Oct. 20, 1970 AKIO WATANABE ET AL 3,535,139
PRESSURE-SENSITIVE COPYING PAPERS
Filed Nov. 14, 1967

FIG. 1

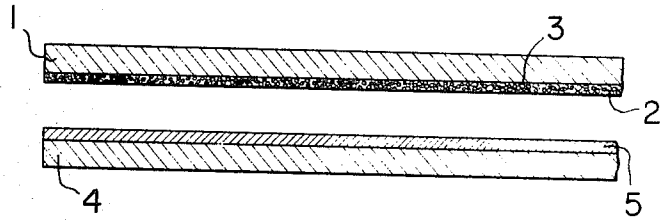
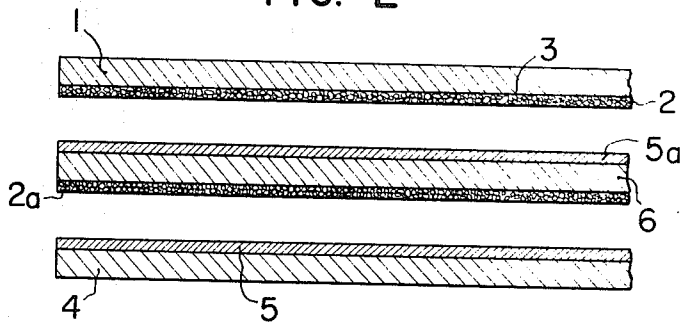


FIG. 2



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PRESSURE-SENSITIVE COPYING PAPERS

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ABSTRACT OF THE DISCLOSURE

Two types of colour formers are used which react with each other to form a durable black coloured chelated compound, one of said colour formers being a derivative of a polyhydric phenol insoluble or scarcely soluble in water and the other consisting of an iron compound or a vanadium compound or mixture thereof. Either one of the colour formers is dissolved in a non-volatile liquid and contained in numerous capsules rupturable under pressure. Base papers coated with respective colour formers are superposed one upon the other with their coated surfaces contacting each other. Pressure due to writing causes capsules in localized areas to rupture, thus providing clear durable copy of black colour.

This invention relates to a pressure-sensitive copying paper capable of forming one or more copies by means of a writing instrument or a typewriter, and more particularly to a pressure-sensitive copying paper wherein two types of colour formers are used which react with each other to form black colour and either one of the colour formers is in the form of a solution and contained in minute capsules which are ruptured when subjected to pressure, whereby the copying paper is not coloured at all in the absence of pressure, but the capsules are ruptured when subjected to pressure to form pure black colour at portions subjected to pressure.

A known pressure sensitive copying of the type referred to above is a colourless capsule type copying paper comprising a first base paper having on one side thereof a transfer coating including numerous minute capsules which are ruptured when subjected to pressure, each capsule containing a colourless solution of a first colour former consisting of a leuco compound such as crystal violet lactone, benzoyl leuco methylene blue and the like; and a second base paper having on one side thereof a receptive coating including a second colour former consisting of an inorganic clay such as activated clay, bentonite, attupulgite and the like, said first and second base papers being superposed one upon the other with the transfer and receptive coatings facing each other, whereby upon application of local pressure and rupture of capsules in localized areas, said two types of colour formers contact each other to produce coloured marks, thus producing a copy. It is also known to use various leuco compounds which form colour upon contact with clay for these copying papers. Various methods of manufacturing minute capsules which are ruptured under pressure are also known in the art.

However, all of these known copying papers can form copies of only blue or red colour, and copying papers that can produce copies of durable real or jet black coloured copies are not yet known.

It is therefore an object of this invention to provide a novel white pressure-sensitive copying paper which can form copies of durable real black colour which does not fade or change colour.

Further, as prior copying papers of this type generally utilize colour formers consisting of derivatives of basic dyes of the leuco type, copied marks are disadvantageous in that their durability is low, the resistance to light is poor, they have a large tendency to fade, their colour tone varies with time, and their concentration, contrast and clearness are low.

Further, these prior copying papers are disadvantageous in that copies produced therefrom cannot be used as originals to produce clear duplicates with diazo type photosensitive copying machines and temperature-sensitive copying machines.

A still further object of this invention is to provide a new and improved capsule type copying paper which can obviate various disadvantages of prior copying papers and can provide black coloured clear copies which can be used as the originals in photosensitive or temperature-sensitive copying machines.

To provide capsule type copying papers capable of producing perfect black coloured copies, it is clear that it is essential to use colour formers which can form especially durable black colour. Presently known basic dye derivatives of leuco type which form blue, red or yellow upon contact with clays such as activated clay, attupulgite, and the like include crystal violet lactone, rhodamine lactone, auramine lactone, etc., and it has been proposed to obtain copying papers which form black colour by combining blue, red and yellow. However, these colour formers generally exhibit different colouring speeds when reacting upon clay, and in addition they have a tendency to fade with time, the speed of fading being different for different colour formers. Consequently, copies obtained immediately after application of pressure do not include marks of uniformly coloured black colour. In addition their colours fade with time and in the extreme cases change to yellow in less than a few days. Further, as three colours are combined, it is very difficult to balance these three colours, with the result that not only is the colour tone of the copies produced poor, but also its concentration is low. Thus, the colour tone of these copies in bluish or grayish so that they cannot be used as originals for use in a photosensitive or temperature-sensitive copying machine.

In addition, since these colour formers are derivatives of basic dyes of the leuco type, the colour tone of the copies varies with time to depart from perfect black. Moreover, as the durability of such copies is low, there is the possibility of copied marks disappearing upon exposure to daylight.

