United States Patent [19]

Hayashi et al.

[11] **3,773,542**

[45] **Nov. 20, 1973**

[54] **SENSITIZING SHEET FOR PRESSURE- OR HEAT-SENSITIVE COPYING PAPER**

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[22] Filed: **Apr. 28, 1971**

[21] Appl. No.: **138,023**

[52] **U.S. Cl.** ..... **117/36.2,** 117/36.8, 117/155 L

[51] **Int. Cl.** **B41m 5/22**

[58] **Field of Search** ..... 117/36.2, 36.8, 155 L

[56] **References Cited**

UNITED STATES PATENTS

3,455,721	7/1969	Phillips et al.	117/36.2
3,516,845	6/1970	Brockett	117/36.2
3,540,913	11/1970	Lin	117/36.2
2,565,152	8/1951	Wachter et al.	117/155 L
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[57] **ABSTRACT**

A sensitizing sheet capable of forming a distinct color when contacted with a substantially colorless color former comprising a support having thereon a layer containing a phenol resin and an alkaline material is disclosed.

10 Claims, 8 Drawing Figures

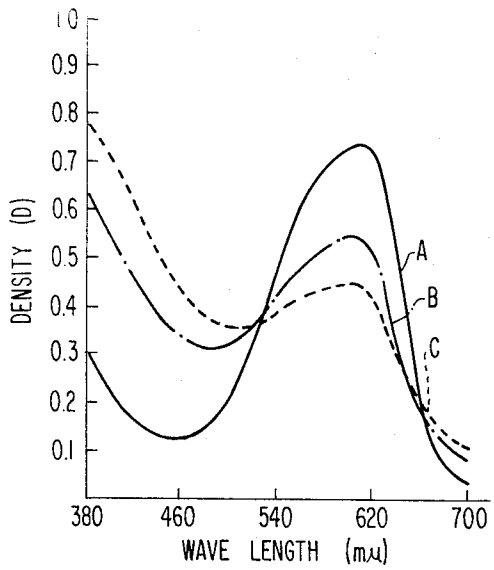


FIG. 1A

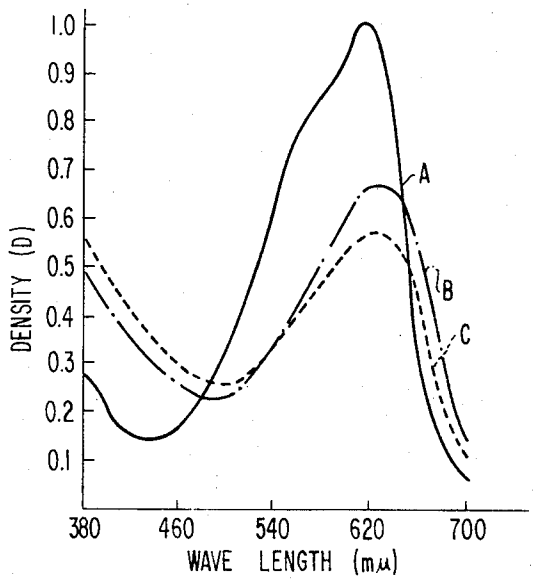


FIG. 2A

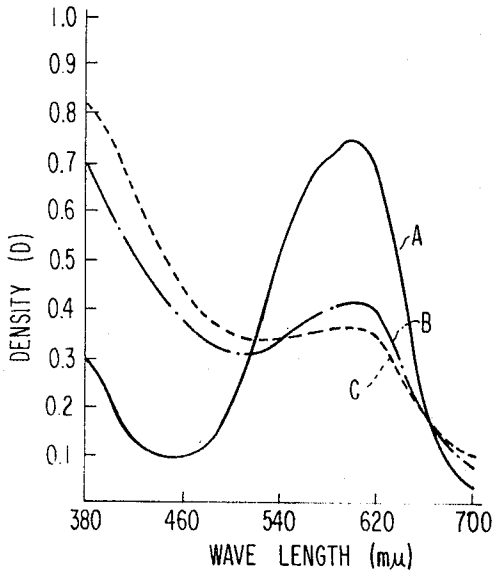


FIG. 1B

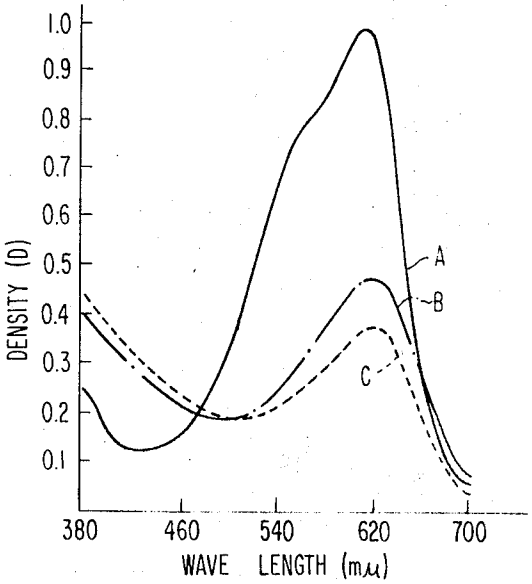


FIG. 2B

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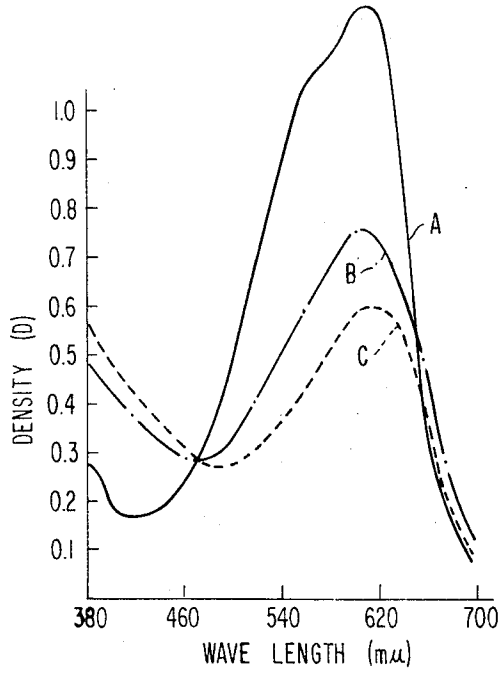


