

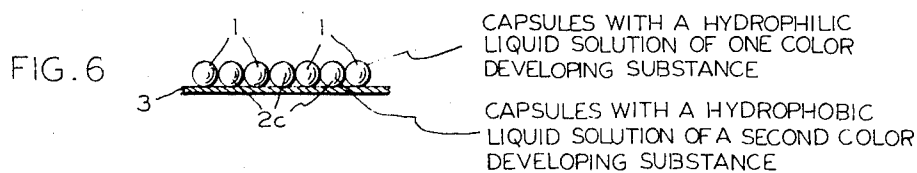
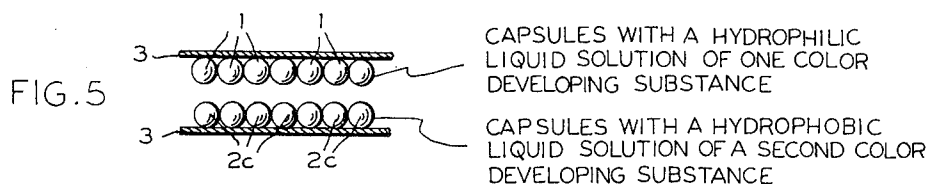
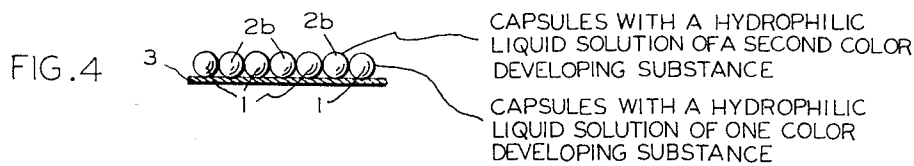
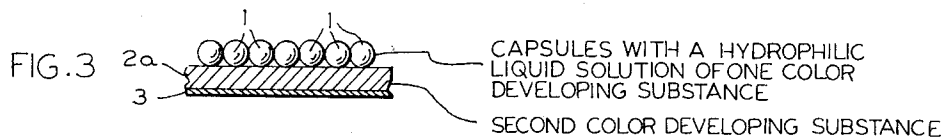
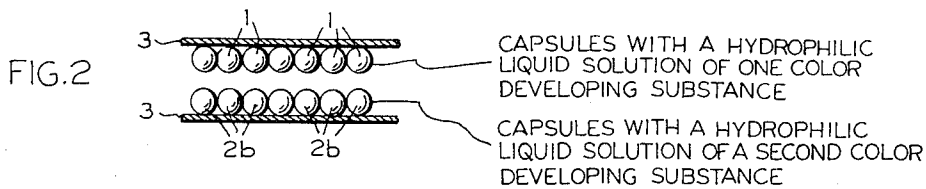
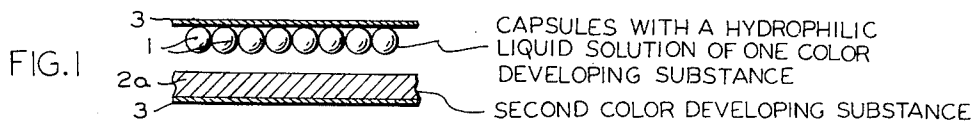
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PRESSURE SENSITIVE COPYING SHEET AND THE PRODUCTION THEREOF

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3,432,327

PRESSURE SENSITIVE COPYING SHEET AND THE PRODUCTION THEREOF

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U.S. Cl. 117—36.2
Int. Cl. B41c

28 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to a pressure sensitive copying sheet wherein a hydrophilic liquid solution of one of two kinds of color-developing substances which react with each other to develop color in the presence of a hydrophilic liquid, is contained in fine capsules, said capsules containing said solution being formed by a novel encapsulation method using the interfacial reaction at the interface of hydrophobic and hydrophilic liquids, and being coated on at least one substratum in combination with the other color-developing substance; and to the production thereof.

This invention relates to a pressure sensitive copying sheet wherein fine capsules containing hydrophilic liquid therein are used and to the production thereof. More particularly, this invention relates to a pressure sensitive copying sheet wherein each fine capsule contains a hydrophilic liquid solution of one color-developing substance of two color-developing substances, which are reacted with each other in the presence of hydrophilic liquid to develop color, said capsule containing said solution being formed by a novel encapsulation method which we have developed, using the interfacial reaction at the interface of hydrophobic and hydrophilic liquids, and being coated at least on a substratum in combination with the other color-developing substance.

While so-called carbon paper has been hitherto used as pressure sensitive copying sheet, it has many disadvantages so that non-carbon papers have been developed recently in place of said carbon paper. For these noncarbon papers, a nonvolatile oil having dissolved therein an electron donative color-developing agent is suspended in water by using a protective colloid such as gum arabic, gelatin and the like to form oil drops, fine capsules are formed by a complex coacervation method in which the oil having dissolved therein the electron donative color-developing agent is coated with the protective colloid, said capsules are coated on one surface of an upper sheet of tissue paper and electron acceptive inorganic clays are coated on a lower sheet of tissue paper. When the coated tissue papers are faced toward each other and pressed, the capsules coated on the upper tissue paper are destroyed, and the oil having dissolved therein the electron donative color-developing agent is exuded and contacts the electron acceptive inorganic clays on the lower tissue paper to develop color and produce handwritings.

However, these previous pressure sensitive copying sheets have the following inevitable disadvantages. Namely, in the first place, for the color-developing agent, when the capsules are exposed to the light, the electron donative color-developing agent, even though it is contained in the capsules, cannot develop color at all or may develop a very light color which is unacceptable owing to the extreme inferiority of said agent in its weather-proofing

2

property. In general, the slow color-developing speed of the electron donative color-developing agent forces the use together of more than two color-developing agents in order to compensate each other for their disadvantages. For colored products formed by contacting these electron donative color-developing agents with electron acceptive inorganic clays, there have been developed only bluish tones so that they have only a few little varieties of colors, and, moreover, their fastness is insufficient. Further, the electron donative color-developing agent is so expensive that it has many disadvantages, for example, that it is not economical in industry.

A capsule containing a non-volatile oil which has dissolved therein an electron donative color-developing agent will now be described. Such a fine capsule has been manufactured by forming a capsule forming film from a protective colloid substance according to a complex coacervation method. This process has disadvantages in that it is a very complicated process, for example, in that it needs many complicated process steps performed with high accuracy and further takes a long period of time. The greatest disadvantage is that the pressure resistance of the capsule is very low since the capsule film is made from a protective colloid substance in the capsule manufactured by this process. Therefore, it often happens that not only during various handlings in the manufacture of copying sheet by coating a substratum with said capsules and cutting or in the use thereof, but also during a simple storage of said sheets during which they are piled up said capsules are very easily destroyed and exude the contained liquid which comes into contact with electron acceptive inorganic clays, placed oppositely to said capsules, to develop color, and the copying sheets are spoiled to a great extent and lose their function as copying sheet. As described above, previous copying sheets have many disadvantages. There is known another process for manufacturing capsules containing oil in which a monomer or intermediate or precondensate is polymerized by adding an initiator, accelerator or catalyst to make capsules containing oil. In this process, the condition of polymerization is adjusted with great difficulty and capsules having uniform and thin film thickness cannot be obtained. Further, since the process is an emulsion or suspension polymerization method, and the substance to be contained in said capsules is only mixed in the emulsion or suspension, a mass of polymer of the resin alone which does not coat oil is formed and there is a very low yield of capsules; and, consequently, a satisfactory result cannot be obtained.

This invention provides a novel pressure sensitive copying sheet and a method for the production thereof, in which all disadvantages described above have been solved.

That is, this invention provides a pressure sensitive copying sheet wherein a hydrophilic liquid solution of one color-developing substance of two color-developing substances, which are reacted with each other in the presence of hydrophilic liquid to develop color, is contained in fine capsules containing said solution and said capsules are coated in combination with the other color-developing substance onto at least one substratum. In manufacturing said copying sheet, capsules containing a solution of said one color-developing substance in a hydrophilic liquid may be prepared as mentioned hereinafter by the novel encapsulation method, which we have developed, using the interfacial reaction at the interface of hydrophilic and hydrophobic liquids.

That is, one substance is selected from the group consisting of hydrophobic liquids, substances which dissolve in hydrophobic liquids and substances which disperse well in hydrophobic liquids and the other substance is selected from the group consisting of hydrophilic liquids, substances which dissolve in hydrophilic liquids and sub-

stances which disperse well in hydrophilic liquids, and both substances are reacted with each other to form a polymer insoluble in both the hydrophilic and hydrophobic liquids. A hydrophilic liquid containing the latter substance and one color-developing substance of two color-developing substances which are reacted with each other in the presence of a hydrophilic liquid to develop color, is dispersed in the form of fine droplets into a hydrophobic liquid containing the former substance, said two substances are reacted with each other at the interface of said hydrophobic and hydrophilic liquids to form a polymer insoluble in both hydrophobic and hydrophilic liquids, whereby capsules containing a solution of said one color-developing substance in hydrophilic liquid may be formed. Said capsules in combination with the other color-developing substance are coated onto at least one substratum to produce a pressure sensitive copying sheet.

The combination of capsules containing one color-developing substance with the other color-developing substance in this invention is formed by the coating of a surface of substratum with capsules and the other color-developing substance by mixing or over-coating, or placing separate coating on the opposed surfaces of two substrata, respectively. The other color-developing substance may be coated as it is or after mixing with a suitable vehicle or may be coated after dissolving or dispersing in a hydrophilic or hydrophobic liquid so as to be contained in capsules.