A more specific object of this invention is to provide a novel capsule type copying paper which can provide one or more copies having marks of real black colour which do not fade with time, have a high concentration, and are durable with respect to daylight and chemicals, so that copies produced therefrom can be used as originals in photosensitive or temperature-sensitive copying machines to form clear duplicates. Although prior copying papers utilizing combinations of previously known colour formers could not provide copies of holographs of black colour, we have found that a greatly improved copying paper can be obtained by utilizing a combination of novel colour formers.

More particularly the novel copying paper according to the invention is characterized in that it utilizes a combination of colour formers radically different from the known combinations of colour formers consisting of colourless derivatives of basic dyes of the leuco type and clay utilized in conventional copying papers.

A pressure sensitive copying paper embodying this invention comprises a first base paper having on one side thereof a transfer coating including numerous microscopic pressure-rupturable capsules, each containing a

non-volatile liquid solution of a first colour forming substance, and a second base paper having on one side thereof a receptive coating including a second colour former, characterized in that one of said first and second colour formers is a polyhydric phenol derivative which is a polyhydric phenol having the atomic group

$$-COOC_nH_{2n+1} \ (n=2\text{–}18)$$

and/or a polyhydric phenol having the atomic group $-SO_3C_nH_{2n+1}$ (n=2–18), and the other of said colour formers is an iron compound and/or a vanadium compound which reacts with said polyhydric phenol derivative to produce a dark black mark of a chelated compound. By sandwiching between said first and second base papers at least one third base paper having a receptive coating on one side thereof and a transfer coating on the other side, two or more copies can be made at a time.

While the specification concludes with claims particularly pointing out and distinctly claiming the subject matter which is regarded as the invention, it is believed that the invention will be better understood from the following description taken in connection with the accompanying drawing in which:

FIG. 1 shows a section of a portion of a copying paper embodying this invention; and

FIG. 2 shows a section of a modified embodiment of this invention.

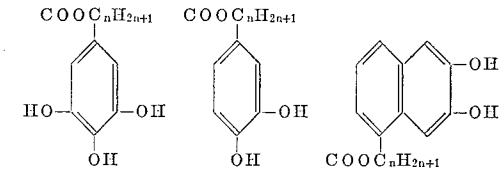
The pressure-sensitive copying paper of this invention illustrated in FIG. 1 consists of two sheets of base papers. One of them is a first base paper **1** having on one side thereof a transfer coating **2** including numerous minute pressure-rupturable capsules **3** each containing a solution of a first colour former which is colourless or only slightly coloured and which reacts with a second colour former to form dark black colour. The other base paper is a second base paper **4** having on one side thereof a receptive coating **5** containing a second colour former which is colourless or only slightly coloured. When using the novel copying paper illustrated in FIG. 1, the first base paper **1** is superposed upon the second base paper **4** with transfer and receptive coatings **2** and **5** contacting each other. When localized pressures by handwriting or typewriting are applied on the superposed base papers, capsules **3** subjected to said localized pressures are ruptured to release the first colour former solution contained therein. The released first colour former reacts with the second colour former contained in the receptive coating **5** to produce dark colour marks which are durable, do not fade, and undergo no colour change.

For the purpose of explanation, the novel copying paper is illustrated as comprising only two base papers to form one copy, and the modification shown in FIG. 2 comprises three base papers for forming two copies at a time. Thus, in this modification, between base papers **1** and **4** identical to those shown in FIG. 1, is interposed a third base paper **6** having a receptive coating 5_a on the upper side and a transfer coating 2_a containing numerous capsules on the lower side. Where more than two sheets of said third base paper **6** are sandwiched between base papers **1** and **4**, more than three copies can be formed simultaneously.

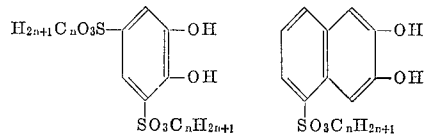
As stated hereinbefore, the novel capsule type copying paper utilizes a new combination of two types of colour formers which have never been known in the art. One of the colour formers is a substance selected from the group consisting of polyhydric phenols having the atom group $-COOC_nH_{2n+1}$ (where n=2–18) and polyhydric phenols having the atom group $-SO_3C_nH_{2n+1}$ (where n=2–18), said substance being insoluble or scarcely soluble in water. The other of the colour formers is a substance selected from the group consisting of iron compounds and vanadium compounds, said substance effecting colour forming reaction when contacted with the first mentioned colour former consisting of a polyhydric

phenol derivative. Thus, when capsules in localized areas are ruptured by the localized pressure applied by handwriting or typewriter said two types of colour formers react with each other to produce dark black marks of a chelated compound having the above described desirable properties.

Examples of the polyhydric phenol having the atomic group $-COOC_nH_{2n+1}$ (n=2–18) employed as one of the colour formers in this invention are as follows:



Examples of the polyhydric phenol having the atomic group $-SO_3C_nH_{2n+1}$ (n=2–18) similarly employed as one of the colour formers are as follows:



Examples of iron compounds employed as the other colour former include iron oleate, iron stearate, iron caprylate, iron naphthenate, ferric chloride, and ferrous sulfate.

Examples of vanadium compounds similarly employed as the other colour former include vanadium naphthenate, vanadium caprylate, vanadium oleate, vanadium stearate, sodium metavanadate, and vanadyl sulfate.

The two types of colour formers react with each other to produce dark black marks of a chelated compound having the above described desirable properties.

