a white precipitate was formed. After stirring the system for one hour and increasing the temperature to 30° C., the precipitate was recovered by filtration under suction, washed with water thoroughly, and dried under reduced pressure at 40° C. to provide 59 g. of a white water-soluble viscous solid. The product was same as the solid prepared in Example 7.

When 2.0 g. of the solid thus obtained was dissolved in 6.0 g. of glycerine and the solution thus prepared was applied to a paper having a layer of pyrogallol, a dark blue image was obtained.

Example 10

In a separate flask equipped with a dropping funnel and a stirrer, 3 g. of ammonium meta-vanadate was dissolved in 400 ml. of distilled water under heating and then the resulting solution was cooled sufficiently by ice water. On the other hand, 10 g. of dimethylhexadecylbenzylammonium chloride was dissolved in 70 ml. of distilled water and the solution thus prepared was added dropwise very slowly to the aqueous ammonium meta-vanadate solution through the dropping funnel. After

11

stirring for about one hour, the temperature of the system was increased to 40° C. to complete the reaction and the precipitate thus formed was separated by filtration under suction, washed sufficiently with water and dried under reduced pressure at 45° C. to provide 10 g. of a yellowish white solid. The compound was coincident with the organo-vanadium compound prepared in Example 9 in infrared absorption spectrum.

The white solid was dissolved in a mixed solvent of 50% by weight of mono-acetin and 50% by weight of chlorinated diphenyl and when a paper coated with 3,4-dihydroxybenzaldehyde was touched with the resulting solution, the layer was colored black.

Example 11

In 62 ml. of distilled water 5 g. of a mixture of sodium ortho-vanadate and sodium meta-vanadate was dissolved by heating and after cooling sufficiently by ice water, the solution was placed in a separate flask equipped with a dropping funnel and a stirrer. A mixture of 18.4 g. of dimethylalkylbenzylammonium chloride (50% aqueous solution, alkyl groups; a mixture of the groups having 12-14 carbon atoms; Nissan Cation F2-50 trade name of Nippon Fats and Oils Co.) was added dropwise slowly into the above-prepared solution with stirring through the dropping funnel. After stirring for about 15 minutes the temperature of the system was increased to 35° C. and the precipitate thus formed was filtered, washed with water sufficiently and dried under reduced pressure to provide 12 g. of a white viscous mass. Into 8.0 g. of ethylene glycol monobenzyl ether was dissolved 20 g. of the mass obtained and when a paper coated with tannic acid was touched with the solution, the paper was colored black.

Example 12

Into 280 g. of distilled water was dissolved under heating 19.4 g. of sodium meta-vanadate and the solution was cooled sufficiently by ice water. On the other hand, 35.3 g. of dodecylbenzyltrimethylammonium chloride was dissolved in 200 ml. of distilled water at 50° C. and after cooling by ice water, the solution was placed in a separate flask equipped with a dropping funnel and a stirrer. When the afore-prepared was very slowly added dropwise to the flask through the dropping funnel, there was formed immediately a precipitate, which was aggregated into a large mass when stirred. After 15 minutes, the mass was separated by filtration, washed with water sufficiently, and dried under reduced pressure at 50° to provide 38.0 g. of a viscous solid.

Into 8.0 g. of benzyl ether was dissolved 2.0 g. of the solid thus obtained and the solution was encapsulated as in Example 1 and then applied to a paper. The paper was placed on a paper coated with 4-octyl catechol so that the coated layers were brought into contact with each other and they were pressed by typewriting, whereby a dark blue image was formed on a white background. The image had a good water resistance and light fastness and was not discolored when heated for 6 hours at 105° C.

Example 13

A solution consisting of 1.5 g. of gallic acid dodecyl ester, 0.1 g. of Turkey red oil and 10 g. of decyl alcohol was dispersed by emulsifying in a solution of 2.0 g. of gum arabic in 20 g. of distilled water for 4 minutes at 50° C. by means of a homogenizer. The diameter of the oil drops in the emulsion was 1-4 microns. The emulsion was mixed with a solution of 2.0 g. of gelatin in 10 g. of distilled water and to the resultant emulsion was added gradually 100 g. of warm water. When the pH of the system was reduced to less than 4.6 by adding 4 g. of 10% acetic acid, microcapsules having about 10-20 microns in diameter were formed around the oil drops. The microcapsules were gelled by cooling and mixed with 2

