

[54] SHEET CONTAINING DEVELOPER FOR PRESSURE-SENSITIVE RECORDING

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[58] Field of Search..... 117/36.2

[56] References Cited

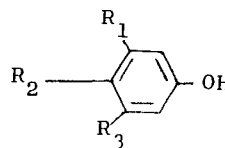
UNITED STATES PATENTS

3,466,185 9/1969 Taylor..... 117/36.2
3,663,256 5/1972 Miller et al. 117/36.2

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[57] ABSTRACT

A pressure sensitive recording developer sheet comprising a phenolic resin developer coating on a support, the improvement which comprises said phenolic resin developer being a resin which is obtained by modifying with an alkylphenol compound represented by the general formula



wherein R₁, R₂ and R₃ which may be the same or different each represents a hydrogen atom or an alkyl group with the proviso that they simultaneously should not be hydrogen atoms, in the condensation of p-phenyl phenol and aldehyde. The coating may also contain microcapsules containing a substantially colorless coupler.

14 Claims, No Drawings

SHEET CONTAINING DEVELOPER FOR PRESSURE-SENSITIVE RECORDING

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a sheet containing a developer for pressure sensitive recording. More particularly, it relates to an improvement in the phenol resin which is used as a developer for pressure sensitive recording.

2. Description of the Prior Art

A pressure sensitive recording sheet utilizes the reaction of an almost colorless organic compound (hereinafter described as the "coupler") and a developing substance which can react with the coupler to form a colored product (hereinafter described as the "developer"). More particularly, it comprises a sheet coated with microcapsules containing a solution of a coupler in an organic solvent (a coupler sheet) and a sheet coated with a developer together with a binder (a developer sheet) and, occasionally a sheet in which a developer is coated on one surface of a support and the microcapsules are coated on the opposite surface (hereinafter described as a pressure sensitive copying sheet). In another embodiment, there is a sheet in which the microcapsules and developer are coated on the same surface of a support.

As couplers, there have been used Malachite Green Lactone, Benzoyl Leuco Methylene Blue, Crystal Violet Lactone, Rhodamine B Lactam, 3-dialkylamino-7-dialkylaminofluorans and 3-methyl-2,2'-spirobi(benzof)cumene), and the like.

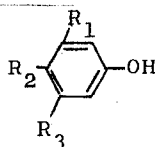
As substances which react with the coupler to form colored products, there have been used generally clays such as acid clay, active earth, attapulgite, zeolite and bentonite; organic acid compounds such as succinic acid, tannic acid and gallic acid. Recently, it has been newly proposed to use a phenol resin as developer. That is, British Pat. No. 1,065,587 describes the combined use of an oil soluble polymer such as a phenol resin and an acid mineral such as attapulgite as a developer and Japanese Pat. No. 511,757 describes also a polymer such as a phenol resin as a developer. While the phenol resin as a developer has excellent properties in that a water stable colored image on reacting with a coupler such as, for example, Crystal Violet Lactone, is formed it has an insufficient developing capacity and tends to change readily to yellow in the daylight or on storage in a room disadvantageously.

An object of this invention is an improved pressure sensitive copying sheet.

Another object of this invention is to use an improved phenol resin as a developer for pressure sensitive recording.

SUMMARY OF THE INVENTION

The above objects of this invention are attained by using a modified phenolic resin as the coupler in the coupler sheet, the phenolic resin being the condensation product of p-phenyl phenol and an alkyl phenol represented by the following general formula



wherein R₁, R₂ and R₃, which may be the same or different, each represents a hydrogen atom or an alkyl group with the proviso that they are not simultaneously hydrogen atoms, and an aldehyde.

DETAILED DESCRIPTION OF THE INVENTION

As examples of phenol compounds represented by the above generally formula which are suitable, there may be mentioned p-cresol, p-ethyl phenol, p-t-butyl phenol, p-t-pentyl phenol, p-nonyl phenol, p-dodecyl phenol, p-octyl phenol, 3,4-xylenol, thymol, and the like.

Wherein R₁, R₂ and R₃, as described above, is an alkyl group, generally the alkyl group will contain from 1 to about 12 carbon atoms. The phenol resin to be used in this invention is obtained by heating p-phenyl phenol, the phenol represented by the above described general formula and an aqueous aldehyde solution in the presence of a catalyst at about 100° to about 200°C for several hours.

In the manufacture of the phenol resin of this invention, from about 0.2 to about 2 mols of the phenol represented by the above general formula are suitable for each mol of p-phenyl phenol. While the amount of aldehyde used has little effect on the resin obtained, from about 0.5 to about 2 mols of aldehyde to each mol of phenol i.e., the sum of the p-phenyl phenol and the alkyl phenol, is preferred.