As described above, one feature of this invention is to manufacture capsules containing a hydrophilic liquid by an interfacial reaction which has not been known previously.

That is, while it was impossible to contain a hydrophilic liquid in capsules at will by the previous capsulation method, the capsulation method using an interfacial reaction which we have developed has made possible the containing of a hydrophilic liquid in capsules at will.

Accordingly, capsules containing one color-developing substance of two color-developing substances which are reacted with each other to develop color in the presence of a hydrophilic liquid may be manufactured at will according to this invention. Moreover, in the present capsulation method, two substances which are reacted with each other to form a new solid polymer are present in both the hydrophilic and hydrophobic liquids separately, and they are reacted at the interface of said hydrophilic and hydrophobic liquids to form a coating film insoluble in both of the hydrophilic and hydrophobic liquids, whereby capsules containing a solution of one color-developing substance in said hydrophilic liquid can be formed. Therefore, the reaction conditions can be adjusted very easily, the capsulation is completed in a short time, the thickness of the capsule coating film is uniform and can be controlled and, further, only capsules which coat perfectly the hydrophilic liquid solution will be manufactured. More advantageously, said capsule coating film is a polymer insoluble in both hydrophilic and hydrophobic liquids so that the high strength of the capsule coating film will provide great protection for the contained liquid, and capsules are not destroyed in various handlings to cause exudation of the contained liquid. Two color-developing substances which are reacted with each other in the presence of a hydrophilic liquid to develop color can be used as color-developing agents for a pressure sensitive copying sheet by employing the capsulation method using said interfacial reaction. This invention is also characterized by the use of two color-developing substances, which are reacted with each other to develop color in the presence of a hydrophilic liquid, as color-developing agents in such a manner as described above.

That is, the principle of the pressure sensitive copying sheet according to this invention is quite different from that of previous non-carbon paper. As shown in the accompanying Table 1, widely varied kinds of color-developing substances can be used. Advantageously, these

color-developing substances are superior in weather proofing property and show a high rate of color-development reaction, and the colored product formed by the interaction of two color-developing substances ranges over every color, has a high color density and is excellent in its fastness.

As described above, the pressure sensitive copying sheet according to this invention, which may be obtained by containing a hydrophilic liquid solution of one color-developing substance of two color-developing substances, which are reacted with each other to develop color in the presence of a hydrophilic liquid, in fine capsules by the interfacial reaction method and coating said capsules in combination with the other color-developing substance onto at least one substratum, has no disadvantage such as those of the previous pressure sensitive copying sheets and has new features.

The nature, principle, and details of the invention will be more clearly apparent by reference to the following detailed description, taken in conjunction with the accompanying drawing in which:

FIGS. 1 through 6 are sectional views showing embodiments of pressure sensitive copying sheet according to this invention.

As shown in FIG. 1, capsules 1 containing a hydrophilic liquid solution of one color-developing substance of two color-developing substances, which are reacted with each other to develop color in the presence of a hydrophilic liquid, are coated on the surface of the upper tissue of two opposed tissue substrata 3, and the other color-developing substance 2a is coated on the surface of the lower tissue of said substrata. The other color-developing substance may be coated as it is or together with a suitable vehicle.

When the upper and lower tissues of the resulting pressure sensitive copying sheet are opposed to each other and pressure exerted thereon by handwriting or typewriting, the capsules coated on the upper tissue are destroyed and exude the contained solution of one color-developing substance in hydrophilic liquid therein, and said solution comes into contact with the other color-developing substance coated on the under tissue and develops color directly to provide letters and figures.

As shown in FIG. 2, the capsules 1 containing a hydrophilic liquid solution of one color-developing substance of two color-developing substances, which are reacted with each other to develop color in the presence of a hydrophilic liquid, may be coated on the surface of the upper tissue of two opposed tissue substrata 3, and the capsules 2b containing a hydrophilic liquid solution containing the other color-developing substance may be coated on the surface of the lower tissue.

When the upper and lower tissues of the resulting pressure sensitive copying sheet are opposed to each other and pressure exerted thereon by handwriting or typewriting, capsules coated on the upper and lower tissues are respectively destroyed to exude the respective contained solutions which come into contact with each other and develop color indirectly to produce letters and figures.

The copying sheet which is shown in FIG. 3 may be obtained by coating capsules 1 containing a hydrophilic liquid solution of one color-developing substance of two color-developing substances, which are reacted with each other to develop color in the presence of a hydrophilic liquid, together with the other color-developing substance 2a which is not encapsulated onto the surface of substratum 3.

When the resulting pressure sensitive copying sheet has pressure exerted thereon by handwriting or typewriting the coated capsules are destroyed to exude the contained solution of one-color-developing substance in a hydrophilic liquid, and the solution comes into contact with the other color-developing substance, which is coated on the same surface, and develops color directly to produce letters and figures.

The example shown in FIG. 4 may be obtained by coating the capsules 1 containing a hydrophilic liquid solution of one color-developing substance of two color-developing substances, which are reacted with each other to develop color in the presence of a hydrophilic liquid, and the capsule 2b containing a hydrophilic liquid solution containing the other color-developing substance onto the surface of substream 3.

When the resulting pressure sensitive copying sheet has pressure exerted thereon by handwriting or typewriting, the coated capsules are destroyed to exude the respective contained liquids, and said respective liquids come into contact with each other and develop color directly to produce letters and figures.

As shown in FIG. 5, the fine capsules 1 containing a hydrophilic liquid solution of one color-developing substance of two color-developing substances, which are reacted with each other to develop color in the presence of a hydrophilic liquid, may be coated on the surface of the upper tissue of two opposed tissue substrata 3, and the fine capsules 2c containing a hydrophobic liquid solution containing the other color-developing substance may be coated on the surface of the lower tissue of said substrata.

When the upper and lower tissues of the resulting pressure sensitive copying sheet are disposed oppositely and pressure is exerted thereon by handwriting or typewriting, respective capsules coated on each surface are destroyed to exude the respective contained liquids, and said liquids come into contact with each other and develop color directly to produce letters and figures.

While fine capsules containing a hydrophobic liquid containing a color-developing substance may be manufactured by various methods, it is preferable to manufacture them by the interfacial reaction method which was developed according to this invention. The reason for this is that, according to this invention, the conditions of manufacture are very simple, and capsules having a uniform and very strong coating film may be obtained easily with good yield.

To illustrate the process for manufacturing said capsules, one substance is selected from the group consisting of hydrophobic liquids, substances which dissolve in hydrophobic liquids and substances which disperse well in hydrophobic liquids, and the other substance is selected from the group consisting of hydrophilic liquids, substances which dissolve in hydrophilic liquids and a substance which disperses well in hydrophilic liquids, both substances being such as will react with each other to form a polymer insoluble in both hydrophobic and hydrophilic liquids solution. A hydrophobic liquid containing said former substance and one color-developing substance of two color-developing substances, which are reacted with each other to develop color in the presence of a hydrophilic liquid, is dispersed in the form of fine droplets into a hydrophilic liquid containing said latter substance, and said two substances are reacted at the interface of said hydrophobic and hydrophilic liquids to form a polymer insoluble in both hydrophobic and hydrophilic liquids, whereby capsules containing a hydrophobic liquid solution containing a color-developing substance are formed.

As shown in FIG. 6, the capsule 1 containing a hydrophilic liquid solution of one color-developing substance of two color-developing substances, which are reacted with each other to develop color in the presence of a hydrophilic liquid, and the capsule 2c containing a hydrophobic liquid solution containing the other color-developing substance may be coated on the surface of substratum 3.

When the resulting pressure sensitive copying sheet has pressure exerted thereon by handwriting or typewriting, the coated capsules are destroyed to exude respective contained liquids, and said respective liquids come into contact with each other and develop color directly to produce letters and figures.

As seen from these examples, the pressure sensitive copying sheet according to this invention may be obtained

by coating a substratum with fine capsules and, in this case, a suitable binder may be used. Said capsules may contain not only a liquid containing the color-developing substance as mentioned above but, in addition, a solution assistant for the color-developing substance, an assistant for color development, an accelerator for development, a stabilizer for stabilization with respect to light or heat, a vapor pressure depressant for contained liquid, an emulsifying agent and other additives.

The hydrophilic liquid to be used in this invention has a relatively strong attractive force for a polar medium of high dielectric constant and is incompatible with the hydrophobic liquid which is used in conjunction with said hydrophilic liquid. Examples of this hydrophilic liquid are: water, methanol, ethanol, propanol, ethylene glycol, glycerine, 1,4-butanol, polyethylene glycol, tert-butanol, 1,2-propylene glycol, 1,3-butylene glycol, cyclohexanol, polypropylene glycol, diacetone alcohol, methyl cyclohexanol, tetrahydrofurfuryl alcohol, monomethylglycol acetate, triethylene glycol, triethylene glycol monomethyl ether, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, acetone, formaldehyde, acetaldehyde, propylaldehyde, butylaldehyde, methyl ethyl ketone, tetrahydrofuran, 1,4-dioxane, cyclohexanone, methyl formate, triethyl phosphate, methyl acetate, α -monoacetin, mono butyrin, ethylene diamine, triethylene diamine, tetramethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, diethyl aminopropylamine, pyridine, acetonitrile, hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, lactic acid, formic acid, acetic acid, butyric acid, ammonium hydroxide, lauryl alcohol sulfate, alkyl benzene sulfonate, polyethylene glycol oleyl ether, polyoxyethylene sorbitane monooleate and the like.

