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RECORD MATERIAL

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ABSTRACT OF THE DISCLOSURE

Sensitized record sheet material, suitable for developing useful color in oily, colorless, chromogenic dye-precursor inks applied thereto. Said record sheet material has a coating comprising an oil-soluble metal salt and an oil-soluble phenol-formaldehyde novolak resin.

This invention relates to record material sheets bearing a coating of an oil-soluble metal salt and an oil-soluble phenol-formaldehyde novolak resin as a combination co-reactant for colorless, chromogenic dye-precursor materials to develop a useful color therein. Oil-soluble phenol-formaldehyde novolak resins, preferably those derived from the condensation of a para-substituted phenol with formaldehyde, have long been used, with great commercial success, in making acid-reactant record material sheets capable of developing color in oil solutions of base-reacting colorless, chromogenic dye-precursor materials. Such resins and the use of them are disclosed in applications for United States patents, Ser. Nos. 44,805, filed June 9, 1970 by Robert E. Miller and Paul S. Phillips, Jr., now U.S. Pat. 3,672,935 and 830,921, filed May 26, 1969 by Robert E. Miller and Bruce W. Brockett, now U.S. Pat. 3,663,256.

U.S. Pat. 3,516,845, which issued June 23, 1970 on application of Bruce W. Brockett, represents an improvement on the known-art acid-reacting record material sheets of the previously cited applications. In the Brockett improvement patent, acidic, water-soluble metal salts, such as zinc chloride, are provided in the sheet coating, intermixed and juxtaposed with particles of oil-absorptive kaolin clay and oil-soluble phenol-formaldehyde resin particles. The metal salt-kaolin-phenolic resin combination gives improved intensity and fade resistance to the developed color of prints made thereon with base-reacting colorless chromogenic dye-precursor materials. A definite synergistic effect was noted wherein the improvement was greater than that which was predicted by the arithmetic combination of intensities and fade rates obtained on prints developed by the three agents (kaolin, zinc chloride and phenolic resin) separately. Thus, certain water-soluble salts and certain oil-soluble resins mixed together with kaolin on a receiving sheet represents an improvement in the art.

Now it is found that the record sheet materials of this invention constitute a further improvement wherein both the metallic moiety and the acidic resin are oil-soluble and both are available for color-developing reaction in oil solution. This improvement can be realized by providing on the sheet surface oil-soluble metal salts and oil-soluble phenol-formaldehyde resins.

It has been found that the amount of color developed in a fixed amount of a colorless chromogen, such as CVL in fixed concentration in oil solution, by a phenolic resin is greatly enhanced by the replacement of part of the resin's phenolic protons with certain metal ions such as zinc(II). Such a proton replacement gives a metal resinate, also called herein a metal-modified resin. The use of metal resinates as co-reactant color-developers for basic color-blocked, chromogenic dye-precursors is taught in the co-pending United States application No. 152,830 filed this day in the names of the present inventors.

It is an object of this invention to give an improved acid-reactant "carbonless copy-paper" receiving sheet without the necessity of providing a separately-manufactured metal-modified resin for use herein.

It is a further object of this invention to provide certain metal salts and certain phenol-formaldehyde resins that are mutually soluble in oily solvents for color-developing reaction with base-reacting, colorless or lightly colored, chromogenic, dye-precursor materials in oil solution.

Furthermore, an object of this invention is to realize improvements in the speed and intensity of print development as well an improvements in stability toward the environment of the coated developing agent prior to print color-development and of the dye color in the developed print without resorting to coatings of water-soluble metal salts together with the commonly-used novolak resins. Novolak powder particles are commonly bound to paper with cooked starch binder and latex binders such as styrene-butadiene latexes, but novolaks in combination with zinc chloride and other useful water-soluble metal salts cannot be successfully bound to paper with latexes and/or cooked starch binder, thereby necessitating the use of other binders such as poly(vinyl alcohol). Adequate adhesion is difficult to achieve with poly(vinyl alcohol) as the sole binder and furthermore such sheets do not give good printing characteristics with offset printing presses and inks.

These and other objects have been realized by this invention.

In general, the metal-modified resins of the above-cited co-pending application give greater improvement in the sheet properties than does the combination of oil-soluble metal salts and oil-soluble novolak resins of the present invention. However, the combination of the present invention can be made more economically and does show performance advantage over the unmodified novolak resins of the known art.

The metal salts and phenol-formaldehyde resins provided herein react with basic chromogens, particularly with Crystal Violet lactone, to give more intense and more fade-resistant prints than do known-art resins alone. The acid-reacting receiving sheets provided herein are also more stable to environmental influences prior to imaging use than are known-art receiving sheets. The rate at which full color-intensity is realized when acid-reacting sheets are treated with oil solutions of base-reacting chromogens, a sheet-property known as "print speed," is comparable for the sheets of this invention to sheets of good commercial quality.