Another feature of the pair of colour formers employed in this invention is that one of the colour formers is substantially insoluble in water but soluble in oil or is dispersible in oil. Heretofore, it has been known that a combination of ammonium metavanadate and gallic acid or of ferric sulfate and tannic acid and other combinations form black colour in aqueous solution. However, when these colour formers are used in copying papers, as both of them are soluble in water, the resistances to water and chemicals of the copying papers are low. In addition, copies obtained therefrom are not durable.

According to this invention, however, instead of using water soluble colour formers such as gallic acid, tannic acid and the like, a colour former which is insoluble or scarcely soluble in water but soluble or dispersible in a hydrophobic liquid, and which is selected from the group consisting of polyhydric phenols having the atomic group $-COOC_nH_{2n+1}$ (n=2–18) and polyhydric phenols having the atomic group $-SO_3C_nH_{2n+1}$ (n=2–18) is used in combination with a colour former selected from the group consisting of iron compounds and vanadium compounds, the two colour formers reacting when placed in contact with each other to form black colour. Therefore with the novel copying paper it is possible to provide copies of durable black colour which have excellent resistance to water and chemicals.

Prior combinations of colour formers consisting of gallic acid and ammonium metavanadate or of tannic acid and ferric sulfate cannot be used as the combination of colour formers for capsule type copying papers. This is because either of these colour formers is water soluble and they can form colours only in the presence of water so that when used in capsule type copying papers, they become incapable of forming colours upon evaporation or freezing of water. Morover, when the copying paper is immersed in water, these colour formers flow out of the paper into the water and thus become incapable of forming colour. According to this invention water soluble gallic acid,

tannic acid or the like is not utilized. We have found that when a polyhydric phenol having the atomic group $-COOC_nH_{2n+1}$ or $-SO_3C_nH_{2n+1}$ (n=2–18) which is insoluble or scarcely soluble in water and has been prepared by esterifying a polyhydric phenol having the atomic group —COOH or $-SO_3H$ with an aliphatic monovalent alcohol containing from 2 to 18 carbon atoms is utilized in combination with an iron compound on a vanadium compound, they can successfully form black colour which has higher concentration and is more durable than the combination of gallic acid and metal which form colour in the presence of water. Thus, said esterified colour former is especially suitable for use in the capsule type copying paper. More particularly, the polyhydric phenol having the atomic group

$$-COOC_nH_{2n+1}$$

or $-SO_3C_nH_{2n+1}$ is essentially insoluble or scarcely soluble in water, and is soluble or dispersible in non-volatile hydrophobic liquids, so that it can react with an iron compound or a vanadium compound in the absence of water to form black colour of sufficiently high concentration. We have found that the polyhydric phenol derivatives can be used as the colour formers in the capsule type copying papers mainly due to their hydrophobic property.

In prior capsule type copying papers, a solution of a colourless colour former prepared by dissolving it in a non-volatile oily liquid is contained in capsules. When ruptured by the pressure applied by a writing instrument, the solution contained in the capsules contacts the other colour former, thus effecting reaction to form a copy. The colour former employed in this invention can be encapsulated by any one of many known methods of encapsulating non-volatile oily liquids. Thus, a non-volatile oily liquid to be encapsulated is emulsified in an aqueous solution of gelatin, and then the gelatin solution is diluted or its pH is adjusted to cause it to coacervate, thus forming walls of capsules. Alternatively, the colour former employed in this invention may be encapsulated by forming walls of capsules either by the polymerization of a monomer in the presence of a catalyst or by an inter-surface reaction. The method of encapsulation should be selected in accordance with the conditions required for a particular copying paper. Both two colour formers employed in this invention may be encapsulated.

Thus, the novel copying papers are classified in the following types dependent upon which one of the colour formers is encapsulated. In one type a non-volatile hydrophobic liquid solution of the colour former selected from the group consisting of polyhydric phenols having the atomic group $-COOC_nH_{2n+1}$ (n=2–18) and polyhydric phenols having the atomic group $-SO_3C_nH_{2n+1}$ (n=2–18) is encapsulated, whereas in the second type a non-volatile liquid solution of the colour former selected from the group consisting of iron compounds and vanadium compounds is encapsulated.

This invention is characterized in that either one or both of two colour formers are insoluble or scarcely soluble in water. Consequently, in addition to an iron compound or vanadium compound insoluble to water, an iron compound or vanadium compound soluble in water may be used in combination with a polyhydric phenol having the atomic group $-COOC_nH_{2n+1}$ or

$$-SO_3C_nH_{2n+1}$$

which is insoluble or scarcely soluble in water to provide durable black coloured copies of holographs with the same desirable properties.

Thus, for example, water insoluble iron compounds or vanadium compounds of naphthenic acid, caprylic acid, stearic acid, oleic acid as well as water soluble ferric chloride, ferrous sulfate, sodium metavanadate, vanadyl sulfate or like metal compound may be used in combination with the polyhydric phenol having the atomic group $-COOC_nH_{2n+1}$ or $-SO_3C_nH_{2n+1}$ (n=2–18).

In this case the novel copying paper comprises a first base paper having on one side thereof a transfer coating including numerous minute pressure rupturable capsules, each containing an aqueous solution of a first colour former consisting of an iron compound or a vanadium compound together with a substance which prevents water from evaporating, and which is selected from the group consisting of calcium chloride, sodium bromide, potassium bromide, magnesium chloride, aluminum chloride, lithium nitrate, potassium carbonate, sodium hydroxide, glycerine, ethylene glycol, polyethylene glycol, sorbitol and the like, and a second base paper having on one side a receptive coating including a second colour former consisting of a polyhydric phenol having the atomic group $-COOC_nH_{2n+1}$ (n=2–18) or

$$-SO_3C_nH_{2n+1}$$

(n=2–18).