FIG. 3A

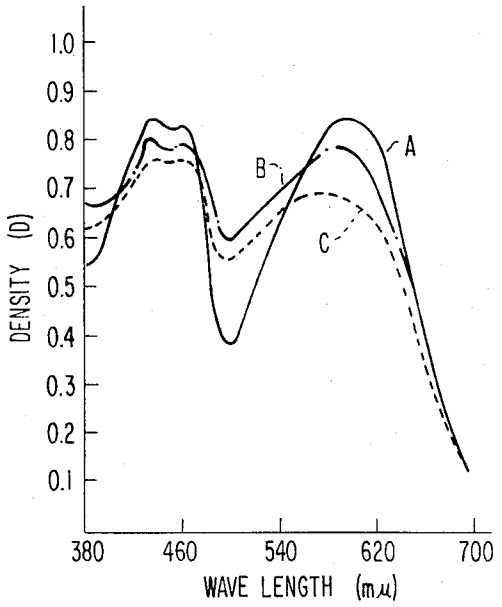


FIG. 4A

FIG. 3B

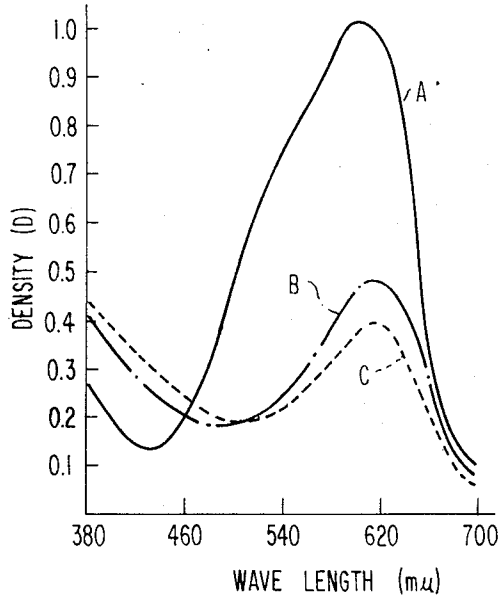
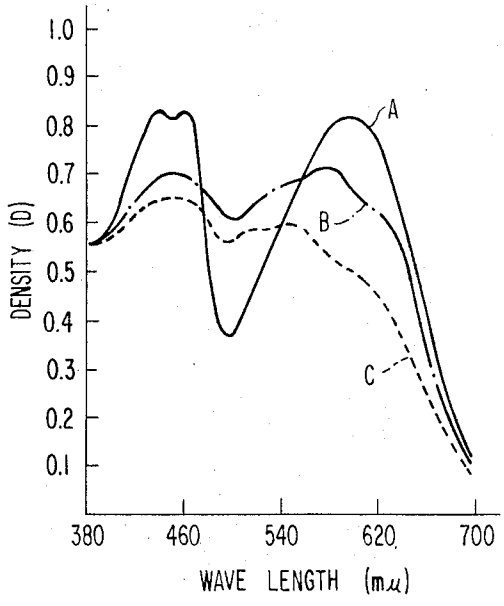


FIG. 4B



SENSITIZING SHEET FOR PRESSURE- OR HEAT-SENSITIVE COPYING PAPER

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a sensitizing sheet for a pressure- or heat-sensitive copying paper. More particularly, the present invention relates to a pressure- or heat-sensitive copying paper using a phenol resin as a sensitizing agent.

2. Description of the Prior Art

Pressure- or heat-sensitive copying papers, as hitherto known, for example, U.S. Pat. Nos. 2,712,507, 2,730,465, 2,730,457 and 3,418,250, utilize a microcapsule containing solution of a substantially colorless organic compound (hereinafter, referred to as the color former) having electron-donating property and coloring reactivity, and an electron accepting adsorbent material (hereinafter referred to as the sensitizing agent).

As typical sensitizing agents, there are, for example, clays, such as acid clay, active clay, attapulgite, zeolite or bentonite, organic acid compounds such as succinic acid, tannic acid or gallic acid and the like.

Recently, the use of a phenol resin has been proposed to increase the stabilities of these sensitizing agents.

That is to say, British Patent No. 1,065,587 discloses the use of an oil-soluble acidic polymer such as a phenol resin together with an acid mineral such as attapulgite as the sensitizing agent, and Japanese Patent No. 511,757 discloses the use of a polymer such as a phenol resin as the sensitizing agent. However, although the phenol resin as the sensitizing agent usually forms a distinct color image stable to water when reacted with a color former, e.g., crystal violet lactone, benzoyl-leucomethylene blue and the like, there are the disadvantages that the color image is inferior in weather resistance, that is, is easily discolored by exposure of sunlight and on standing in a room.

An object of the present invention is to provide an improved pressure- or heat-sensitive copying paper.

Still another object of the present invention is to provide a novel sensitizing agent.

A further object of the present invention is to provide an improved phenol resin useful as the sensitizing agent.

Another object of the invention is to provide a process for making useful, practical pressure-sensitive copying papers and a process for improving the weather-resistance of the phenol resin as a sensitizing agent.

SUMMARY OF THE INVENTION

The foregoing purposes of the present invention can easily be achieved by adding an alkaline material to the phenol resin.

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWINGS

The accompanying drawings, FIGS. 1 to 4, show the spectro-absorbance characteristics in terms of the relationship of density to wavelength of embodiments of the present invention in which an alkaline material was used with a phenol resin in the preparation of a sensitizing sheet in comparison with the comparative examples of sensitizing sheets not prepared in accordance with this invention, as described hereinafter in greater detail.

In each of the Figures, Curves A, B and C represent the spectroabsorption fresh (Curve A), after exposure to sunlight for 1 hour (Curve B), and after exposure to sunlight for 3 hours (Curve C).

DESCRIPTION OF THE INVENTION

The alkaline material is generally dissolved in a solvent such as water, methanol, ethanol and the like, but in case of using an oil-soluble phenol resin, it may be desirable to dissolve it in methanol, ethanol and the like.