The hydrophobic liquid to be used in this invention has a relatively strong attractive force for a nonpolar medium of low dielectric constant and is incompatible with the hydrophilic liquid which is used in conjunction with said hydrophobic liquid. Examples of this hydrophobic liquid are: castor oil, arachis oil, whale oil, turpentine oil, lard oil, dynamo oil, spindle oil, dichlorodiphenyl, silicone oil, chlorinated paraffin, oleic acid, diethyl phosphate, tricresyl phosphate, ethyl acetate, butyl acetate, butyl oleate, methyl isobutyl ketone, cyclohexanone, octyl alcohol, benzyl alcohol, cyclohexanol, benzene, xylene, cyclohexane, monochlorobenzene, benzyl chloride, methylene chloride, cresol, epichlorohydrin, carbon tetrachloride, trichlene, tetrachloroethane, heptane, octane, carbon bisulfide, benzaldehyde, caproyl aldehyde, sorbitane monooleate and the like. Pairs of color-developing substance which will react with each other to develop color in the presence of a hydrophilic liquid and the color developed are listed in the accompanying Table 1, but this invention is by no means limited to only the substances so listed.

TABLE 1

Combinations of two kinds of color-developing substances which are reacted with each other in the presence of a hydrophilic liquid	Shade of colored product
1 Potassium ferrocyanide..... Ammonium ferric sulfate.....	Blue.
2 Same as above..... Cupric sulfate.....	Brown.
3 Potassium thiocyanate..... Ammonium ferric sulfate.....	Red.
4 Sodium sulfide..... Same as above.....	brown.
5 Same as above..... Lead acetate.....	Black.
6 Potassium iodide..... Mercuric acetate.....	Brown.
7 Same as above..... Cupric sulfate.....	Orange.
8 Same as above..... Cupric sulfate-starch.....	Brown.
9 Same as above..... Cupric sulfate-benzidine.....	Black.
10 Dimethyl glyoxime..... Nickel acetate.....	Violet.
11 α -Benzoinoxime..... Cupric sulfate.....	Blue.
12 Same as above..... Copper oleate.....	Red.
13 Salicyl aldoxime..... Ammonium ferric sulfate.....	Yellow-green.
14 Same as above..... Cupric sulfate.....	Do.
15 Catechol..... Ammonium ferric sulfate.....	Brown.
16 Same as above..... Ferric oleate.....	Yellow-green.
	Black.
	Violet-black.

TABLE 1—Continued

Combinations of two kinds of color-developing substances which are reacted with each other in the presence of a hydrophilic liquid			Shade of colored product
17	Dihydroxynaphthalene.....	Ferric oleate.....	Violet.
18	Same as above.....	Ammonium ferric sulfate.....	Do.
19	Catechol disulfonic acid.....	Same as above.....	Brown.
20	Gallic acid.....	Same as above.....	Black.
21	Same as above.....	Ammonium metavanadate.....	Do.
22	Tannic acid.....	Same as above.....	Do.
23	Same as above.....	Ammonium ferric sulfate.....	Do.
24	Salicylic acid.....	Ferric sulfate.....	Violet.
25	Sulfosalicylic acid.....	Ammonium ferric sulfate.....	Brown.
26	Thiosalicylic acid.....	Same as above.....	Do.
27	Kojic acid.....	Ammonium ferric sulfate.....	Orange.
28	1-amino-2-naphthol-4-sulfonic acid.....	Ferric sulfate.....	Brown.
29	1-nitroso-2-naphthol.....	Cobalt acetate.....	Red brown.
30	Same as above.....	Nickel acetate.....	Green.
31	Same as above.....	Cupric acetate.....	Red brown.
32	Same as above.....	Ammonium ferric sulfate.....	Brown.
33	Same as above.....	Ferric oleate.....	Green.
34	Nitroso R salt.....	Cobalt acetate.....	Red brown.
35	Same as above.....	Ferric sulfate.....	Green.
36	2-nitroso-1-naphthol-4-sulfonic acid.....	Cobalt chloride.....	Red brown.
37	Same as above.....	Cupric sulfate.....	Yellow-brown.
38	Same as above.....	Ammonium ferric sulfate.....	Brown.
39	2,4-dinitrophenol.....	Same as above.....	Do.
40	2,4-dinitro-1-naphthol.....	Cobalt chloride.....	Do.
41	Same as above.....	Ferric sulfate.....	Black.
42	8-hydroxyquinoline.....	Ammonium ferric sulfate.....	Do.
43	Same as above.....	Ferric oleate.....	Do.
44	Ferron.....	Ferric sulfate.....	Brown.
45	2,2'-bipyridine.....	Ferrous sulfate.....	Red.
46	Dithiooxamide.....	Nickel acetate.....	Blue-violet.
47	Same as above.....	Cupric sulfate.....	Black.
48	Same as above.....	Copper oleate.....	Do.
49	Sodium diethyl dithiocarbamate.....	Same as above.....	Brown.
50	Same as above.....	Ferric oleate.....	Black.
51	Same as above.....	Ammonium ferric sulfate.....	Brown.
52	Same as above.....	Chromium sulfate.....	Green.
53	Same as above.....	Cupric sulfate.....	Do.
54	Diphenylcarbazone.....	Same as above.....	Violet.
55	Same as above.....	Lead nitrate.....	Red.
56	Diphenylcarbazide.....	Cupric sulfate.....	Violet.
57	Same as above.....	Ammonium ferric sulfate.....	Brown.
58	2-mercaptobenzothiazole.....	Cupric acetate.....	Blue.
59	Same as above.....	Nickel acetate.....	Brown.
60	Same as above.....	Cobalt chloride.....	Red brown.
61	Benzotriazol.....	Cupric sulfate.....	Yellow-green.
62	Sodium rhodizonate.....	Lead acetate.....	Red.
63	Same as above.....	Stannic chloride.....	Do.
64	Quinaldine acid.....	Ferrous sulfate.....	Orange.
65	Rhodanine.....	Cupric sulfate.....	Yellow.
66	p-Dimethylaminobenzalrhodanine.....	Silver nitrate.....	Violet.
67	Azo violet.....	Magnesium sulfate.....	Do.
68	Gallocyanine.....	Lead acetate.....	Do.
69	Same as above.....	Ammonium ferric sulfate.....	Do.
70	Aluminon.....	Ammonium aluminum sulfate.....	Red.
71	Alizarin.....	Cupric sulfate.....	Blue.
72	Same as above.....	Copper oleate.....	Violet red.
73	Same as above.....	Ammonium ferric sulfate.....	Green.
74	Same as above.....	Ammonium ferric sulfate.....	Green.
75	Same as above.....	Ammonium aluminum sulfate.....	Brown.
76	Quinalizarin.....	Nickel acetate.....	Violet.
77	Same as above.....	Magnesium acetate.....	Do.
78	Same as above.....	Copper oleate.....	Violet red.
79	Alizarine Red S.....	Ammonium ferric sulfate.....	Brown.
80	Same as above.....	Chromium sulfate.....	Blue.
81	Same as above.....	Cupric sulfate.....	Do.
82	Chrome Red B.....	Same as above.....	Red.
83	Chrome Cyanine R.....	Cupric sulfate.....	Blue.
84	Alizarine Blue S.....	Same as above.....	Do.
85	Picryl chloride.....	Thiourea.....	Yellow.
86	Indigosol-O.....	Oxidizing agent.....	Blue.
87	Naththol AS-OL.....	Fast Blue RR Base salt.....	Do.
88	Naphthol AS.....	Fast Scarlet LG Base salt.....	Red.
89	Bromocresol purple.....	Potassium hydroxide.....	Violet.
90	Chlorphenol Red.....	Sodium hydroxide.....	Red.
	Bromothymol Blue.....	Triethanol amine.....	Blue.

Pairs of substances forming the coating film of the capsule in preparing the aforesaid capsule containing a hydrophilic liquid containing a color-developing substance by the interfacial reaction method in this invention are listed in the accompanying Table 2, in combinations of a substance soluble or dispersible in a hydrophobic liquid with a substance soluble or dispersible in a hydrophilic liquid. These two kinds of substances are separated

in a hydrophilic and hydrophobic liquid respectively before the reaction. After their interaction at the interface of both liquids, they yield a polymer insoluble in both liquids and form the coating film of the capsules. A hydrophilic liquid containing a substance soluble or dispersible in a hydrophilic liquid is dispersed in the form of fine droplets into a hydrophobic liquid containing a substance soluble or dispersible in a hydrophobic liquid. On the other hand, to contain a hydrophobic liquid in the capsules, a hydrophobic liquid containing a substance soluble or dispersible in a hydrophobic liquid is dispersed in the form of fine droplets into a hydrophilic liquid containing a substance soluble or dispersible in a hydrophilic liquid.