While formaldehyde, acetaldehyde, propionaldehyde and other aldehydes may be used as the aldehyde employed, the reaction takes place with greater difficulty as the number of carbon atoms of the aldehyde increases. Generally, aliphatic monoaldehydes having from 1 to about 3 carbon atoms are preferred. Formaldehyde is especially preferred.

In general, an acid may be used as catalyst; for example, hydrochloric acid, sulfuric acid, oxalic anhydride and the like are suitable.

The amount of the catalyst used can be varied and in general from about 5 to about 20cc of 37% hydrochloric acid and from about 1 to about 10g for oxalic anhydride can be used. In the use of a solid catalyst, it may be dissolved in a solvent for use.

The resulting modified phenol resin is separated from the liquid phase, dissolved in an organic solvent such as acetone, methyl ethyl ketone, butyl acetate, benzene, toluene, xylene and the like or dispersed in an aqueous binder solution and coated on a paper surface. In another embodiment, the modified phenol resin can be dissolved in an organic solvent, dispersed in aqueous binder solution and coated on a paper surface.

As binders, styrene-butadiene latex, maleic anhydride-styrene copolymer, polyvinyl alcohol, starch, casein, ethyl cellulose, styrene-butadiene copolymer, polyvinyl acetate, polyvinylidene chloride, vinyl chloride-vinylidene chloride copolymer and the like are suitable.

The amount of binder generally used ranges from about 5 to about 30 parts by weight per 100 parts by weight of the modified phenol resin.

The developer layer of this invention may contain clay minerals having a developing capacity, e.g., Japanese acid clay or active clay or an inorganic pigment having an adsorption capability or a mixture thereof.

In comparison with developer sheets using previous phenol resins, the developer sheet using the phenol resin obtained in this invention has a strong developing

capacity with respect to the coupler and excellent properties in that it changes to yellow in the daylight or on storage in a room with difficulty.

The phenol resins described in the above referred British Pat. No. 1,065,587 and Japanese Pat. No. 511,757 were obtained by the condensation of a single phenol compound with an aldehyde. As discussed above, however, the developer sheet for pressure sensitive copying using this phenol resin of a single phenol compound does not have sufficient developing capacity and tends to be discolored into yellow in the daylight or on storage in a room.

The phenol resin according to this invention is obtained by the condensation of at least two phenol compounds with an aldehyde. The developer sheet for pressure sensitive copying using the phenol resin obtained by the method as described above employing at least two phenol compounds has excellent properties in that it has a strong developing capacity and changes with difficulty into yellow in the daylight or on storage in a room.

When the relation between the chemical composition of the phenol resin of this invention and developing capacity and yellow discoloration resistance of the developer sheet for pressure sensitive copying based on the fact as mentioned above, it is obvious that a useful effect is obtained by the use of the phenol resin prepared by using more than two kinds of phenol compounds as in this invention.

The following examples illustrate in greater detail the and practical advantages brought by a developer sheet for pressure sensitive copying which comprises a phenol resin prepared using at least two phenol compounds as in this invention. These examples are not to be interpreted as limiting the invention described herein.

The effect of the developer sheet according to this invention was demonstrated with the following coupler sheet:

A microcapsule containing coupler was prepared, for example, according to disclosure in U.S. Pat. No. 2,800,457 and an example thereof is described as follows:

10 parts of pig leather acid-treated gelatin and 10 parts of gum arabic are dissolved in 400 parts of water, 0.2 part of Turkey red oil is added as an emulsifier and 40 parts of oil coupler are emulsified therein. The coupler oil contains 2% of Crystal Violet Lactone dissolved in an oil consisting of 4 parts of diphenyl chloride and 1 part of kerosene.

When the size of the oil droplets is on an average of 5μ , the emulsification is ceased. Water at 40°C is added thereto to make 900 parts total and the stirring is continued, during which time the liquid temperature should fall below 40°C . 10% acetic acid is then added to adjust the pH-value of liquid to 4.0 - 4.2 resulting in coacervation. After stirring for a 20 minute period, it is cooled by ice water to gel the coacervate film deposited around the oil droplets. When the liquid temperature is 20°C , 7 parts of 37% formaldehyde are added. 15% aqueous sodium hydroxide is added dropwise at 10°C to adjust the pH-value to 9, during which time the addition of the sodium hydroxide should be carried out with the utmost care. Successively, it is heated for 20 min with stirring to make the liquid temperature 50°C .