12

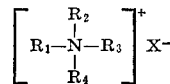
ml. of 10% chromium alum solution. After stirring for about 30 minutes, an aqueous 2% sodium carbonate solution was added to the system to adjust the pH thereof to 5-6, whereby the microcapsules were hardened. The coating composition containing the microcapsules was applied to a paper having a thickness of 50 g./sq. m. in a thickness of 5 microns. On the other hand, 4.0 g. of the reaction product of sodium metavanadate and dimethylhexadecylbenzylammonium chloride prepared in Example 1 was dissolved in 4.0 g. of ethanol and the solution was added dropwise to 30 g. of a polyacrylate resin emulsified dispersion (40% aqueous solution) with stirring vigorously to provide a white coating composition, which was applied to a paper in a thickness of 6 microns.

When the coated layers were brought into contact with each other and the sheets were partially pressed by a stylus, a clear dark blue image was obtained. The image had high water resistance and light fastness.

What is claimed is:

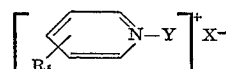
1. A pressure sensitive recording system comprising two supported layers, one layer containing an organo-vanadium compound and the other layer containing an aromatic hydroxy compound capable of reacting with the organo-vanadium compound to form a color when brought into contact with each other, at least one of said color-forming compounds being in a state of a solution in an organic solvent encapsulated by microcapsules rupturable by printing pressure, said organo-vanadium compound being one prepared by the reaction of a member selected from the group consisting of a nitrogen compound represented by general Formula I

Formula (I)



wherein R_1 represents a member selected from the group consisting of a hydrocarbon group having 6-21 carbon atoms and a derivative thereof, wherein said hydrocarbon group may have at least one side chain or at least one unsaturated bond; R_2 , R_3 , and R_4 , which may be the same or different, each represents a hydrogen atom and a mono-valent hydrocarbon group; and X^- represents an anion and a nitrogen-containing compound represented by general Formula II

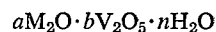
Formula (II)



wherein R_5 represents a member selected from the group consisting of a hydrogen atom, an alkyl group having 1-3 carbon atoms, a methoxy group, and an ethoxy group; Y represents a member selected from an alkyl group having 1-12 carbon atoms, a benzyl group, COOR_7 and



(wherein R_7 represents an alkyl group having 1-6 carbon atoms); and X^- represents an anion with an inorganic vanadium compound represented by general Formula III



wherein M represents a member selected from the group consisting of a mono-valent metal and ammonium; a and b each represents an integer; and n represents 0-18.

2. The pressure sensitive recording material as claimed in claim 1 wherein the layers are supported on paper.

3. The pressure sensitive recording material as claimed in claim 1 wherein said hydrocarbon group represented by R_1 is selected from an alkyl group having 6-21 carbon atoms, a phenyl group, a cyclohexyl group, a benzyl group, a p-tolyl group, a p-methoxyphenyl group, a p-methoxybenzyl group, a dodecylbenzyl group, a p-chlorobenzyl group, a phenethyl group, a p-methylphenethyl group, a 3-phenylpropyl group, and a 4-phenylbutyl group.

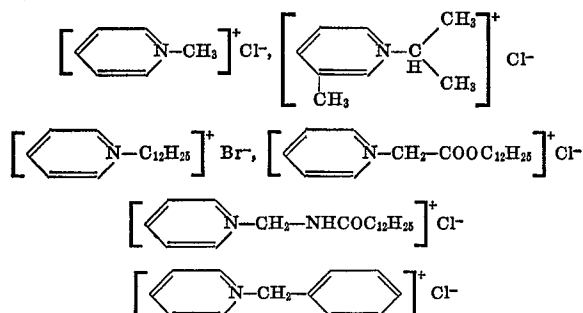
4. The pressure sensitive recording material as claimed in claim 1 wherein said mono-valent hydrocarbon group

13

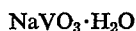
represented by each of R_2 , R_3 and R_4 is selected from an alkyl group having 1-4 carbon atoms, a phenyl group, a benzyl group, a dodecylbenzyl group, and a 2-hydroxyethyl group.