TABLE 2

Substances Soluble or Dispersible in a Hydrophobic Liquid		Substances Soluble or Dispersible in a Hydrophilic Liquid
1	Toluylene diisocyanate Hexamethylene diisocyanate Triphenylmethane triisocyanate Toluylene diisocyanate-hexane triol addition compound Diphenylmethane diisocyanate Polyurethane containing isocyanate groups Etc.	Water Ethylene glycol 1,4-butanediol Etc.
2	Same as above	Ethylenediamine Trimethylenediamine Tetramethylenediamine Pentamethylenediamine Hexamethylenediamine p-Phenylenediamine m-Phenylenediamine Piperazine 2-methyl piperazine 2,5-dimethyl piperazine 2-hydroxytrimethylene diamine Diethylenetriamine Triethylene tetramine Diethyleneaminopropyl amine Tetraethylene pentamine Epoxy resin-amine addition compounds Etc.
3	Tetramethylenediisothiocyanate Hexamethylenediisothiocyanate p-Phenylenediisothiocyanate Etc.	Same as above
4	Oxaloyl chloride Succinoyl chloride Adipoyl chloride Sebacoyl chloride Phthaloyl chloride Isophthaloyl chloride Terephthaloyl chloride Fumaroyl chloride 1,4-cyclohexane dicarbonyl chloride 4,4'-biphenyl dicarbonyl chloride Phosgene 4,4'-sulfonyldibenzoyl chloride Polyester containing acyl chloride groups Polyamide containing acyl chloride groups Etc.	Same as above
5	Same as above	Ethylene glycol 1,4-butane diol Hexamethylene glycol Hydroquinone Resorcinol Alkali salts of 4-chlororesorcinol Glycerol Pentaerythritol Alkali salts of 2,2'-bis(4-hydroxyphenyl)propane Alkali salts of 1,5-dihydroxynaphthalene Alkali salts of phenolphthalein Alkali salts of phenol formaldehyde precondensates Melamine formaldehyde precondensates Urea formaldehyde precondensates Etc.
6	Same as above	Alkali salts of ethylene dithioglycol Alkali salts of dithiohydroquinone Etc.

TABLE 2—Continued

Substances Soluble or Dispersible in a Hydrophobic Liquid	Substances Soluble or Dispersible in a Hydrophilic Liquid
7 1,3-benzenedisulfonyl chloride 1,4-benzenedisulfonyl chloride 1,5-naphthalenedisulfonyl chloride 1,5-naphthalenedisulfonyl chloride 2,7-naphthalenedisulfonyl chloride 4,4'-biphenyldisulfonyl chloride p-oxybis (benzenesulfonyl chloride) 1,6-hexanedisulfonyl chloride Etc.	Ethylenediamine Trimethylenediamine Tetramethylenediamine Hexamethylenediamine ph-Phenylenediamine m-Phenylenediamine Piperazine 2-methyl piperazine 2,5-dimethyl piperazine 2-hydroxytrimethylenediamine Diethylene triamine Triethylene tetramine Diethylaminopropyl amine Tetraethylene pentamine Epoxy resin-amine addition compounds Polyamide (curing agent for epoxy resin) Etc.
8 Ethylene bis (chloroformate) Tetra methylene bis(chloroformate) Hexamethylene bis(chloroformate) 2,2'-dimethyl-1,3-propane bis(chloroformate) p-Phenylene bis(chloroformate) Etc.	Same as above
9 Polyester containing epoxy group Epoxy resin, etc.	Same as above
10 Same as above	Alkali salts of Ethylene dithioglycol Alkali salts of Dithiohydroquinone Etc.
11 Dichloroethane 1,4-dichlorobutane Dibromoethane Etc.	Sodium polysulfide Alkali salts of Ethylene dithioglycol Etc.
12 Epichlorohydrin, etc.	Tetramethylene diamine Pentamethylenediamine Hexamethylenediamine Epoxy resin-amine addition compounds Etc.
13 Oxaloyl chloride Succinoyl chloride Adipoyl chloride Sebacoyl chloride Phthaloyl chloride Isophthaloyl chloride Terephthaloyl chloride Fumaroyl chloride 1,4-cyclohexane dicarbonyl chloride 4,4'-biphenyl dicarbonyl chloride Phosgene 4,4'-sulfonyl dibenzoyl chloride Butyryl chloride Benzoyl chloride Benzene sulfonyl chloride p-Toluenesulfonyl chloride Naphthalene sulfonyl chloride 1,3-benzene disulfonyl chloride 1,4-benzene disulfonyl chloride 1,5-naphthalene disulfonyl chloride 2,7-naphthalene disulfonyl chloride 4,4'-biphenyl disulfonyl chloride p,p'-Oxybis(benzene sulfonyl chloride) 1,6-hexane disulfonyl chloride Etc.	Methyl cellulose Ethyl cellulose Carboxymethyl cellulose Etc.
14 Same as above	Polyvinyl pyrrolidone, etc.
15 Same as above	Albumin Globulin Glutenin Gelatin Casein Etc.
16 Capryl aldehyde Heptyl aldehyde Benzaldehyde Etc.	Polyvinyl alcohol, etc.

TABLE 2—Continued

Substances Soluble or Dispersible in a Hydrophobic Liquid	Substances Soluble or Dispersible in a Hydrophilic Liquid
17 Oxaloyl chloride Succinoyl chloride Adipoyl chloride Sebacoyl chloride Phthaloyl chloride Isophthaloyl chloride Terephthaloyl chloride Fumaroyl chloride 1,4-cyclohexane dicarbonyl chloride 4,4'-biphenyl dicarbonyl chloride Phosgene 4,4'-sulfonyl dibenzoyl chloride 1,3-benzene disulfonyl chloride 1,4-benzene disulfonyl chloride 1,4-naphthalene disulfonyl chloride 2,7-naphthalene disulfonyl chloride 4,4'-biphenyl disulfonyl chloride p,p'-Oxybis(benzene sulfonyl chloride) 1,6-hexane disulfonyl chloride Butyryl chloride Benzoyl chloride Benzene sulfonyl chloride p-Tulene sulfonyl chloride Naphthalene sulfonyl chloride Etc.	Polyvinyl alcohol, etc.
18 Styrene-maleic acid Copolymer Styrene-maleic anhydride copolymer	Alkali salts of 2,2'-bis(4-hydroxyphenyl)propane Alkali salts of 1,5-dihydroxy naphthalene Alkali salts of phenolphthalein
30 Acrylic ester-maleid acid copolymer Vinylacetate-Methacrylic acid copolymer Ethylene-maleic acid copolymer Ethylene-maleic anhydride copolymer Etc.	Alkali salts of phenol-formaldehyde precondensates Urea-formaldehyde precondensates Etc.
35	
19 Same as above	Tetramethylene diamine Pentamethylenediamine Hexamethylenediamine p-Phenylenediamine m-Phenylenediamine Diethylaminopropylamine Tetraethylene pentamine Epoxy resin-amine addition compounds Etc.
40	
20 Polyurea containing amino groups Polyurea containing isocyanate groups Polyamide containing amino groups Polyurethane containing isocyanate groups	Water-soluble epoxy resin etc.
45	

Among substances forming the coating film of the capsule shown in Table 2, the combination of an epoxy compound with a polyvalent amine and its derivatives, of a polyvalent isocyanate and its derivatives with water and a polyvalent amine, and of polyacyl halides and their derivatives with a polyvalent hydroxy compound, give good performances. When the substance soluble or dispersible in a hydrophobic liquid shown in Table 2 is a hydrophobic liquid itself, it may be used as it is without dissolving or dispersing in another hydrophobic liquid. When the substance soluble or dispersible in a hydrophilic liquid is a hydrophilic liquid itself, it may be used as it is without dissolving or dispersing in another hydrophilic liquid.

As a substratum for the copying sheet according to this invention, not only paper but cotton cloth, synthetic fiber cloth, unwoven fabric, plastic film and foam sheet, etc., may be used.

The following examples illustrate this invention, which is by no means limited to these examples.

EXAMPLE 1

0.9 g. of potassium ferrocyanide and 5 g. of hardener U for epoxy resin (an amine compound manufactured by Shell Petroleum Co., U.S.A.), were dissolved in a mixed solvent of 10 cc. of water and 12 cc. of glycerine to form the first liquid. Separately, 15 g. of Epikote 834

(an epoxy resin manufactured by Shell Petroleum Co., U.S.A.), 1 g. of S-Leck BMS (polyvinyl acetal manufactured by Sekisui Chemical Co., Ltd., Japan, and 4 g. of Soluol K100 (a nonionic surface active agent manufactured by Kao Soap Co., Ltd., Japan), were dissolved in 380 cc. of benzene to form the second liquid. The first liquid was added to the second liquid to emulsify the first liquid into fine droplets. Subsequently, when the temperature of the liquid was adjusted to 40° C. and the emulsion was maintained thus for about 6 hrs., the hardener U for epoxy resin reacted with Epikote 834 at the interface of each fine droplet of the first liquid and the dispersion medium of the second liquid to form a coating film insoluble in both the first and second liquids, and the coating film coated the first liquid to form capsules containing the first liquid. The suspension of capsules was coated on the surface of a substratum such as paper and thereafter dried. An aqueous 20% solution of ammonium ferric sulfate was then prepared, coated or wetted on the surface of another substratum and thereafter dried.

When the two surfaces of substrata obtained in the manner as mentioned above were opposed and pressure exerted thereon by handwriting or typewriting, capsules coated on one surface were destroyed to exude an aqueous glycerine solution of potassium ferrocyanide, and the solution came into contact with the ammonium ferric sulfate coated on the surface of the other substratum and reacted directly to yield a blue color. After exposure for two days to light, the resulting pressure sensitive copying sheet provided a dense and sharp copy which was the same as that before the exposure. Further, the copy was in particular superior in weather proofing property and water resistance, and it showed no change upon exposure to light for a long period of time or in contact with water. A sharp copy could be obtained on a Recopy light sensitive paper (a diazo light sensitive paper manufactured by Riken Optical Industries Co., Ltd., Japan), using Recopy 500 (a diazo copying press manufactured by Riken Optical Industries Co., Ltd., Japan).

EXAMPLE 2

A suspension of capsules containing an aqueous glycerine solution of potassium ferrocyanide prepared in Example 1 was coated on the surface of a substratum and thereafter dried.