Thus, the resulting microcapsules are conditioned at 30°C , coated in an amount of $6\text{g}(\text{solid})/\text{m}^2$ on a paper of $40\text{g}/\text{m}^2$ and dried.

Other coupler containing sheets using microcapsules containing Malachite Green Lactone, Benzoyl Leuco Methylene Blue, Rhodamine B Lactum, 3-dialkylamino-7-dialkylamino-fluorans and 3-methyl-2,2'-spiro (benzo (f) cumene) or mixtures thereof as the couplers were prepared in the same manner as described above for the Crystal Violet Lactone.

EXAMPLE 1

85g of p-phenyl phenol, 75g of p-t-butyl phenol, 100g of aqueous 37% formaldehyde, 10 ml of conc. hydrochloric acid (37%) and 50 ml of water were placed in a kettle to prepare the resin and heated at 140°C for 10 hrs. The resulting resin was cooled and then ground. 10g of the resulting resin were dissolved in 40 ml of acetone, coated in an amount of $2\text{g}/\text{m}^2$ and dried.

CONTROL 1

170g of p-phenyl phenol, 100g of aqueous 37% formaldehyde, 10 ml of conc hydrochloric acid (37%) and 50cc of water were placed in a kettle for to prepare a resin and heated at 140°C for 10 hrs. The resulting resin was cooled and then ground. 10g of the resulting resin were dissolved in 40 ml of acetone, coated in an amount of $2\text{g}/\text{m}^2$ on a paper of $40\text{g}/\text{m}^2$ and dried.

EXAMPLE 2

85g of p-phenyl phenol, 55g of p-nonyl phenol, 50g of aqueous 37% formaldehyde, 10g of oxalic anhydride and 50 ml of water were placed in a kettle to prepare the resin and heated at 180°C for 5 hrs. The resulting resin was cooled and then ground. 10g of the resulting resin were dissolved in 40 ml of benzene, coated in an amount of $2\text{g}/\text{m}^2$ on a paper of $40\text{g}/\text{m}^2$ and dried.

CONTROL 2

127.5g of p-phenyl phenol, 50g of aqueous 37% formaldehyde, 10g oxalic anhydride and 50 ml of water were placed in a kettle to prepare the resin and heated at 180°C for 5 hrs. The resulting resin was cooled and then ground. 10g of the resulting resin were dissolved in 40 ml of benzene, coated in an amount of $2\text{g}/\text{m}^2$ on a paper of $40\text{g}/\text{m}^2$ and dried.

EXAMPLE 3

85g of p-phenyl phenol, 91.5g of 3,4-xyleneol, 50g of aqueous 37% formaldehyde, 10 ml of conc. hydrochloric acid (37%), 1g of oxalic anhydride and 50 ml of water were placed in a kettle to prepare the resin and heated at 160°C for 8 hrs. The resulting resin was cooled and then ground. 10g of the resulting resin were dissolved in 40 ml of methyl ethyl ketone, coated in an amount of $2\text{g}/\text{m}^2$ on a paper of $40\text{g}/\text{m}^2$ and dried.

CONTROL 3

212.5g of p-phenyl phenol, 50g of aqueous 37% formaldehyde, 10 ml of conc. hydrochloric acid (37%), 1g of oxalic anhydride and 50 ml of water were placed in a kettle to prepare the resin and heated at 160°C for 8 hrs. 10g of the resulting resin were dissolved in 40 ml of methyl ethyl ketone, coated in an amount of $2\text{g}/\text{m}^2$ on a paper of $40\text{g}/\text{m}^2$ and dried. In order to compare the samples prepared as described above, the following procedure was followed.

1. A microcapsule-coated paper containing Crystal Violet Lactone as a coupler was placed respectively on the developer sheet of Examples 1, 2 and 3 and Con-

trols 1, 2 and 3 and developed by applying a load pressure of 600 kg/cm². After standing for 1 hour in the dark, the spectral absorption curve in the wave length range of 700 - 400 mμ was measured and the developing capacity of each developer sheets was examined using the density (D₁) at the maximum adsorption (610 mμ).

2. After exposing each developer sheet of Examples 1, 2 and 3 and Controls 1, 2 and 3 to the sun for 5 hrs, the whiteness of each sheet was determined using a Hunter Brightness Meter and the yellowing tendency of developer sheet was measured based on the whiteness value.

The results of (1) and (2) are shown in Table I.

Table I

	Developing Capacity (D ₁) for Crystal Violet Lactone	Whiteness after Sun Exposure for 5 hrs.
Example 1	0.934	57.4
Control 1	0.713	41.8
Example 2	0.877	52.5
Control 2	0.640	37.3
Example 3	0.878	55.7
Control 3	0.795	40.6

The same effect was obtained for the other couplers described herein before.