The metal salts found useful herein for use with oil-soluble phenol-formaldehyde resins in pressure-sensitive copy-papers of the "NCR Paper" type include the oil-soluble salts of aluminum(III), barium(II), cadmium(II), calcium(II), cerium(III), cesium(I), cobalt(II), copper (III), indium(III), iron(II) and (III), lead (II), magnesium (II), manganese (II), molybdenum(V), nickel(II), sodium(I), strontium(II), tin(II), titanium(IV), vanadium(IV), zinc(II), and zirconium(IV). The great diversity of the oil-soluble metal resinates tested and found useful herein should be noted inasmuch as they include metals from Periodic Groups I–A and B, II–A and B, III–A and B, IV–A and B, V–B, VI–B, VII–B, and VIII.

Eligible anions of the useful metal salts include acetylacetonate, hexafluoroacetylacetonate, benzoate, naphthenate, salicylate, 2-ethylhexanoate, abietate, oleate, and palmitate. In order to be eligible, the candidate anion should confer on the metal salt ready solubility in the oily solvents used as the core-material in encapsulated chromogenic inks in carbonless copy-papers. Exemplary of the oils in use are hydrocarbons such as paraffin oils, aromatic oils such as xylene and alkylated biphenyls, high

molecular weight esters such as dioctyl adipate and dioctyl phthalate, halocarbons such as trichlorobiphenyl, and aromatic ethers such as diphenyl oxide. The metal-modified resins of this invention are designed to operate and do operate well in developing oily dye-precursor inks of the type described. The oily vehicle preferred herein is one of low volatility, such as chlorinated or alkylated biphenyl, which leaves an essentially wet print on the paper surface rather than a more volatile one such as xylene that readily evaporates to leave a dry print. The enhancement of print intensity by the metal-modified resins of this invention is considerably greater in wet prints than in dry prints. Rapid and substantial solubility is required to give satisfactory print speed in use. To fulfill this requirement, the metal salt anion should have a carbon content of at least four carbon atoms and preferably six or more carbon atoms. Metal salts of anions of less than four carbon atoms will operate to enhance color intensity and/or fade resistance provided they are still oil-soluble. However, as the anionic carbon content goes below about four carbon atoms, the metal salts tend toward water solubility, and the imaged prints. developed thereon, become spotty and uneven due to the effect of atmospheric moisture on stored sheets. Therefore metal salts of carbon content below about four carbon atoms, which are both oil-soluble and water soluble, are to be avoided in the record material sheets of this invention.

Of the metal ions set out above as having been found useful herein, zinc(II) is preferred. All of the cited metal ions improve the fade resistance of the developed prints. In addition to improved fade resistance, print intensity is markedly improved over known-art sheets by the preferred zinc(II) and furthermore, print intensity is improved or at least comparable to good commercial quality known-art sheets in sheets containing aluminum(III), cerium(III), cobalt(II), iron(II), iron(III), indium(III), manganese(II), and tin(II).

A further object of this invention is to make a color-developing agent for basic-chromogens that is completely oil-soluble (unlike acidic clays and the combination agents exemplified by paraphenylphenol-formaldehyde resin together with zinc chloride and other water-soluble metal salts) so that it may be used in a variety of ways including particulate coating on a sheet, solution coating on a sheet and coating as encapsulated droplets of an oil solution. Either or both of the two-color-developing co-reactant materials, the selected oil-soluble novolak and the selected oil-soluble metal salt may be dissolved in oil for encapsulation or for coating as a solution residue on substrate sheets. When both the selected novolak and the selected metal salt are dissolved in oil in mutual solution, at least some, that is appreciable amounts, of metal resinate material is formed in the solution, depending in part on the selection of the oil and the two color-developing materials. As is taught in the co-pending application of this date, zinc naphthenate and para-phenylphenol - formaldehyde resin in 1,2,4 - trimethylbenzene readily form the zinc resinate in solution.

The objects set out above and other objects have been realized by the embodiments of this invention.

In general, it has been found that the effectiveness of metal salts in enhanching acidic resin color-production, in chromogenic dye-precursors such as CVL, is inversely related to the chelating ability of the metal in the metal salt. For instance, metals that form very stable chelates with acetylacetone, having stability constant logs ($\log_{10} K_{stability}$ corrected to zero ionic strength) greater than about 5.5 do not enhance CVL color-production when used in conjunction with acidic resins. The metals of more unstable metal-acetylacetone chelates, having stability constant logs less than about 5.5, will be found to enhance CVL-resin color intensity in solution. Such metallic ions are designated herein as color-enhancing metals. That is to say, solutions of CVL, metals salts and novolak resins will show higher optical densities as the stability constants of the chelates of the chosen metals and acetylacetone decrease. However, it should be noted that there will be wide variance among the oil-solubilities of these color-enhancing metal salts which will affect the maximum concentration of the colored species attainable in the chosen vehicle oil. In any chosen record-material system, the most useful metal salts will be those of color-enhancing metals which are readily soluble in the liquid vehicle droplets used in the record material system capsules. For a metal to be useful as a color-enhancer with a novolak resin in a record material copy sheet, the metal must be a color enhancer and must be present as a metal salt which is readily soluble, in the presence of the chosen novolak, in the oil droplets included in the copy paper.