An aqueous 20% solution of copper sulfate was then prepared, coated or wetted on the surface of another substratum and then dried.

When two surfaces of the resulting substrata obtained as mentioned above were opposed and pressure exerted by handwriting or typewriting, capsules coated on one surface were destroyed to exude the aqueous glycerine solution of potassium ferrocyanide, and the solution came into contact with the copper sulfate coated on the surface of the other substratum and reacted directly to yield a sharp and fast brown color. The pressure sensitive copying sheet was in particular superior in weather proofing property and stability and showed no change after storage for a long period of time or on exposure to light, and the copy was also superior in weather proofing property and water resistance, a sharp copy obtained on a diazo light sensitive paper.

EXAMPLE 3

3 g. of ammonium ferric sulfate was dissolved in a mixed solvent of 12 cc. of water and 13 cc. of glycerine to form the first liquid. 1 g. of polystyrene and 0.5 g. of dibutyl tin dilaurate were dissolved in 250 cc. of chlorobenzene to form the second liquid. Finally, 20 g. of Desmodur L (an adduct of toluylene diisocyanate and hexanetriol manufactured by Bayer A.G., Germany), were dissolved in 50 cc. of chlorobenzene to form the third liquid. The first liquid was added dropwise into the second liquid to emulsify the first liquid into fine

droplets, the third liquid was then added dropwise, the temperature of the liquid was adjusted to 40° C. and the emulsion was so maintained for about 5 hrs. The water reacted then with the Desmodur L at the interface of each fine droplet of the first liquid and the dispersion medium of the second and third liquids to form a coating film insoluble in both said fine droplet and dispersion medium. The film coated the first liquid to form capsules containing the first liquid. The suspension of capsules was coated on the surface of substratum and then dried.

An ethyl alcohol 5% solution of 8-oxyquinoline was then prepared, coated or wetted on the surface of another substratum and then dried. When the two faces of the substrata obtained as described above were opposed and pressure exerted by handwriting or typewriting, capsules coated on one surface were destroyed to exude an aqueous glycerine solution of ammonium ferric sulfate which came into contact with the 8-oxyquinoline coated on the surface of the other substratum and reacted directly to yield a sharp and fast black color. The copy was stable and showed no change after storage for a long period of time or upon exposure to light. A very sharp copy was obtained on a diazo light sensitive paper.

EXAMPLE 4

0.4 of nickel acetate was dissolved in a mixed solvent of 8 cc. of water and 11 cc. of glycerine to form the first liquid. Separately, 10 g. of Desmodur L, 0.3 g. of Saran F-220 (copolymer of vinylidene chloride and acrylonitrile manufactured by Sekisui Chemical Co., Ltd., Japan), and 0.25 g. of dibutyl tin dilaurate were dissolved in 150 cc. of butyl acetate to form the second liquid. The first liquid was added dropwise to the second liquid to emulsify the first liquid into fine droplets, and subsequently the temperature of the liquid was adjusted to 40° C., the emulsion being so maintained for about 4 hrs. The water reacted with the Desmodur L at the interfaces of fine droplets of the first liquid and the dispersion medium of the second liquid to form a coating film insoluble in both the first and second liquids, and the film coated the first liquid to form capsules containing the first liquid. The suspension of said capsules was coated on the surface of a substratum such as paper and then dried.

An acetone 3% solution of dimethyl glyoxime was then prepared, coated or wetted on the surface of another substratum and then dried. When the two surfaces of the substrata obtained as described above were opposed to each other and pressure exerted thereon by handwriting or typewriting, capsules coated on one surface were destroyed to exude an aqueous glycerine solution of nickel acetate, which came into contact with the dimethylglyoxime coated on the surface of the other substratum and reacted directly to yield a sharp and fast red color. The resulting pressure sensitive copying sheet was in particular superior in weather proofing property and stability and showed no change upon exposure for a long period of time or after storage, and the color of the copy was very sharp.

EXAMPLE 5

0.3 g. of p-diazoethyl hydroxyethyl aniline chloride zinc chloride was dissolved in a mixed solvent or 4 cc. of water and 3 cc. of ethylene glycol to form the first liquid. 3 g. of Desmodur L was then dissolved in 70 cc. of trichlorodiphenyl to form the second liquid. The third liquid was 0.05 g. of triethylamine. Finally, the fourth liquid was 0.05 g. of dibutyl tin dilaurate. The first liquid was added dropwise to the second liquid to emulsify the first liquid into fine droplets, the third and fourth liquids were then added dropwise, and subsequently the temperature of liquid was adjusted to 40° C. for about 2 hrs. and to 25° C. for 15 hrs. The water, Desmodur L, and ethylene glycol reacted at the interfaces of the fine droplets of the first liquid and the dispersion medium of the second liquid to form a coating film insoluble in the first and

second liquids. The film coated the first liquid to form capsules containing the first liquid. The suspension of said capsules was coated on the surface of a substratum such as paper and then dried.

An aqueous 5% caustic soda solution of 1-phenyl-3-methyl-5-pyrazolone was then prepared, coated or wetted on the surface of another substratum and then dried.

When the two surfaces obtained as described above were mutually opposed and pressure exerted thereon by handwriting or typewriting, capsules coated on one surface were destroyed to exude an aqueous ethylene glycol solution of p-diazoethyl hydroxyethyl aniline chloride zinc chloride, which came into contact with the 1-phenyl-3-methyl-5-pyrazolone coated on the surface of the other substratum and in this instance reacted immediately to yield a sharp and fast red color.

EXAMPLE 6

0.8 g. of bisphenol A, 0.1 g. of Indigosol-O and 0.4 g. of caustic soda were dissolved in 7 cc. of water to form the first liquid. 1 g. of S-Leck BMS was then dissolved in 100 cc. of benzene to form the second liquid. Finally, 0.8 g. of terephthalic acid chloride was dissolved in 50 cc. of benzene to form the third liquid. The first liquid was added dropwise to the second liquid to emulsify the first liquid into fine droplets, the third liquid was then added dropwise, the temperature of the liquid was adjusted to 25° C. and the emulsion was so maintained for about 4 hrs. The bisphenol A reacted with the terephthalic acid chloride at the interfaces of the fine droplets of the first liquid and the dispersion medium of the second and third liquids to form a coating film insoluble in the first, second and third liquids. The film coated the first liquid to form capsules containing the first liquid. The suspension of said capsules was coated on the surface of substratum such as paper and then dried.

Acid clay was then dispersed to in an amount of 10% by weight in an aqueous solution of diluted sulfuric acid, coated or wetted on the surface of another substratum and then dried.

When the two surfaces of the substrata obtained as described above were mutually opposed and pressure exerted thereon by handwriting or typewriting, capsules coated on one surface were destroyed to exude an aqueous solution of Indigosol-O, which was oxidized on the acid clay on the surface of the other substratum to yield a sharp and fast blue color.

EXAMPLE 7

0.3 g. of caustic soda, 0.6 g. of bisphenol A and 0.03 g. of Sunchromine Pure Blue B Extra (a mordant dye manufactured by Sumitomo Chemical Co., Ltd., Japan), were dissolved in 10 cc. of aqueous 50% glycerine solution to form the first liquid. 50 cc. of carbon tetrachloride was then mixed with 40 cc. of petroleum benzene to form the second liquid. Separately, 0.8 g. of terephthalic acid dichloride was dissolved in 45 cc. of trichlene to form the third liquid. The first liquid was added dropwise to the second liquid to emulsify the first liquid into fine droplets, the third liquid was then added dropwise, the temperature of the liquid was adjusted to 25° C. and the emulsion was so maintained for about 3 hrs. The bisphenol A reacted with the terephthalic acid dichloride at the interfaces of the fine droplets of the first liquid and the dispersion medium of the second and third liquids to form a coating film insoluble in said fine droplets and dispersion medium. The film coated the first liquid to form capsules containing the first liquid. The suspension of said capsules was coated on the surface of a substratum such as paper and then dried.

An aqueous 20% solution of copper sulfate was then prepared, coated or wetted on the surface of another substratum and then dried. When the two surfaces of the substrata obtained as described above were opposed to each other and pressure was exerted thereon by hand-

writing or typewriting, capsules coated on one surface were destroyed to exude an aqueous glycerine solution of Sunchromine Pure Blue B Extra, which came into contact with the copper sulfate coated on the surface of the other substratum and reacted immediately to yield a sharp and very fast blue color. The resulting pressure sensitive copying sheet was in particular superior in weather proofing property and showed no change upon exposure to light for a long period of time.

EXAMPLE 8

0.5 g. of Chlorophenol Red was dissolved in a mixed solvent of 5 cc. of water and 16 cc. of glycerine to form the first liquid. Separately, 15 g. of Desmodur L and 1 g. of polystyrene were dissolved in 200 cc. of chlorobenzene to form the second liquid. The first liquid was added dropwise to the second liquid to emulsify the first liquid into fine droplets, the temperature of the liquid was then adjusted to 42° C. and the emulsion was so maintained for about 7 hrs. The water reacted with the Desmodur L at the interfaces of the fine droplets of the first liquid and the dispersion medium of the second liquid to form a coating film insoluble in both the first and second liquids. The film coated the first liquid to form capsules containing the first liquid. The suspension of said capsules was coated on the surface of a substratum such as paper and then dried.

An aqueous 2% solution of caustic potash was then prepared, coated or wetted on the surface of another substratum and then dried.