Like a copying paper utilizing a colour former consisting of a water insoluble iron compound or vanadium compound, the above described copying paper provides a copy which instantaneously forms pure black colour which is durable and does not fade or change colour with time, and which can be used as an original to produce excellent replicas of holographs by means of a heat-sensitive or photosensitive copying machine. The colour former consisting of a water soluble iron compound or vanadium compound is perfectly protected by capsule walls, and the other polyhydric phenol having the atomic group $-COOC_nH_{2n+1}$ or $-SO_3C_nH_{2n+1}$ (n=2–18) is insoluble in water or scarcely soluble in water, so that the novel copying papers have high resistance to evaporation and water. Further, as the copy of the holograph produced from this copying paper is comprised by a compound produced by the reaction between the water insoluble polyhydric phenol having the atomic group

$$-COOC_nH_{2n+1}$$

or $-SO_3C_nH_{2n+1}$ (n=2–18) and a metal compound, it is extremely durable.

The invention can be modified in various ways. For example, a substance or substances may be added to one or both of the colour formers in order to add various characteristics to the novel copying paper. It is intended that all such modifications are included in the scope of this invention.

Thus, for example to supplement or increase the colour tone of the copy produced, another combination of colour formers consisting of a known colour former of a colourless derivative of a basic dye of the leuco type such as crystal violet lactone, benzoyl leuco methylene blue or the like and the other colour former consisting of clay that forms a colour when placed in contact with said colour former may be used together with a pair of colour formers according to this invention.

Thus, this invention includes the following two types as its variations.

In one type the pressure sensitive copying paper comprises a first base paper having on one side a transfer coating including numerous minute pressure-rupturable capsules each containing a nonvolatile hydrophobic liquid solution of a mixture of first and second colour formers, said first colour former being selected from the group consisting of polyhydric phenols having the atom group $-COOC_nH_{2n+1}$ (n=2–18) and polyhydric phenols having the atomic group—$SO_3C_nH_{2n+1}$ (n=2–18) and said second colour former consisting of a colourless leuco compound which causes a colour change when placed in contact with an inorganic substance selected from the group consisting of attapulgite, zeolite, halloysite, bentonite, kaolinite, activated clay, colloidal silica, and aluminosilicate; and a second base paper having on one side thereof a receptive coating including a mixture of third and fourth colour formers, said third colour former being selected from the group consisting of iron compounds and vanadium compounds which are insoluble in hydro-

philic liquid, and which cause colour forming reaction upon contact with said first colour former, and said fourth colour former being an inorganic substance selected from the group mentioned above, said first and second base papers being superposed one upon the other with said transfer and receptive coatings contacting each other, whereby upon application of localized pressure and rupture of said capsules in localized areas, the two types of colour undergo reactions, namely the colour forming reaction between said first and third colour formers and that between said second and fourth colour formers, which occur simultaneously to produce dark coloured marks.

The other type of the pressure sensitive copying paper comprises a first base paper having on one side thereof a transfer coating including numerous minute pressure-rupturable capsules, each containing a non-volatile hydrophobic liquid solution of a mixture of first and second colour formers, said first colour former being selected from the group consisting of iron compounds and vanadium compounds which are soluble in hydrophobic liquid, and which cause colour forming reaction when placed in contact with a polyhydric phenol derivative selected from the group consisting of polyhydric phenols having the atomic group $-COOC_nH_{2n+1}$ (n=2–18) and polyhydric phenols having the atomic group

$$-SO_3C_nH_{2n+1}$$

(n=2–18), and said second colour former consisting of a colourless leuco compound which causes a colour change when placed in contact with an inorganic substance selected from the group consisting of attapulgite, zeolite, halloysite, bentonite, kaolinite, activated clay, colloidal silica, and aluminosilicate; and a second base paper having on one side thereof a receptive coating including a mixture of third and fourth colour formers, said third colour former consisting of the same polyhydric phenol derivative as that mentioned above, and said fourth colour forming substance consisting of the same inorganic substance as that mentioned above; said first and second base papers being superposed with the transfer and receptive coatings contacting each other, whereby upon application of localized pressure and rupture of capsules in localized areas, two types of colour forming reactions, namely the colour forming reaction between said first and third colour formers and that between said second and fourth colour formers occur simultaneously to produce dark coloured marks.

Since some of the polyhydric phenols having the atomic group $-COOC_nH_{2n+1}$ or $-SO_3C_nH_{2n+1}$

(n=2–18)

are oxidized to decompose by the oxygen in air when they come into direct contact with air, there is the problem of degrading when they are stored over a long period of time. We have found that it is possible to provide copying papers which are stable over a long period without any degrading by incorporating a sulfur compound such as thiourea, 2-mercaptoimidazoline, mercaptobenzimidazole, mercaptobenzothiazole, and the like into the polyhydric phenol derivative.

These sulfur compounds act to prevent a portion of the polyhydric phenol derivative from being gradually oxidized by the oxygen in air, thus colouring the surface of the copying paper to a pale yellowish brown without decreasing the copying ability of the copying paper. Gradual oxidation of the polyhydric phenol derivative results in a decrease in the concentration of the copied holograph, but a suitable quality of said sulfur compound prevents such phenomenon, thus assuring the production of copying papers which do not degrade. In this case a mixture of the polyhydric phenol derivative and sulfur compound may be used for the novel copying paper, directly or after encapsulation. Alternatively, capsules containing the polyhydric phenol derivative may be mixed with a sulfur compound.