Embodiments of the alkaline material include hydroxides or carbonates of alkali metals, such as sodium, potassium and the like, or alkaline earth metals, such as calcium,magnesium and the like.

In the addition of the alkaline material solution to the phenol resin solution, the amount of said alkaline material added may preferably range from 0.5 to 5 parts per 100 parts of said phenol resin. The phenol resin solution can be prepared by dissolving in a solvent such as benzene, toluene, xylene and the like, the phenol resin, which is described in the foregoing British Patent and Japanese Patent, for example, a phenol-aldehyde resin, a phenol-acetylene resin and the like.

The foregoing two types of solvents are not especially limited in the quantitative relation between the solute and the solvent because they are dried and evaporated after applying the solutions to a support. For the purpose of increasing the absorbing property of the phenol resin, it may also be effective to incorporate an adsorbent material, which is only slightly colored even on contact with a color-former, e.g., talc or China clay and or an absorbent material, which is hitherto known as a sensitizing agent, for example, acid clay, active clay, attapulgite and the like, into the solution of the phenol resin and the alkaline material.

The activity in use of these sensitizing agents is increased by the alkaline material, whereby a useful pressure-sensitive copying paper capable of forming a distinct color having a higher density is produced. However, it is most important in the process of the present invention to improve the weather resistance of the color images formed on the phenol resin by the alkaline material, and it is a secondary advantage to increase the activity of the known sensitizing agent.

The foregoing fact is easily clarified since the weather-resistance of the color images is increased even in case of adding less coloring adsorbent material to the coating solution.

One embodiment of the so-obtained phenol resin-containing solution is by coating it singly or together with a microcapsule containing a color former, as described hereinafter, to a support such as paper.

And furthermore, a second embodiment which is also successful involves the steps of applying or laminating the phenol resin onto the support previously and then coating the solution of the alkaline material thereon.

As the color former, there may be used, alone or in combination, crystal violet lactone, benzoyl leucomethylene blue, Malachite green lactone, rhodamine-β-lactam, 3-dialkylamino-7-dialkylaminofluoranes, 3-methyl-2,2-spirobi(benzo-[f]-chromene) and other known compounds.

In general, color formers for the pressure-sensitive copying paper may be generally used as a mixture to complete the instantaneous color formation and the light-resistance of the color image.

Thus, for example, there is well-known the combination of a high speed color former such as crystal violet lactone as the primary color former with a low speed color former having excellent light-resistance such as benzoyl leucomethylene blue.

However, when the combined color formers are contacted with the phenol resin and pressurized, crystal violet lactone rapidly forms a color of the phenol resin layer, but a long time is required until the benzoyl leucomethylene is colored and the color image formed from the crystal violet lactone is easily discolored.

In the case of using a sensitizing agent of the present invention, the foregoing disadvantages are improved and will be clarified by the following Examples.

Generally, although a pressure-sensitive copying paper which forms a black color image is prepared by using mixtures of several color formers imparting several color hues, a pressure-sensitive copying paper of the present invention is capable of forming a pure black image which is not changed under sunlight.

The conventional process of making the microcapsules containing the color former may be conducted by a method disclosed in U.S. Pat. No. 2,800,457, and this embodiment is shown as follows:

10 parts of acid-treated pig-skin gelatin and 10 parts of gum arabic are dissolved in 400 parts of water at 40°C. After adding 0.2 part of Turkey red oil as an emulsifier thereto, 40 parts of a color former oil is emulsified and dispersed therein. The color former oil is prepared by dissolving 2 percent of crystal violet lactone and 1.5 percent of benzoyl leucomethylene blue in an oil consisting of 4 parts of chlorinated diphenyl and 1 part of kerosene.

When the oil droplets obtain an average particle size of 5μ the emulsification is stopped and water heated to 40°C is added to make 900 parts with stirring. In this case, the temperature of the solution should be maintained so that it does not drop below 40°C. Thereafter, the pH value of the solution is adjusted to 4.0–4.2 by adding 10 percent acetic acid to effect the coacervation.

After 20 minutes of continuing to stir the system, the coacervate around the oil droplet is gelled.