EXAMPLE 4

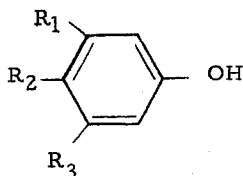
100 g of the resin obtained in Example 1 is mixed with 10g of styrene-sodium maleic anhydride using a ball-mill for a period of 24 hours. The resulting composition is coated in an amount of 3g/m² on a dye-containing microcapsule coated paper and then dried. A single-sheet type pressure recording paper was obtained.

EXAMPLE 5

The resins obtained as in Examples 2 and 3 are coated in the same manner as described in Example 4 to obtain a single-sheet type pressure-sensitive recording paper. While the above invention has been described in detail and with reference to certain embodiments thereof, it will be recognized that modifications and variations can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. In a pressure sensitive recording developer sheet comprising a phenolic resin developer coated on a support, the improvement which comprises said phenolic resin developer being the condensation product of p-phenyl phenol and at least one alkyl phenol represented by the general formula



wherein R₁, R₂ and R₃, which may be the same or different, each represents a hydrogen atom or an alkyl group, said alkyl group containing from 1 to 12 carbon atoms, with the proviso that R₁, R₂ and R₃ are not simultaneously a hydrogen atom, with an aldehyde, wherein said alkyl phenol is present in said condensation product at a level of from about 0.2 to about 2

moles of said alkyl phenol per mole of p-phenyl phenol and said aldehyde is present at a level of from about 0.5 to about 2.0 moles of aldehyde per total moles of phenol.

2. The sheet of claim 1 wherein said alkyl phenol is selected from the group consisting of p-cresol, p-ethyl phenol, p-t-butyl phenol, p-t-pentyl phenol, p-nonyl phenol, p-dodecyl phenol, p-octyl phenol, 3,4-xylenol, and thymol.

3. The sheet of claim 1, wherein said aldehyde is selected from the group consisting of formaldehyde, acetaldehyde and propionaldehyde.

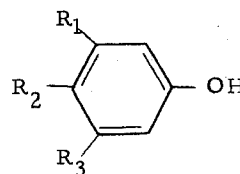
4. The sheet of claim 3, wherein said aldehyde is formaldehyde.

5. The sheet of claim 1, wherein said phenolic resin developer is incorporated into a binder coated on said support.

6. The sheet of claim 5, wherein said binder is selected from the group consisting of styrene-butadiene latex, maleic anhydride-styrene copolymer, polyvinyl alcohol, starch, casein, polyvinylidene chloride and vinyl chloride-vinylidene chloride copolymer.

7. The sheet of claim 5 wherein said binder is present at a level of from about 5 to about 30 parts by weight for each 100 parts by weight of said phenolic resin.

8. In a pressure sensitive recording sheet comprising a support having coated thereon microcapsules containing a substantially colorless coupler and a phenolic resin developer, said coupler being one which forms a color upon contact with said phenolic resin developer, the improvement which comprises said phenolic resin developer being the condensation product of p-phenyl phenol and at least one alkyl phenol represented by the general formula



where R₁, R₂ and R₃, which may be the same or different, each represents a hydrogen atom or an alkyl group having 1 to 12 carbon atoms, with the proviso that R₁, R₂ and R₃ are not simultaneously a hydrogen atom, with an aldehyde, wherein said alkyl phenol is present in said condensation product at a level of from about 0.2 to about 2 moles of said alkyl phenol per mole of p-phenyl phenol and said aldehyde is present at a level of from about 0.5 to about 2.0 moles of aldehyde per total moles of phenol.

9. The sheet of claim 8 wherein said alkyl phenol is selected from the group consisting of p-cresol, p-ethyl phenol, p-t-butyl phenol, p-t-pentyl phenol, p-nonyl phenol, p-dodecyl phenol, p-octyl phenol, 3,4-xylenol, and thymol.

10. The sheet of claim 8, wherein said aldehyde is selected from the group consisting of formaldehyde, acetaldehyde and propionaldehyde.

11. The sheet of claim 10, wherein said aldehyde is formaldehyde.

12. The sheet of claim 8, wherein said phenolic resin developer is incorporated into a binder coated on said support.

13. The sheet of claim 12, wherein said binder is selected from group consisting of styrene-butadiene latex, maleic anhydride-styrene copolymer, polyvinyl alcohol, starch, casein, polyvinylidene chloride and vinyl chloride-vinylidene chloride copolymer.

14. The sheet of claim 12 wherein said binder is present at a level of from about 5 to about 30 parts by weight for each 100 parts by weight of said phenolic resin.