The speed of colour forming of receptive surface which forms black colour upon contact with the liquid contained in capsules is very slow, and, in addition, the concentration is low where the colour former is merely applied thereto. Accordingly in order to improve the colour forming speed and concentration of copying papers required to have higher copying capability, it is advantageous to incorporate a white inorganic powder which will absorb the liquid contained in the capsules, such as a powder of silicon oxide, calcium carbonate, titanium oxide, zinc oxide, barium sulfate, magnesium carbonate, and the like into the receptive coating together with the colour former. While these white powders do not directly participate in the colour forming reaction they absorb the liquid contained in the capsules to accelerate the colour forming reaction on the surface of the powder thus providing a clear copy having high concentration. In addition, where the colour former employed in this invention is slightly coloured, the white powder improves the whiteness of the surface of copying paper.

Where the above described colour former, sulfur compound, and white powder are applied to the transfer coating or receptive coating, directly or after encapsulation, it is necessary, of course, to use a suitable bonding agent. For the bonding agent, any one of many well known bonding agents may be used including water soluble binder such as gelatin, dextrin, etc., emulsions of a synthetic resin such as polyvinyl acetate, acrylic resin, etc., a volatile organic solvent solution of polyvinyl acetate, vinyl chloride-vinyl acetate copolymer, and the like.

The following examples are illustrative only and should not be construed as limiting the invention which is properly set forth in the appended claims.

EXAMPLE 1

12 g. of vanadium naphthenate was dissolved in 150 g. of dibutyl phthalate, and 20 g. of the initial polymerization product of epoxy resin was added to the solution to obtain a homogeneous solution. This solution was homogeneously emulsified in 600 g. of a 10% aqueous solution of gelatin containing 8 g. of diethylene triamine and the resulted emulsion was heated to a temperature of 60° C. for 8 hours under agitation to form capsules containing a solution of vanadium naphthenate and dibutyl phthalate.

500 g. of a 20% aqueous solution of dextrin was added to the capsules thus formed, and the mixture was uniformly applied to one side of a base paper by means of a suitable coating machine so that a dry or solid content of 5 g./m.^{2} could be obtained after drying. The resulting paper was designated as paper A. Further, 200 g. of dodecyl-3,4,5-trihydroxy benzoate, 60 g. of polyvinyl acetate emulsion, and 800 g. of water were mixed. The mixture was uniformly dissolved and dispersed and then applied to another base paper by a suitable coating machine so that a dry content of 6 g./m.^{2} could be obtained. The paper thus prepared was designated as paper B.

The paper A was superposed upon paper B with their coated surfaces contacting each other. When handwriting was made on the top of paper A, a durably black colour copy of the holograph was obtained.

EXAMPLE 2

8 g. of iron stearate, 1 g. of crystal violet lactone, 1 g. of benzoyl leuco methylene blue, and 1 g. of Apo rhodamine were dissolved and dispersed in 80 g. of diphenyl chloride, and then the solution was emulsified in an aqueous solution consisting of 320 g. of water, 20 g. of gum arabic, and 20 g. of gelatin. 500 g. of water was added to the emulsion thus obtained, and the pH thereof was adjusted to 4.5 by using a 10% acetic acid aqueous solution, thus causing coacervation to precipitate thin walls of gelatin-gum arabic around miniature drops of diphenyl chloride containing said colour former dissolved therein.

The above process steps were all carried out at a tem-

perature of 50° C. for the purpose of preventing gelation. The temperature was rapidly decreased to 10° C., and after the pH was adjusted to a value of from 7 to 9, 4 g. of a 37% aqueous solution of formaldehyde was added to form thin walls, thereby producing capsules containing a diphenyl chloride solution containing four types of colour formers, i.e., iron stearate, crystal violet lactone, benzoyl leuco methylene blue, and Apo rhodamine. 300 g. of an 8% aqueous solution of polyvinyl alcohol was added to separated capsules and the mixture was applied to one side of a base paper by means of a suitable coating machine so that a dry content of 5 g./m.^{2} could be obtained. The coated paper was designated as paper A.

On one hand, 150 g. of activated clay, 50 g. of 2,3-dihydroxy naphthalene-6-sulfonic acid ethyl ester, 5 g. of 2-mercaptoimidazoline and 1 kg. of a 5% aqueous solution of polyvinyl alcohol were uniformly dissolved and dispersed. The mixture was uniformly applied on one side of another base paper by a suitable coating machine to obtain a dry content of 6 g./m.^{2}. The treated paper was designated as paper B.

Paper A was superposed upon paper B with the thinly coated surfaces in contact with each other. Upon writing on the top of paper A, a durable black coloured copy of the holograph was obtained.

The 2-mercaptoimidazoline utilized in this example may be omitted where the completed copying paper is not required to be stored over a long period.

EXAMPLE 3

8 g. of 1,2-dihydroxy benzene-3,5-disulfonic acid-dipropyl ester, 1 g. of mercapto benzothiazole, 1 g. of crystal violet lactone, 1 g. of benzoyl leuco methylene blue, and 1 g. of Apo rhodamine were dissolved and dispersed in 80 g. of diphenyl chloride, and the mixture was emulsified in an aqueous solution in 320 g. of water of 20 g. of gum arabic and 20 g. of gelatin dissolved therein. 50 g. of water was added to the emulsion, and the pH thereof was adjusted to 4.5 by using an aqueous solution of 10% acetic acid to effect coacervation, thus precipitating thin walls of gelatin-gum arabic around minute particles of diphenyl chloride containing said colour formers dissolved therein.