7 parts of 37 percent formaldehyde is added when the temperature of the solution becomes 20°C, and when it becomes 10°C the mixture is adjusted to a pH of 9 by adding carefully a 15 percent aqueous caustic soda solution.

Then, the resultant mixture is heated to 50°C with stirring for 20 minutes.

The thus obtained microcapsule mixture is adjusted to 30°C and coated on a paper of 40 g/m² in a proportion of 6 g/m² based on the solids content and then dried.

The following examples will serve to set forth more specifically the present invention without intending to limit it to the examples themselves.

EXAMPLE 1

A phenol resin was obtained by the following polymerization.

170 g of p-phenyl phenol, 65 g of 37 percent aqueous formaldehyde soultion, 10 cc of concentrated (37 percent) hydrochloric acid, 19 g of oxalic anhydride and 40 cc of water were introduced into a reactor and refluxed for 10 hours at the boiling point of water. Thereafter, the reactant was cooled to separate the aqueous layer, and the phenol resinous material was distilled under a reduced pressure until the temperature of the flask became 120°–130°C. The resin was placed in a vessel of stainless steel and cooled to obtain the phenol resin.

10 g of the phenol resin dissolved in 40 cc of xylene was mixed with 0.1 g of caustic soda dissolved in 10 cc of methanol and applied to a paper of 40 g/m² in a proportion of 5 g/m² based on the phenol resin using a coating rod, and dried.

COMPARATIVE EXAMPLE 1

For comparative purposes, a solution of 10 g of said phenol resin in 50 cc of xylene was applied to a paper of 40 g/m², such that 40 g/m² of the phenol resin was coated, using a coating rod and dried.

COMPARATIVE TEST RESULT 1

A capsule sheet having coated thereon a layer of microcapsule containing crystal violet lactone was piled on the sheets of Example 1 and Comparative Example 1, respectively, and pressurized with a pressure of 60 kg/cm² to form a distinct color.

The spectroabsorption curves of the color image after 1 hour were measured at 380–700 mμ wave length, and the curves of the color images after being exposed to sunlight for 1 hour and 3 hours respectively were measured and the results are shown in FIG. 1.

The measurement of the spectroabsorption curves were conducted using a Beckman D B type spectrophotometer produced by Tokyo Shibaura Electric Co., Ltd.

In FIG. 1, FIG. 1A shows Example 1 and FIG. 1B shows Comparative Example 1, in which Curve A shows the fresh density, Curve B shows the density after exposure to sunlight for 1 hour, and Curve C shows the density after exposure to sunlight for 3 hours (these designations are referred to similarly in the following Examples and Comparative Examples).

The values of the light-fastness calculated from the following equation are shown in Table 1.

$$\text{Value of Light Fastness} = \frac{\text{Density at the Maximum Absorption after Exposure to Sunlight}}{\text{Fresh Density at the Maximum Absorption}} \times 100$$

TABLE 1

	Sunlight (1 hr.)	Sunlight (3 hrs.)
Example 1	67.1%	60.8%
Comparative Example 1	54.5%	48.5%

It was confirmed that by incorporation of the alkaline material into the phenol resin, the fastness to light of the crystal violet lactone was markedly improved based on the results shown in the foregoing table and the change of the color hue was reduced based on the absorption curve in the accompanying FIG. 1. On the other hand, a sheet coated with microcapsules containing crystal violet lactone and benzoyl leucomethylene blue was piled on the foregoing sensitizing sheet and pressurized with a pressure of 600 kg/cm² to form a color image. The change of the image density in the maximum absorption (610 mμ) after being allowed to stand in a room was as shown in Table 2.

TABLE 2

Room Storage Time (Days)	Example 1	Comparative Example 1
0	0.750	0.747
5	0.680	0.510
10	0.630	0.470
20	0.560	0.430

Since in the case of a sensitized sheet containing no alkaline material, the formed color image of the crystal violet lactone thereon was markedly discolored on storage for 5 days in a room, and the benzoyl leucomethylene blue was not colored after storing it in a room for 5 days, the color image was markedly faded after 5 days. On the contrary, with a sensitizing sheet with the alkaline material it was difficult to discolor the crystal violet lactone and therefore the density of the color image was not reduced after storing for 5 days.