In the preceding discussion, the metal salts and novolak resins of this invention are viewed as being coated on a receiving sheet for the receipt and development of color in liquid dye-precursor materials, but they are not so-limited in use. As is taught in the previously-cited application of Miller and Phillips, there are various ways of arranging, in a record material, the different components of a color-developing system comprising oil-soluble dye-precursor material, oil-soluble polymeric resin co-reactant material and mutual-solvent oil. FIG. 2 of the Miller-Phillips application shows a number of such arrangements. Any and all of the metal salts and novolak resins of this invention, either taken separately or together, may be coated on paper or dissolved in oil and encapsulated as solution droplets prior to being coated on paper so as to operate in the record-material constructions of the Miller-Phillips application's FIG. 2. The metal salts and novolak resins of this invention are oil-soluble, are grindable to a fine powder, and are encapsulatable as fine oil-solution droplets either separately or together. So they are adaptable for use in any of the ways Miller and Phillips envisioned and taught that oil-soluble polymeric resin co-reactants could be used.

Similarly, the metal salts and novolak resins of this invention may be (1) applied to a sheet from a printing solution as taught in the aforementioned Miller-Phillips application and in U.S. Pat. No. 3,466,184 which issued Sept 9, 1969 on the application of Richard G. Bowler and Robert E. Miller, (2) applied as a substratum below the surface of a fibrous record material as taught and claimed in U.S. Pat. No. 3,466,185 which issued Sept. 9, 1969 on the application of John E. G. Taylor, (3) applied as a particulate, finely ground powder as taught in the aforementioned Miller-Phillips application or in combination with an oil-adsorbent coating-clay such as kaolin as taught and claimed in U.S. Pat. No. 3,455,721, which issued July 15, 1969 on the application of Paul S. Phillips, Jr., and Gerald M. Hein, and (4) applied as a coating on individual particles of paper-coating pigment material as taught and claimed in United States application Ser. No. 807,960 which was filed Mar. 17, 1969 in the name of Bruce W. Brockett.

The use of oil-soluble novolak resins together with oil-soluble metal salts as herein described offers somewhat more versatility in mode of aplication to a substrate sheet than does the use of the metal resinates described in the aforementioned co-pending application of this date. For instance, a solution of a novolak resin may be applied to a sheet as encapsulated droplets together with finely ground particles of an oil-soluble metal salt which may be interspersed with the resin-containing microcapsules or coated on a dye-sensitized receiving sheet to be used in conjunction with the resin-containing microcapsule-coated sheet.

As with the metal-modified resins or metal resinates, the selection of the metal of the metal salt for use herein is of little consequence as far as improving fade resistance of the developed print is concerned. Selection for good print intensity is more important. Some metals found to work well in improving print intensity as metal resinates

do not work well as oil-soluble metal salts mixed with resins and vice versa. Furthermore, mixtures of metal salt and phenolic resin appear to be more limited than metal resinates in their application to different base-reacting chromogenic dyes. The mixtures described herein serve to improve the prints made with Crystal Violet lactone (CVL) and its structural analogs (namely color-blocked 4,4' - diaminodiphenylmethane derivatives) more markedly than prints made with base-reacting chromogenic fluoran dyes. This selectivity with respect to useful dyes suggests that at least part of the beneficial effects observed with the resin-salt mixtures described herein is due to direct chemical reaction between the chromogenic dye and the metal salt, rather than chemical combination between the resin and the metal salt to make a metal resinate which then reacts with the chromogenic dye, as one would suppose on the assumption of strict analogy between the resin-salt mixture and the above discussed metal resinates.