When the two surfaces of the substrata obtained as described above were opposed to each other and pressure was exerted thereon by handwriting or typewriting, capsules coated on one surface were destroyed to exude an aqueous glycerine solution of Chlorophenol Red, which came into contact with the caustic potash coated on the surface of the other substratum and, at the same time, reacted immediately to yield a bright red color.

EXAMPLE 9

0.075 g. of ammonium metavanadate was dissolved in 15 cc. of aqueous 70% solution of glycerine to form the first liquid. 10 g. of Desmodur L, 4 g. of S-Neal P-42 (polyvinyl acetate resin manufactured by Sekisui Chemical Industries Co., Ltd., Japan), and 2 g. of Soluol K-100 were then dissolved in 150 cc. of chlorobenzene to form the second liquid. Separately, 0.01 g. of di-n-butyl tin dilaurate was dissolved in 10 cc. of chlorobenzene to form the third liquid.

The first liquid was added dropwise to the second liquid to emulsify the first liquid into fine droplets, the temperature of the liquid was adjusted to 40° C., after about 30 min. the third liquid was added dropwise and the emulsion was then so maintained for about 6 hrs. The water reacted with the Desmodur L at the interfaces of the fine droplets of the first liquid and the dispersion medium of the second and third liquid to form a coating film insoluble in both said fine droplets and dispersion medium. The film coated the first liquid to form capsules containing the first liquid. The suspension of said capsules was coated on the surface of a substratum such as paper and then dried.

An ethanolic 10% solution of 2,3-dihydroxynaphthalene was then prepared, coated or wetted on the surface of another substratum and then dried. When the two surfaces of the substrata obtained as described above were opposed to each other and pressure was exerted thereon by handwriting or typewriting, capsules coated on one surface were destroyed to exude an aqueous glycerine solution of ammonium metavanadate, which came into contact with the 2,3-dihydroxynaphthalene coated on the surface of the other substratum and reacted immediately to yield a sharp and very fast black color. The resulting pressure sensitive copying sheet was superior in that it preserved well and showed no change after storage for

a long period of time. The copy was stable, and a sharp copy was obtained on a diazo light sensitive paper.

EXAMPLE 10

The suspension of capsules containing an aqueous glycerine solution of potassium ferrocyanide prepared in Example 1 was coated on the surface of a substratum such as paper and then dried.

The suspension of capsules containing an aqueous glycerine solution of ammonium ferric sulfate prepared in Example 3 was coated on the surface of another substratum and then dried.

When the two surfaces of the substrata obtained as described above were opposed to each other and pressure was exerted thereon by handwriting or typewriting, the capsules coated on said respective surfaces were destroyed to exude an aqueous glycerine solution of ammonium ferric sulfate and an aqueous glycerine solution of potassium ferrocyanide, which came into contact with each other and reacted immediately to yield a sharp and fast blue color.

The resulting pressure sensitive copying sheet was in particular superior in weather proofing property and showed no change after exposure to light for a long period of time.

EXAMPLE 11

0.1 g. of dimethylglyoxime was dissolved in 4 cc. of water and 16 g. of ethylene glycol to form the first liquid. Separately, 10 g. of Desmodur L was dissolved in 200 g. of trichlorodiphenyl to form the second liquid. The first liquid was added dropwise to the second liquid to emulsify the first liquid into fine droplets, the temperature of the liquid was adjusted to 40° C. and the emulsion was so maintained for about 10 hrs. The water reacted with the Desmodur L at the interfaces of the fine droplets of the first liquid and the dispersion medium of the second liquid to form a coating film insoluble in the first and second liquids. The film coated the first liquid to form capsules containing the first liquid. The suspension of said capsules was coated on the surface of a substratum such as paper and then dried.

The suspension of capsules containing an aqueous glycerine solution of nickel acetate prepared in Example 4 was then coated on the surface of another substratum and then dried.

When the two surfaces of the substrata obtained as described above were opposed to each other and pressure was exerted thereon by handwriting or typewriting, the capsules coated on said respective surfaces were destroyed to exude an aqueous glycerine solution of nickel acetate and an aqueous ethylene glycol solution of dimethylglyoxime, which came into contact with each other and reacted immediately to yield a sharp and fast pink color.

The resulting pressure sensitive copying sheet was in particular superior in weather proofing property and showed no change after exposure to light for a long period of time.

EXAMPLE 12

1.0 g. of thiourea and 5.0 g. of hardener U for epoxy resin were dissolved in a mixed solvent of 12 cc. of water and 18 cc. of glycerine to form the first liquid. Separately, 15.0 g. of Epikote 834 and 3.6 g. of S-Leck BMS were dissolved in 450 cc. of benzene to form the second liquid. The first liquid was added dropwise to the second liquid to emulsify the first liquid into fine droplets, the temperature of the liquid was adjusted to 40° C. and the emulsion was so maintained for about 15 hrs. The hardener U for epoxy resin reacted with the Epikote 834 at the interfaces of the fine droplets of the first liquid and the dispersion medium of the second liquid to form a coating film insoluble in the first and second liquids. The film coated the first liquid to form capsules containing the first liquid. The suspension of said capsules was coated on the surface of a substratum and then dried.

0.15 g. of picryl chloride, 1.5 g. of Desmodur R (triphenylmethane trisocyanate manufactured by Bayer A.G., Germany), and 0.02 g. of Emulgen 810 (nonionic surface active agent manufactured by Kao Soap Co., Ltd., Japan), were dissolved in 17 cc. of xylene to form the third liquid. 0.1 g. of polyvinyl alcohol was dissolved in 100 cc. of water to form the fourth liquid, and 0.8 g. of hexamethylenediamine was dissolved in 35 cc. of water to form the fifth liquid. The third liquid was added dropwise to the fourth liquid to emulsify the third liquid into fine droplets, the fifth liquid was then added dropwise, the temperature of the liquid was adjusted to 25° C. and the emulsion was so maintained for about 4 hrs. The Desmodur R reacted with the hexamethylenediamine at the interfaces of the fine droplets of the third liquid and the dispersion medium of the fourth and fifth liquids to form a coating film insoluble in the third, fourth and fifth liquids. The film coated the third liquid to form capsules containing the third liquid. The suspension of said capsules was coated on the surface of another substratum and then dried.

When the two surfaces of the substrata obtained as described above were opposed to each other and pressure was exerted thereon by handwriting or typewriting, the capsules coated on said respective surfaces were destroyed to exude an aqueous glycerine solution of thiourea and an xylene solution of picryl chloride, which came into contact and reacted with each other to yield a sharp and fast yellow color.

The resulting pressure sensitive copying sheet was superior in weather proofing property, the copy was very fast and a very sharp copy could be obtained on a Recopy light sensitive paper.

EXAMPLE 13

An ethanolic 0.5% solution of Bromothymol Blue was coated or wetted on the surface of a substratum such as paper and then dried. 0.5 g. of bisphenol A and 0.2 g. of caustic soda were dissolved in a mixed solvent of 2 cc. of polypropylene glycol #200 and 8 cc. of water to form the first liquid. The second liquid was 60 cc. of hexane. Finally, 0.5 g. of terephthalic acid chloride was dissolved in 60 cc. of hexane to form the third liquid. The first liquid was added dropwise to the second liquid to emulsify the first liquid into fine droplets, subsequently the third liquid was added dropwise, the temperature of the liquid was adjusted to 20° C. and the emulsion was maintained for about 3 hrs. The bisphenol A reacted with the terephthalic acid chloride at the interfaces of the fine droplets of the first liquid and the dispersion medium of the second and third liquids to form a coating film insoluble in both said fine droplets and dispersion medium. The film coated the first liquid to form capsules containing the first liquid. The suspension of said capsules was coated on the surface, which had been previously coated with Bromothymol Blue, of a substratum and then dried.

When the surface of the substratum obtained as described above had pressure exerted thereon by handwriting or typewriting, the coated capsules were destroyed to exude an aqueous caustic soda solution of polypropylene glycol, which came into contact with the Bromothymol Blue which was coated on the same surface and directly after the contact, reacted immediately to yield a sharp and bright blue color.

EXAMPLE 14

An aqueous caustic potash solution as prepared in Example 8 was coated or wetted on the surface of a substratum and dried. The suspension of capsules containing an aqueous glycerine solution of Chlorophenol Red prepared in Example 8 was then coated on the same surface and then dried.

When the resulting surface of the substratum had pressure exerted thereon by handwriting or typewriting, the coated capsules were destroyed to exude an aqueous glycerine solution of Chlorophenol Red, which came into

contact with the caustic potash which was coated on the same surface and, directly after the contact, reacted immediately to yield a sharp and bright red color.

EXAMPLE 15

The suspension of capsules containing an aqueous glycerine solution of potassium ferrocyanide prepared in Example 1 was coated on the surface of a substratum and then dried. The suspension of capsules containing an aqueous glycerine solution of ammonium ferric sulfate prepared in Example 3 was further coated on the same surface of the substratum and then dried.

When the resulting surface of the substratum obtained as described above had pressure exerted thereon by handwriting or typewriting, the respective coated capsules were destroyed to exude an aqueous glycerine solution of potassium ferrocyanide and an aqueous glycerine solution of ammonium ferric sulfate, which came into contact with each other and reacted immediately to yield a sharp and fast blue color.

EXAMPLE 16

The suspension of capsules containing an ethylene glycol solution of dimethylglyoxime prepared in Example 11 was coated on the surface of a substratum and dried. The suspension of capsules containing an aqueous glycerine solution of nickel acetate prepared in Example 4 was further coated on the same surface and then dried.