As described above, it could be clarified that the disadvantages of Comparative Example 1 were markedly improved according to the process of the present invention.

EXAMPLE 2

To a dispersion of 10 g of talc dispersed in 40 cc of xylene was gradually added 10 g of a phenol resin, the same as in Example 1, dissolved in 40 cc of xylene with stirring thereof.

Thereafter, 0.2 g of caustic potash dissolved in 10 cc of methanol was gradually added thereto prepare the paint. The paint was applied to a paper of 40 g/m² in a proportion of 10 g/m² based on the solids content using a coating rod and dried.

COMPARATIVE EXAMPLE 2

To a dispersion of 10 g of talc dispersed in 40 cc of xylene was gradually added 10 g of phenol resin, the same as in Example 1, dissolved in 50 cc of xylene with stirring thereof to prepare the paint. The paint was applied to a paper of 40 g/m² in a proportion of 10 g/m² based on the solid content using a coating rod and dried.

COMPARATIVE TEST RESULT 2

The test was carried out in the same manner as in Comparative Test Result 1, and the absorption curve of the color image after exposure to sunlight was measured using the same spectrophotometer as above and represented in the accompanying FIG. 2. The light fastness value is shown in Table 3.

TABLE 3

	Sunlight (1 hr.)	Sunlight (3 hrs.)
Example 1	66.4%	56.5%
COmparative Example 2	47.3%	38.5%

It could be confirmed, from the foregoing results, that the fastness to light of the crystal violet lactone was markedly improved as in Comparative Test Result 1.

On the other hand, a sheet coated with microcapsules containing crystal violet lactone and benzoyl leucomethylene blue was piled on the foregoing sensitizing sheet and pressurized with a pressure of 600 kg/cm² to form a color image.

The change of the image density at the maximum asorption (610 mμ) after being stored in a room is shown in Table 4.

TABLE 4

Room Storage Time (Delays)	Example 2	Comparative Example 2
0	1.003	0.995
5	0.910	0.860

10	0.850	0.590
20	0.780	0.530

As in Comparative Test Result 1, the effects of incorporating the alkaline material into the phenol resin could be confirmed therefrom.

EXAMPLE 3

To 0.2 g of caustic soda dissolved in 40 cc of water were added 10 g of acid clay and gradually further a solution of the phenol resin, the same as in Example 1, dissolved in 50 cc of a xylene-methyl alcohol mixed solvent (1:1) with stirring of the system. Successively, styrene-butadiene rubber latex (Trade Name: DOW 620), was added in a proportion of 4 g based on the solids content to prepare the applying solution.

The solution was applied to a paper of 40 g/m² in a proportion of 8 g/m² based on the solids content using a coating rod and dried.

COMPARATIVE EXAMPLE 3

10 g of acid clay was gradually added to 50 cc of water with stirring thereof and gradually then mixed with 10 g of the same phenol resin as in Example 1 dissolved in a xylene-methanol mixed solvent (1:1) with stirring thereof.

Successively, styrene-butadiene rubber latex (Trade Name: DOW 620), was added thereto in a proportion of 4 g based on the solids content to prepare the solution.

The solution was applied to a paper of 40 g/m² in a proportion of 8 g/m² based on the solids content using a coating rod and dried.

COMPARATIVE TEST RESULT 3

The test was carried out in the same manner as in Comparative Test Result 1, and the results were as shown in the accompanying FIG. 3 and Table 5.

TABLE 5

	Sunlight (1 hr.)	Sunlight (3 hrs.)
Example 3	61.5%	48.5%
Comparative Example 3	47.3%	39.1%

It could be confirmed, from the foregoing results, that the fastness to light of the crystal violet lactone was markedly improved as in Comparative Test Results 1 and 2.