5. The pressure sensitive recording material as claimed in claim 1 wherein the group forming said anion is selected from a chlorine atom, a bromine atom, an iodine atom, hydroxyl group, and an acetoxy group.

6. The pressure sensitive recording material as claimed in claim 1 wherein said nitrogen compound represented by general Formula II is selected from



7. The pressure sensitive recording material as claimed in claim 1 wherein said inorganic vanadium compound is selected from Na_3VO_4 , $\text{Na}_3\text{VO}_4 \cdot 16\text{H}_2\text{O}$, NaVO_3 ,



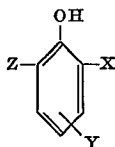
$\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$, $\text{NaV}_2\text{O}_7 \cdot n\text{H}_2\text{O}$, NH_4VO_3 , KVO_3 , and $\text{LiVO}_3 \cdot 2\text{H}_2\text{O}$.

8. The pressure sensitive recording material as claimed in claim 1 wherein said organo-vanadium compound is prepared by reacting the nitrogen compound and the inorganic vanadium compound is an aqueous phase.

9. The pressure sensitive recording material as claimed in claim 8 wherein the pH of the aqueous reaction system is adjusted to about 8-9.

10. The pressure sensitive recording material as claimed in claim 1 wherein said aromatic hydroxy compound is selected from m-di-gallic acid and tannic acid.

11. The pressure sensitive recording material as claimed in claim 1 wherein said aromatic hydroxy compound is represented by general Formula IV

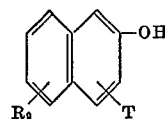


wherein X represents a member selected from the group consisting of a hydrogen atom, a hydroxyl group, COOM (where M is an alkali metal), and COOR_8 (where R_8 is a member selected from the group consisting of a hydrogen atom, an alkali metal, ammonium, and a mono-valent hydrocarbon group having 1-12 carbon atoms, Y represents a member selected from the group consisting of a hydrogen atom, CHO , SO_3H , a halogen atom, a nitro group, and COOR_8 (where R_8 is same as above); and Z

14

represents a member selected from the group consisting of a hydrogen atom and hydroxyl group.

12. The pressure sensitive recording material as claimed in claim 1 wherein said aromatic hydroxy compound is represented by general Formula V



wherein T represents a member selected from the group consisting of a hydrogen atom, a hydroxyl group, and COOR_6 (R_6 is same as defined above), said two groups each being present at the 1- or 3-position of the compound, and R_9 represents a member selected from the group consisting of a hydrogen atom and SO_3H .

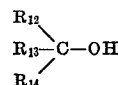
13. The pressure sensitive recording material as claimed in claim 1 wherein said organic solvent is selected from aromatic solvents, ester solvents, amide solvents, polyol solvents and ether solvents.

14. The pressure sensitive recording material as claimed in claim 1 wherein said organic solvent is represented by general Formula VI



wherein X represents a member selected from a hydrogen atom and a hydroxyl group; R_{10} represents a member selected from the group consisting of a hydrogen atom, an alkyl group having 1-6 carbon atoms and an acetyl group; R_{11} represents a member selected from the group consisting of a phenyl group, a halogen-introduced phenyl group, a benzyl group, an alkyl group having 1-6 carbon atoms, and a hydrogen atom; and m is 1-3.

15. The pressure sensitive recording material as claimed in claim 1 wherein said organic solvent is represented by



wherein R_{12} represents a member selected from the group consisting of a hydrogen atom, a phenyl group, a hydrogen-introduced phenyl group, and CH_2OH ; R_{13} represents a member selected from the group consisting of a hydrogen atom, a methyl group, and CH_2OH ; and R_{14} represents an alkyl group having 1-16 carbon atoms and $\text{C}_3\text{H}_7\text{CH}(\text{CH})\text{CH}(\text{C}_2\text{H}_5)$, said R_{14} being an alkyl group when R_{12} and R_{13} each represents a hydrogen atom.

References Cited

UNITED STATES PATENTS

2,712,507	7/1955	Green.
2,864,720	12/1958	Maguire et al.
3,432,327	3/1969	Kan et al.
3,435,759	4/1969	Lueck et al.
3,467,658	9/1969	Lipka.

MURRAY KATZ, Primary Examiner

U.S. Cl. X.R.

117-36.8, 36.9, 155; 252-316