When the resulting surface of the substratum obtained as described above had pressure exerted thereon by handwriting or typewriting, the respective coated capsules were destroyed to exude an ethylene glycol solution of dimethylglyoxime and an aqueous glycerine solution of nickel acetate, which came into contact with each other and reacted immediately to yield a sharp and fast pink color.

EXAMPLE 17

The suspension of capsules containing an aqueous glycerine solution of thiourea prepared in Example 12 was coated on the surface of a substratum and dried. The suspension of capsules containing a xylene solution of picryl chloride prepared in Example 12 was additionally coated on the same surface and then dried.

When the resulting surface of the substratum obtained as described above had pressure exerted thereon by handwriting or typewriting, the respective coated capsules were destroyed to exude an aqueous glycerine solution of thiourea and a xylene solution of picryl chloride, which came into contact with each other and reacted to yield a sharp and fast yellow color.

In the pressure sensitive copying sheet according to this invention, the capsules are not destroyed by storage and various handlings, and the contained liquid in the capsules does not leak out due to the high strength of the coating film of said capsules containing a liquid containing a color-developing substance. Therefore, there is no contamination of the copying sheet, and a sharp copy having a high color contrast can be obtained. Further, the pressure sensitive copying sheet according to this invention is very superior in that it can be preserved for a long period of time, is stable and weatherproof and can produce a variety of selectable colors, etc., as compared to the previous copying paper and may be used in many applications.

We claim:

1. A pressure sensitive copying sheet comprising at least one substratum, a coating thereon comprising capsules containing a hydrophilic liquid solution of one color-developing substance of two color-developing substances which react with each other to develop color in the presence of a hydrophilic liquid, said coating further containing the other color-developing substance, said capsules containing said solution being the reaction product of a process which comprises dispersing into a first

solution of a hydrophobic liquid and one substance which is reactive with a second substance to form a polymer insoluble in both hydrophobic and hydrophilic liquids and which one substance is taken from the group consisting of polyisocyanates, polyisothiocyanates, acyl halides, sulfonyl halides, polychloroformates, epoxy compounds, polyhalides of hydrocarbons, water-insoluble aldehydes, prepolymers having isocyanate groups, prepolymers having acyl halide groups, water-insoluble prepolymers having amino groups, water-insoluble polymers having carboxyl groups and water-insoluble polymers having acid anhydride groups, a second solution of said one color-developing substance, the second substance which is reactive with said one substance, and a hydrophilic liquid, said second substance being taken from the group consisting of water, polyhydroxy compounds and their alkali salts, polyamines, piperazine and its derivatives, epoxy resin-amine addition compounds, polyamide curing agents for epoxy resins, alkali salts of polyhydric thioalcohols, alkali salts of polyhydric thiophenols, polysulfides of alkali metals, water-soluble epoxy resins, precondensates, water-soluble polymers having hydroxyl groups, polyvinyl pyrrolidone and proteins, said dispersion of the said second solution being in the form of fine droplets, and reacting said two substances at the interfaces of the hydrophobic and hydrophilic liquids to form the polymer insoluble in both hydrophobic and hydrophilic liquids as a coating around said fine droplets.

2. A pressure sensitive copying sheet as claimed in claim 1 in which order color-developing substance is present in a layer on said substratum and is uncapsulated.

3. A pressure sensitive copying sheet as claimed in claim 1 in which said other color-developing substance is encapsulated in a hydrophilic liquid in fine capsules on said substratum.

4. A pressure sensitive copying sheet as claimed in claim 1 in which said other color-developing substance is encapsulated in a hydrophobic liquid in fine capsules on said substratum.

5. A pressure sensitive copying sheet comprising at least one substratum, a coating thereon comprising capsules, some containing a hydrophilic liquid solution of one color-developing substance of two color-developing substances which react with each other to develop color in the presence of a hydrophilic liquid, and the remainder containing a hydrophilic liquid solution of the other color-developing substance, said capsules containing said solutions being the reaction products of processes each of which comprises dispersing into a first solution of a hydrophobic liquid and one substance which is reactive with a second substance to form a polymer insoluble in both hydrophobic and hydrophilic liquids and which one substance is taken from the group consisting of polyisocyanates, polyisothiocyanates, acyl halides, sulfonyl halides, polychloroformates, epoxy compounds, polyhalides of hydrocarbons, water-insoluble aldehydes, prepolymers having isocyanate groups, prepolymers having acyl halide groups, water-insoluble prepolymers having amino groups, water-insoluble polymers having carboxyl groups and water-insoluble polymers having acid anhydride groups, a second solution of the respective color-developing substance, the second substance which is reactive with said one substance, and a hydrophilic liquid, said second substance being taken from the group consisting of water, polyhydroxy compounds and their alkali salts, polyamines, piperazine and its derivatives, epoxy resin-amine addition compounds, polyamide curing agents for epoxy resins, alkali salts of polyhydric thioalcohols, alkali salts of polyhydric thiophenols, polysulfides of alkali metals, water-soluble epoxy resins, precondensates, water-soluble polymers having hydroxyl groups, polyvinyl pyrrolidone and proteins, said dispersion of the said second solution being in the form of fine droplets, and reacting said two substances at the interfaces of the hydrophobic and hydrophilic liquids to form the polymer insoluble in both hydro-

phobic and hydrophilic liquids as a coating around said fine droplets.

6. A pressure sensitive copying sheet comprising a first substratum, a coating thereon comprising capsules containing a hydrophilic liquid solution of one color-developing substance of two color-developing substances which react with each other to develop color in the presence of a hydrophilic liquid, a second substratum having a coating thereon containing the other color developing substance, the coated sides of said substrata being opposed to each other, said capsules containing said solution being the reaction product of a process which comprises dispersing into a first solution of a hydrophobic liquid and one substance which is reactive with a second substance to form a polymer insoluble in both hydrophobic and hydrophilic liquids and which one substance is taken from the group consisting of polyisocyanates, polyisothiocyanates, acyl halides, sulfonyl halides, polychloroformates, epoxy compounds, polyhalides of hydrocarbons, water-insoluble aldehydes, prepolymers having isocyanate groups, prepolymers having acyl halide groups, water-insoluble prepolymers having amino groups, water-insoluble polymers having carboxyl groups and water-insoluble polymers having acid anhydride groups, a second solution of said one color developing substance, the second substance which is reactive with said one substance, and a hydrophilic liquid, said second substance being taken from the group consisting of water, polyhydroxy compounds and their alkali salts, polyamines, piperazine and its derivatives, epoxy resin-amine addition compounds, polyamide curing agents for epoxy resins, alkali salts of polyhydric thioalcohols, alkali salts of polyhydric thiophenols, polysulfides of alkali metals, water-soluble epoxy resins, precondensates, water-soluble polymers having hydroxyl groups, polyvinyl pyrrolidone and proteins, said dispersion of the said second solution being in the form of fine droplets, and reacting said two substances at the interfaces of the hydrophobic and hydrophilic liquids to form the polymer insoluble in both hydrophobic and hydrophilic liquids as a coating around said fine droplets.

7. A pressure sensitive copying sheet as claimed in claim 6 in which other color-developing substance is present in a layer on said second substratum and is unincapsulated.

8. A pressure sensitive copying sheet as claimed in claim 6 in which said other color-developing substance is encapsulated in a hydrophilic liquid in fine capsules on said second substratum.

9. A pressure sensitive copying sheet as claimed in claim 6 in which said other color-developing substance is encapsulated in a hydrophobic liquid in fine capsules on said second substratum.

10. A pressure sensitive copying sheet comprising a first substratum, a coating thereon comprising capsules containing a hydrophilic liquid solution of one color-developing substance of two color-developing substances which react with each other to develop color in the presence of a hydrophilic liquid, a second substratum having a coating thereon comprising capsules containing a hydrophilic liquid solution of the other color-developing substance, said capsules containing said solution being the reaction products of processes each of which comprises dispersing into a first solution of a hydrophobic liquid and one substance which is reactive with a second substance to form a polymer insoluble in both hydrophobic and hydrophilic liquids and which one substance is taken from the group consisting of polyisocyanates, polyisothiocyanates, acyl halides, sulfonyl halides, polychloroformates, epoxy compounds, polyhalides of hydrocarbons, water-insoluble aldehydes, prepolymers having isocyanate groups, prepolymers having acyl halide groups, water-insoluble prepolymers having amino groups, water-insoluble polymers having carboxyl groups and water-insoluble polymers having acid anhydride groups, a second solution of the

respective color developing substance, the second substance which is reactive with said one substance, and a hydrophilic liquid, said second substance being taken from the group consisting of water, polyhydroxy compounds and their alkali salts, polyamines, piperazine and its derivatives, epoxy resin-amine addition compounds, polyamide curing agents for epoxy resins, alkali salts of polyhydric thioalcohols, alkali salts of polyhydric thiophenols, polysulfides of alkali metals, water-soluble epoxy resins, precondensates, water-soluble polymers having hydroxyl groups, polyvinyl pyrrolidone and proteins, said dispersion of the said second solution being in the form of fine droplets, and reacting said two substances at the interfaces of the hydrophobic and hydrophilic liquids to form the polymer insoluble in both hydrophobic and hydrophilic liquids as a coating around said fine droplets.