The above operations were all performed at a temperature of 50° C. for the purpose of preventing gelation. The temperature was rapidly decreased to 10° C., and after the pH was adjusted to a value of from 7 to 9, 4 g. of a 37% aqueous solution of formaldehyde was added to to form thin wall capsules containing four types of colour formers, viz. 1,2-dihydroxy benzene-3,5-disulfonic acid dipropyl ester, crystal violet lactone, benzoyl leuco methylene blue, and Apo rhodamine. 300 g. of an 8% aqueous solution of polyvinyl alcohol was added to separated capsules, and the mixture was uniformly applied to one side of a base paper by means of a suitable coating machine to obtain a dry content of 5 g./m.^{2}. The resulting paper was designated as paper A. Further, 150 g. of bentonite, 50 g. of iron stearate and 1 kg. of a 5% aqueous solution of polyvinyl alcohol were uniformly dissolved and dispersed, and the mixture was uniformly applied onto one side of another base paper by means a suitable coating machine to obtain a dry content of 6 g./m.^{2}. The resulting paper was designated as paper B.

Then paper A was superposed upon paper B with their coated surfaces in contact with each other. Upon writing on the top of paper A, a durable black coloured copy of the holograph was obtained.

Where the copying paper of this example is not required to be stored over a long period, the mercaptobenzothiazole may be omitted.

EXAMPLE 4

8 g. of 2,3-dihydroxy naphthalene-5-carboxylic acid dodecyl ester and 1 g. of mercaptobenzothiazole were dissolved and dispersed in 80 g. of diphenyl chloride. The mixture was then emulsified in an aqueous solution in 320 g. of water of 20 g. of gum arabic and 20 g. of gelatin dissolved therein. 500 g. of water was added to the emulsion, and the pH thereof was adjusted to 4.5 by using a 10% aqueous solution of acetic acid to cause coacervation, thus forming thin walls around small particles of diphenyl chloride containing said colour formers dissolved therein.

The above operations were all effected at a temperature of 50° C. for the purpose of preventing gelatin. When the temperature was rapidly decreased to 10° C., and after the pH was adjusted to a value of from 7 to 9, 4 g. of 37% aqueous solution of formaldehyde was added, capsules were formed containing diphenyl chloride including 2,3-dihydroxy naphthalene-5-carboxylic acid dodecyl ester. 300 g. of a 20% aqueous solution of dextrine was added to separated capsules, and the mixture was uniformly applied to one side of another base paper by means of suitable coating machine to obtain a dry content of 5 g./m.^{2}. The treated paper was designated as paper A. On one hand, 150 g. of vanadium naphthenate, 50 g. of iron oleate, 70 g. of ethyl methacrylate-styrene copolymer, and 1 kg. of toluene were uniformly dissolved and dispersed. Then the mixture was uniformly applied onto one side of another base paper by means of a suitable coating machine to obtain a dry content of 6 g./m.^{2}. The resulting paper was designated as paper B.

Paper A was superposed upon paper B with their coated surfaces in contact with each other. Upon writing on the top of paper A, a durable black coloured copy of the holograph was obtained.

EXAMPLE 5

10 g. of vanadium caprylate, 8 g. of styrene monomer, 2 g. of divinyl benzene monomer, and 0.003 g. of benzoylperoxide were dissolved and dispersed in 140 g. of diphenyl chloride, and the mixture was maintained at a temperature of 85° C. for 8 minutes to initiate polymerization. Then the mixture was emulsified in 182 g. of 11% aqueous solution of gelatin. The emulsion was incorporated into a solution in 1,220 g. of water of 0.12 g. of potassium persulfate and 20 g. of gum arabic. After the pH was adjusted to 6.5 at a temperature of 55° C., the pH was gradually decreased to 4.6, thus causing coacervation. Finally the mixture was cooled to 15° C. to form double walled capsules each consisting of an inner wall of styrene-divinyl benzene copolymer and an outer wall of gelatin-gum arabic and containing diphenyl chloride containing vanadium caprylate. 500 g. of a 20% aqueous solution of dextrin was added to separated capsules, and then the mixture was uniformly applied onto one side of another base paper by means of a suitable coating machine to obtain a dry content of 5 g./m.^{2}. The treated paper was designated as paper A. On one hand, 150 g. of calcium carbonate, 50 g. of stearyl-3,4-dihydroxy-benzoate, 100 g. of dextrin, and 1 kg. of water were uniformly dissolved and dispersed, and then the mixture was applied onto one side of another base paper by means of an appropriate coating machine to obtain a dry content of 6 g./m.^{2}. The coated paper was designated as paper B.

Paper A was superposed upon paper B with their coated surfaces in contact with each other. Upon writing on the top of paper A, a durable black coloured copy of the holograph was obtained.

EXAMPLE 6

4 g. of ammonium metavanadate was dissolved in 150 g. of a 67% aqueous solution of glycerine. Further, 15 g. of bisphenol A and 30 g. of sodium hydroxide were incorporated into the solution to obtain a homogenous solution. The solution was then emulsified in 250 g. of toluene, and 200 g. of a toluene solution containing 14 g. of terephthaloyl chloride was added dropwisely to the emulsion while it was stirred. After stirring of about 5

hours, capsules were formed containing an aqueous solution of glycerine containing ammonium metavanadate. After the capsules were separated, 300 g. of a 5% toluene solution containing polyvinyl acetate dissolved therein was added to the capsules, and the mixture was uniformly applied onto one side of another base paper by means of a suitable coating machine to obtain a dry content of 5 g./m.^{2}. The treated paper was designated as paper A.