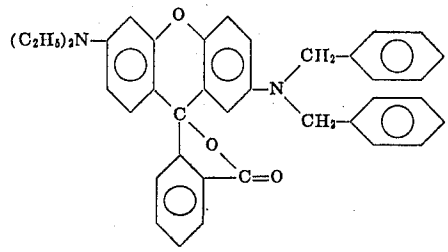
On the other hand, a sheet coated with microcapsules containing crystal violet lactone and benzoyl leucomethylene blue was piled on the foregoing sensitized sheet and pressurized with a pressure of 600 kg/cm² to form a color image. The change of the image density at the maximum absorption (610 mμ) after being stored in a room as shown in Table 6.

TABLE 6

Room Storage Time (Days)	Example 3	Comparative Example 3
0	1.26	1.02
5	1.12	0.780
10	0.960	0.710
20	0.910	0.65

The same effects as in Comparative Test Result 1 could be confirmed.

A sheet coated with microcapsules containing a compound represented by the formula:



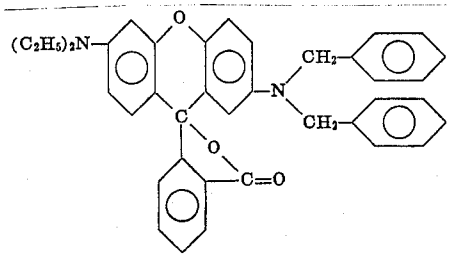
was piled on the foregoing sensitized sheet and pressurized at a pressure of 600 kg/cm² to form an image.

The spectroabsorption curve of said specimen after 1 hour had elapsed was measured, and successively that of the specimen after being exposed to sunlight for 1 hour and 3 hours, respectively, was measured. These results are shown in the accompanying FIG. 4.

From the spectroabsorption curves, it was confirmed that the maximum absorption in Example 3 transferred from initially observed 600 mμ to 570 mμ on exposure to sunlight for 1 hour and further to 589 mμ on exposure to sunlight for 3 hours.

However, for the sensitizing sheet of Comparative Example 3 the maximum absorption transferred from the initially observed 600 mμ to 570 mμ on exposure to sunlight for 1 hour and further to 560 mμ on exposure to sunlight for 3 hours.

As described above, the compound represented by the formula:



exhibited less of a change in hue to the sensitized sheet of Example 3.

What is claimed is:

1. A pressure sensitive copying assembly comprising a color forming sheet containing a substantially colorless color forming, election donating, organic compound and a sensitizing sheet for said color former for use therewith for color formation, comprising a support having thereon a sensitizing layer containing an oil soluble acidic phenol resin and an alkali material selected from the group consisting of sodium hydroxide and potassium hydroxide whereby color formation occurs upon pressurization of said assembly and the contacting of said color former and said sensitizing layer.

2. A pressure sensitive copying assembly comprising a support having thereon a layer of a substantially colorless color forming, election donating, organic compound, and a sensitizing layer for said color former for use therewith for color formation, comprising an oil soluble acidic phenol resin and an alkali material selected from the group consisting of sodium hydroxide and potassium hydroxide whereby color formation occurs upon pressurization of said assembly and the contacting of said color former and said sensitizing layer.

3. The pressure sensitive copying assembly of claim 1, wherein said sensitizing layer comprises a layer of said oil soluble acidic phenol resin and a layer of said alkali material.

4. The pressure sensitive copying assembly of claim 2, wherein said sensitizing layer comprises a layer of said oil soluble acidic phenol resin and a layer of said alkali material.

5. The pressure sensitive copying assembly of claim 3, wherein at least one of said oil soluble phenol resin layer or said alkali material layer additionally contains an adsorbent substance.

6. The pressure sensitive copying assembly of claim 2, wherein at least one of said oil soluble phenol resin layer or said alkali material layer additionally contains an adsorbent substance.

7. The pressure sensitive copying assembly of claim 5, wherein said adsorbent substance is a color-forming substance when contacted with said substantially colorless color former.

8. The pressure sensitive copying assembly of claim 5, wherein said adsorbent substance is a substantially non-color forming substance when contacted with said substantially colorless color former.

9. The pressure sensitive copying assembly of claim 6, wherein said adsorbent substance is a color-forming substance when contacted with said substantially colorless color former.

10. The pressure sensitive copying assembly of claim 6, wherein said adsorbent substance is a substantially non-color forming substance when contacted with said substantially colorless color former.

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