11. A process for making a pressure sensitive copying sheet, comprising dispersing into a first solution of hydrophobic liquid and one substance which is reactive with a second substance to form a polymer insoluble in both hydrophobic and hydrophilic liquids and which one substance is taken from the group consisting of polyisocyanates, polyisothiocyanates, acyl halides, sulfonyl halides, polychloroformates, epoxy compounds, polyhalides of hydrocarbons, water-insoluble aldehydes, prepolymers having isocyanate groups, prepolymers having acyl halide groups, water-insoluble prepolymers having amino groups, water-insoluble polymers having carboxyl groups and water-insoluble polymers having acid anhydride groups, a second solution containing one color-developing substance of two color-developing substances which react with each other to develop color in the presence of a hydrophilic liquid, and further containing the second substance which is reactive with said one substance, and a hydrophilic liquid, said second substance being taken from the group consisting of water, polyhydroxy compounds and their alkali salts, polyamines, piperazine and its derivatives, epoxy resin-amine addition compounds, polyamide curing agents for epoxy resins, alkali salts of polyhydric thioalcohols, alkali salts of polyhydric thiophenols, polysulfides of alkali metals, water-soluble epoxy resins, precondensates, water-soluble polymers having hydroxyl groups, polyvinyl pyrrolidone and proteins, said dispersion of said second solution being in the form of fine droplets, reacting said two substances at the interfaces of said hydrophobic and hydrophilic liquids to form the polymer insoluble in both the hydrophobic and hydrophilic liquids as a coating around said fine droplets to form capsules containing said one color-developing substance in a hydrophilic liquid, coating said capsules on at least one substratum, and coating on said substratum the other color-developing substance.

12. A process as claimed in claim 11 in which the step of coating on said substratum the other color developing substance comprises incorporating it in a liquid material and coating the liquid material on the substratum in unincapsulated form.

13. A process as claimed in claim 11 in which the step of coating on said substratum the other color-developing substance comprises encapsulating it and coating the capsules on the substratum.

14. A process as claimed in claim 13 in which the other color-developing substance is encapsulated in a hydrophilic liquid solution.

15. A process as claimed in claim 13 in which the other color-developing substance is encapsulated in a hydrophobic liquid solution.

16. A process as claimed in claim 11 wherein one of the two substances which react with each other to form a polymer insoluble in both hydrophilic and hydrophobic liquids is an epoxy compound and is contained in the hydrophobic liquid, and the other substance is a substance selected from the group consisting of polyamines and their derivatives and is contained in the hydrophilic liquid.

17. A process as claimed in claim 11, wherein one of the two substances which react with each other to form a polymer insoluble in both hydrophilic and hydrophobic liquids is a substance selected from the group consisting of polyisocyanates and their derivatives and is contained in the hydrophobic liquid, and the other substance is a substance selected from the group consisting of water and polyamines and is contained in the hydrophilic liquid.

18. A process as claimed in claim 11, where one of the two substances which react with each other to form a polymer insoluble in both hydrophilic and hydrophobic liquids is a substance selected from the group consisting of polyacyl halides and their derivatives and is contained in the hydrophobic liquid, and the other substance is a polyhydroxy compound and is contained in the hydrophilic liquid.

19. A process for making a pressure sensitive copying sheet, comprising dispersing into two respective first solutions of a hydrophobic liquid and one substance which is reactive with a second substance to form a polymer insoluble in both hydrophobic and hydrophilic liquids and which one substance is taken from the group consisting of polyisocyanates, polyisothiocyanates, acyl halides, sulfonyl halides, polychloroformates, epoxy compounds, polyhalides of hydrocarbons, water-insoluble aldehydes, prepolymers having isocyanate groups, prepolymers having acyl halide groups, water-insoluble prepolymers having amino groups, water-insoluble polymers having carboxyl groups and water-insoluble polymers having acid anhydride groups, two respective second solutions, one second solution containing one color-developing substance of two color-developing substances which react with each other to develop color in the presence of a hydrophilic liquid, and the other second solution containing the other color-developing substance, and each second solution further containing the second substance which is reactive with said one substance, and a hydrophilic liquid, said second substance being taken from the group consisting of water, polyhydroxy compounds and their alkali salts, polyamines, piperazine and its derivatives, epoxy resin-amine addition compounds, polyamide curing agents for epoxy resins, alkali salts of polyhydric thioalcohols, alkali salts of polyhydric thiophenols, polysulfides of alkali metals, water-soluble epoxy resins, precondensates, water-soluble polymers having hydroxyl groups, polyvinyl pyrrolidone and proteins, said dispersion of said second solutions being in the form of fine droplets, reacting said two substances at the interfaces of said hydrophobic and hydrophilic liquids to form the polymer insoluble in both the hydrophobic and hydrophilic liquids as a coating around said fine droplets to form one group of capsules containing said one color-developing substance in a hydrophilic liquid, and a second group of capsules containing the other color-developing substance in a hydrophilic liquid, and coating said two groups of capsules on at least one substratum.

20. A process for making a pressure sensitive copying sheet, comprising dispersing into a first solution of a hydrophobic liquid and one substance which is reactive with a second substance to form a polymer insoluble in both hydrophobic and hydrophilic liquids and which one substance is taken from the group consisting of polyisocyanates, polyisothiocyanates, acyl halides, sulfonyl halides, polychloroformates, epoxy compounds, polyhalides of hydrocarbons, water-insoluble aldehydes, prepolymers having isocyanate groups, prepolymers having amino groups, water-insoluble polymers having carboxyl groups and water-insoluble polymers having acid anhydride groups, a second solution containing one color developing substance of two color-developing substances which react with each other to develop color in the presence of a hydrophilic liquid, and further containing the second substance which is reactive with said one substance, and a hydrophilic liquid, said second substance being taken

from the group consisting of water, polyhydroxy compounds and their alkali salts, polyamines, piperazine and its derivatives, epoxy resin-amine addition compounds, polyamide curing agents for epoxy resins, alkali salts of polyhydric thioalcohols, alkali salts of polyhydric thiophenols, polysulfides of alkali metals, water-soluble epoxy resins, precondensates, water-soluble polymers having hydroxyl groups, polyvinyl pyrrolidone and proteins, said dispersion of said second solution being in the form of fine droplets, reacting said two substances at the interfaces of said hydrophobic and hydrophilic liquids to form the polymer insoluble in both the hydrophobic and hydrophilic liquids as a coating around said fine droplets to form capsules containing said one color developing substance in a hydrophilic liquid, coating said capsules on one substratum, coating on a second substratum the other color developing substance, and then placing the substratum against each other with the coated surfaces opposed.

21. A process as claimed in claim 20 in which the step of coating on said second substratum the other color-developing substance comprises incorporating it in a liquid material and coating the liquid material on the substratum in unincapsulated form.

22. A process as claimed in claim 20 in which the step of coating on said second substratum the other color developing substance comprises encapsulating it and coating the capsules on the second substratum.

23. A process as claimed in claim 22 in which the other color developing substance is encapsulated in a hydrophilic liquid solution.

24. A process as claimed in claim 22 in which the other color-developing substance is encapsulated in a hydrophobic liquid solution.

25. A process as claimed in claim 20 wherein one of the two substances which react with each other to form a polymer insoluble in both hydrophilic and hydrophobic liquids is an epoxy compound and is contained in the hydrophobic liquid, and the other substance is a substance selected from the group consisting of polyamines and their derivatives and is contained in the hydrophilic liquid.

26. A process as claimed in claim 20, wherein one of the two substances which react with each other to form a polymer insoluble in both hydrophilic and hydrophobic liquids is a substance selected from the group consisting of polyisocyanates and their derivatives and is contained in the hydrophobic liquid, and the other substance is a substance selected from the group consisting of water and polyamines and is contained in the hydrophilic liquid.

27. A process as claimed in claim 20, wherein one of the two substances which react with each other to form a polymer insoluble in both hydrophilic and hydrophobic liquids is a substance selected from the group consisting of polyacyl halides and their derivatives and is contained in the hydrophobic liquid, and the other substance is a polyhydroxy compound and is contained in the hydrophilic liquid.

28. A process for making a pressure sensitive copying sheet, comprising dispersing into two respective first solutions of a hydrophobic liquid and one substance which is reactive with a second substance to form a polymer insoluble in both hydrophobic and hydrophilic liquids and which one substance is taken from the group consisting of polyisocyanates, polyisothiocyanates, acyl halides, sulfonyl halides, polychloroformates, epoxy compounds, polyhalides of hydrocarbons, water-insoluble aldehydes, prepolymers having isocyanate groups, prepolymers having acyl halide groups, water-insoluble prepolymers having amino groups, water-insoluble polymers having carboxyl groups and water-insoluble polymers having acid anhydride groups, two respective second solutions, one second solution containing one color-developing substance of two color-developing substances which react with each other to develop color in the presence of a hydrophilic

liquid, and the other second solution containing the other color-developing substance, and each second solution further containing the second substance which is reactive with said one substance, and a hydrophilic liquid, said second substance being taken from the group consisting of water, polyhydroxy compounds and their alkali salts, polyamines, piperazine and its derivatives, epoxy resin-amine addition compounds, polyamide curing agents for epoxy resins, alkali salts of polyhydric thioalcohols, alkali salts of polyhydric thiophenols, polysulfides of alkali metals, water-soluble epoxy resins, precondensates, water-soluble polymers having hydroxyl groups, polyvinyl pyrrolidone and proteins, said dispersion of said second solution being in the form of fine droplets, reacting said two substances at the interfaces of said hydrophobic and hydrophilic liquids to form the polymer insoluble in both the hydrophobic and hydrophilic liquids as a coating around said fine droplets to form one group of capsules containing said one color-developing substance in a hydrophilic liquid, and a second group of capsules contain-

ing the other color-developing substance in a hydrophilic liquid, coating said one group of capsules on one substratum, coating on a second substratum said second group of capsules, and then placing the substrata against each other with the coated surfaces opposed.

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