Further, 150 g. of a fine powder of silica, 30 g. of cetyl-3,4-dihydroxy-benzoate, 20 g. of 2,3-dihydroxy naphthalene-5 sulfonic acid propyl ester, 5 g. of mercapto-benzimidazole, 100 g. of vinyl chloroide-vinyl acetate copolymer, and 1 kg. of ethyl acetate were uniformly dissolved and dispersed, and the mixture thus obtained was uniformly applied to one side of another base paper to obtain a dry content of 6 g./m.^{2}. The treated paper was designated as paper B.

Paper A was superposed on paper B with their coated surfaces in contact with each other. Upon writing on the top of paper A, a durable black coloured copy of the holograph was obtained.

While in the foregoing examples, an iron compound, a vanadium compound, or a mixture thereof is used as one of the colour formers, a vanadium compound may be substituted for a portion or the whole of the iron compound in Examples 2 and 3 wherein only an iron compound is used. Similarly, a portion or the whole of the vanadium compound utilized in Examples 1, 5, and 6 may be substituted by an iron compound. Further in Example 4, where both iron compound and vanadium compound are used they can be substituted by either an iron compound or a vanadium compound.

Copied holographs obtained by using copying papers prepared according to various embodiments of the invention manifest a clear durable dark black colour which does not fade, change colour, and is resistant to water and chemicals. Accordingly, these copies can be used as originals to obtain clear replicas in a diazo photosensitive copying machine, a temperature-sensitive copying machine, or the like.

These unique characteristics could never be realized by conventional copying papers utilizing colour formers consisting of derivatives of basic dyes. More particularly, with conventional methods utilizing derivatives of basic dyes, copied holographs of only blue, red or gray could be obtained, but utilization of colour formers according to this invention results in pure black coloured copied holographs. Upon exposure to daylight, the former copied holographs greatly fade in less than one week, whereas the latter obtained from the novel copying papers exhibit no fading whatsoever and retain their clear black colour over an extended period.

It should be understood that the method of encapsulation, combination of colour formers utilized, and ratio of components according to the invention may be varied dependent upon the application of the copying paper and for the purpose of providing desirable characteristics.

It should be understood, of course, that the foregoing disclosure relates principally to only preferred embodiments of the invention and that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purposes of the disclosure, which do not constitute departures from the spirit and scope of the invention as set forth in the appended claims.

What is claimed is:

1. Pressure-sensitive copying paper comprising a first base paper having on one side thereof a transfer coating including numerous minute pressure-rupturable capsules each containing a non-volatile liquid solution of a first colour former and a second base paper having on one side thereof a receptive coating including a second colour former said first and second colour formers being insoluble or scarcely soluble in water, one of said first and second colour formers being a polyhydric phenol derivative selected from the group consisting of polyhydric phenols having the atomic group $-COOC_nH_{2n+1}$ where n=2–18, and polyhydric phenols having the atomic group $-SO_3C_nH_{2n+1}$ where n=2–18, the other of said colour formers being selected from the group consisting of iron compounds and vanadium compounds which react with said polyhydric phenol derivative to produce a dark black coloured mark of a chelated compound, and said first and second base papers being superposed one upon the other with said transfer coating and said receptive coating in contact with each other.

2. Pressure-sensitive copying paper comprising a first base paper having on one side thereof a transfer coating including numerous microscopic pressure-rupturable capsules, each capsule containing a non-volatile hydrophobic liquid solution of a first colour former which is selected from the group consisting of polyhydric phenols having the atomic group $-COOC_nH_{2n+1}$, n=2–18, and polyhydric phenols having the atomic group $-SO_3C_nH_{2n+1}$, n=2–18, and a second base paper having on one side thereof a receptive coating including a second colour former selected from the group consisting of iron compounds and vanadium compounds which are insoluble in hydrophilic liquids, and which cause colour-forming reaction when placed in contact with said first colour former said first and second colour formers being insoluble or scarcely soluble in water, said first and second base papers being superposed one upon the other with said transfer and receptive coatings in contact with each other, whereby, upon application of local pressure and rupture of said capsules in localized areas, said first and second colour formers react with each other to produce a dark black coloured mark of a chelated compound.

3. The pressure-sensitive copying paper according to claim 2 in which, in addition to said numerous capsules containing a solution of the first colour former substance, the transfer coating includes a sulphur compound selected from the group consisting of thiourea, 2-mercapto-imidazoline, mercapto-benzimidazole, and mercaptobenzothiazole.

4. The pressure-sensitive copying paper according to claim 2 in which, addition to the first colour former substance, the solution in the capsules contains a sulphur compound selected from the group consisting of thiourea, 2-mercapto-imidazoline, mercapto - benzimidazole, and mercapto-benzothiazole.

5. The pressure-sensitive copying paper according to claim 2 in which, in addition to the second colour former, the receptive coating includes a white fine powder of a compound selected from the group consisting of silicon oxide, calcium carbonate, titanium oxide, zinc oxide, barium sulfate, and magnesium carbonate.

6. The pressure-sensitive copying paper according to claim 2 in which the transfer coating includes a sulphur compound selected from the group consisting of thiourea, 2-mercapto-imidazoline, mercapto - benzimidazole and mercapto-benzothiazole in addition to said numerous capsules containing a solution of the first colour former, and the receptive coating includes a white fine powder of a compound selected from the group consisting of silicon oxide, calcium carbonate, titanium oxide, zinc oxide, barium sulfate, and magnesium carbonate in addition to the second colour former.

7. The pressure-sensitive copying paper according to claim 2 in which the solution in the capsules contains a sulphur compound selected from the group consisting of thiourea, 2-mercapto - imidazoline, mercapto-benzimidazole, and mercapto-benzothiazole in addition to the first colour former, and the receptive coating includes a white fine powder of a compound selected from the group consisting of silicon oxide, calcium carbonate titanium oxide, zinc oxide, barium sulfate, and magnesium carbonate in addition to the second colour former.

8. Pressure-sensitive copying paper, comprising a first base paper having on one side thereof a transfer coating including numerous microscopic pressure-rupturable capsules, each capsule containing a non-volatile liquid solution of a first colour former selected from the group con-

sisting of iron compounds and vanadium compounds which cause colour-forming reaction when placed in contact with a polyhydric phenol derivative selected from the group consisting of polyhydric phenols having the atomic group $—COOC_nH_{2n+1}$, n=2–18, and polyhydric phenols having the atomic group $—SO_3C_nH_{2n+1}$, n=2–18, and a second base paper having on one side thereof a receptive coating including a second colour former which consists of said polyhydric phenol derivative said first and second colour formers being insoluble or scarcely soluble in water, said first and second base papers being superposed one upon the other with said transfer and receptive coatings in contact with each other, whereby upon application of local pressure and rupture of said capsules in localized areas, said first and second colour formers react with each other to produce a dark black coloured mark of a chelated compound.

9. The pressure-sensitive copying paper according to claim **8** in which, in addition to the second colour former, the receptive coating includes a sulphur compound selected from the group consisting of thiourea, 2-mercapto-imidazoline, mercapto-benzimidazole, and mercapto-benzothiazole.

10. The pressure-sensitive copying paper according to claim **8** in which, in addition to the second colour former, the receptive coating includes a white fine powder of a compound selected from the group consisting of silicon oxide, calcium carbonate, titanium oxide, zinc oxide, barium sulfate, and magnesium carbonate.

11. The pressure-sensitive copying paper according to claim **8** in which, in addition to the second colour former, the receptive coating includes a sulphur compound selected from the group consisting of thiourea, 2-mercapto-imidazoline, mercapto-benzimidazole and mercapto-benzothiazole and a white fine powder of a compound selected from the group consisting of silicon oxide, calcium carbonate, titanium oxide, zinc oxide, barium sulfate, and magnesium carbonate.

12. Pressure-sensitive copying paper comprising a first base paper having on one side thereof a transfer coating including numerous microscopic pressure-rupturable capsules, each capsule containing a non-volatile hydrophobic liquid solution of a mixture of a first and a second colour former said first and second colour formers being insoluble or scarcely soluble in water, said first colour former being selected from the group consisting of polyhydric phenols having the atomic group $—COOC_nH_{2n+1}$, n=2–18, and polyhydric phenols having the atomic group $—SO_3C_nH_{2n+1}$, n=2–18, said second colour former consisting of a colourless leuco compound which causes a colour change when placed in contact with an inorganic substance selected from the group consisting of attapulgite, zeolite, halloysite, bentonite, kaolinite, activated clay, colloidal silica, and almino-silicate, and a second base paper having on one side thereof a receptive coating including a mixture of third and fourth colour formers, said third colour former being selected from the group consisting of iron compounds and vanadium cmpounds which are insoluble in hydrophilic liquids, and which cause colour-forming reaction when placed in contact with said first colour former, said fourth colour former consisting of said inorganic substance, said first and second base papers being superposed one upon the other with said transfer and receptive coatings in contact with each other whereby upon application of local pressure and rupture of said capsules in localized areas, two types of colour-forming reactions, namely, a colour-forming reaction between said first and third colour formers and that between said second and fourth colour formers, occur simultaneously to produce a dark coloured mark.

13. Pressure-sensitive copying paper according to claim **12** in which besides the mixture of the first and second colour formers, the solution in the capsule contains a sulphur compound selected from the group consisting of thiourea, 2-mercapto-imidazoline, mercapto - benzimidazole, and mercapto-benzothiazole.

14. Pressure-sensitive copying paper comprising a first base paper having on one side thereof a transfer coating including numerous microscopic pressure-rupturable capsules, each capsule containing a non-volatile hydrophobic liquid solution of a mixture of first and second colour formers said first and second colour formers being insoluble or scarcely soluble in water, said first colour former being selected from the group consisting of iron compounds and vanadium compounds which are soluble in hydrophobic liquids, and which cause colour-forming reaction when placed in contact with a polyhydric phenol derivative selected from the group consisting of polyhydric phenols having the atomic group $—COOC_nH_{2n+1}$, n=2–18 and polyhydric phenols having the atomic group $—SO_3C_nH_{2n+1}$, n=2–18, and said second colour former consisting of a colourless leuco compound which causes a colour change when placed in contact with an inorganic substance selected from the group consisting of attapulgite, zeolite, halloysite, bentonite, kaolinite, activated clay, colloidal silica, and alumino-silicate and a second base paper having on one side thereof a receptive coating including a mixture of third and fourth colour formers, said third colour former consisting of said polyhydric phenol derivative, said fourth colour former consisting of said inorganic substance, said first and second base papers being superposed one upon the other with said transfer and receptive coatings in contact with each other, whereby upon application of local pressure and rupture of said capsules in localized areas, two types of colour-forming reactions, namely a colour-forming reaction between said first and third colour formers and that between said second and fourth colour formers, occur simultaneously to produce a dark coloured mark.

15. The pressure-sensitive copying paper according to claim **14** in which, in addition to the mixture of the third and fourth colour formers, the receptive coating includes a sulphur compound selected from the group consisting of thiourea, 2-mercapto - imidazoline, mercapto-benzimidazole, and mercapto-benzothiazole.

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