It is not known whether or not reaction actually occurs between the metal salts of this invention and chromogens such as CVL or whether the product of such reaction, if it occurs, is colorless or colored. Zinc salicylate, which has a phenolic group in addition to the metallated carboxy group, gives a blue color with CVL in oil solution. Oil solutions of some of the other eligible metal salts occasionaly give a light blue color when CVL is added to the solution, but this is thought to be due to excess acid present as a contaminant in the metal salt. At any rate, a solution of a metal salt in an oil, preferably a volatile oil, can be printed over a CVL-containing sheet coating without observable development of color therein. The resulting colorless over-printed sheet coating gives a good surface, containing two color-forming reactants (namely metal salt and CVL), to receive an oil solution of a novolak resin and give an improved print. Furthermore, as in Example 4, both the colorless chromogenic dye-precursor materials and the metal salts of this invention can be dissolved in oil together, without substantial coloration, and be encapsulated and coated onto paper sheets for use as transfer sheets with standard phenolic resin-containing receiving sheets. Zinc salicylate and any other metal salt that gives some degree of color-development with CVL in oil solution can be used for the metal-salt over-print preparation and for the preparation of microcapsules containing droplets of oil solution of CVL and metal salt material, but these materials are not preferred because color-development therein with acidic novolak resin material gives a dark-blue print on a light-blue background. Preferred for use in constructions where CVL and metal salts actually come into oil-solution contact prior to color-development-use are the following zinc(II) salts: acetylacetonate, caprylate, laurate, 2-ethylhexanoate, oleate, abietate, and naphthenate, which give little or no observable coloration when dissolved in oily CVL solutions.

Useful weights of materials for the practice of this invention fall within the range of one part of metal ion as an oil-soluble metal salt to one to twenty parts of an oil-soluble phenol-formaldehyde novolak resin. Weights in this range of the color-developing co-reactant materials in combination operate well to develop chromogenic dye-precursor materials such as Crystal Violet lactone present to the extent of one-half to ten parts. A good practical combination of color-forming reactants is ten parts of resin to one part of metal ion to one part of chromogenic dye-precursor.

In the following examples, all parts are parts by weight and all solution percents are weight percents unless otherwise stated.

EXAMPLE 1

Novolak-metal salt coated receiving (CF) sheets.—A

paper-coating slurry of 30 percent solids content was prepared by mixing the following ingredients:

	Parts (dry)	Parts (wet)
para-Phenylphenol-formaldehyde resin	381	381
Zinc acetylacetonate	190	190
Kaolin clay	3,429	3,429
Silica gel	165	165
Calcium carbonate	500	500
Styrene-butadiene latex binder	360	720
Cooked starch binder	510	2,550
Water		9,600

Bond paper (33 pound base stock) was coated on an air knife coater (air-pressure 2.75 pounds/square inch) and dried, by a 12-second pass through a high-velocity-air oven at an average temperature of about 190 degrees Fahrenheit, to give a dry-coat weight of 4 pounds per ream of 500 sheets (25 by 38 inches) having a total area of 3,300 square feet.

Commercial "NCR Paper" CB sheets, having capsular coatings containing oily solution droplets of Crystal Violet lactone (CVL) and benzoyl leuco methylene blue (BLMB), were coupled with the above CF sheets to make a mark-producing, transfer-receiving sheet couple.

Alternatively, a solution of zinc salt, such as zinc acetylacetonate in a volatile organic solvent such as acetone, can be applied to the kaolin clay particles which can then be dried to give a free flowing powder of kaolin particles having the zinc salt adsorptively held thereon. The zinc salt-coated kaolin particles can then be applied to the sheet in place of the zinc acetylacetonate and kaolin clay in the above paper-coating slurry. This latter method is particularly useful for non-crystalline zinc salts that are difficult to grind, such as zinc naphthenate, zinc oleate and zinc 2-ethylhexanoate.

EXAMPLE 2

Metal salt-novolak transfer (CB) sheets.—A paper-coating slurry was prepared by mixing the following ingredients:

	Parts (dry)	Parts (wet)
Zinc abietate	12	12
Novolak-containing microcapsules	38	130
Alpha-cellulose floc fibers	16	16
Poly(vinyl alcohol) binder (5 percent, aqueous)	6	120
Water		122

The microcapsules were made with core material of para-phenylphenol-formaldehyde resin (17 percent in xylene), according to the method of Robert G. Bayless and Donald D. Emrick taught and claimed in U.S. patent application Ser. No. 701,124, filed Jan. 29, 1968.

The above slurry was coated onto paper sheets and dried to give a dry-coat weight of 4.5 pounds per specified ream. The so-coated sheets were used as transfer sheets against receiving sheets, sensitized by being dipped into a 1.5 percent solution of CVL in acetone and dried. The transfer-receiving sheet couples gave good transfer prints that were remarkably fade-resistant.

EXAMPLE 3

CVL-metal salt coated receiving (CF) sheets.—A thick slurry of 99 parts of calcium carbonate in 400 parts of a 1 percent solution of CVL in acetone was stirred occasionally in an open tray to allow evaporation of the acetone to give a free-flowing powder of calcium carbonate particles having CVL adsorbed thereon. A paper coating slurry was prepared by mixing 203 parts of the CVL-coated calcium carbonate particles prepared above with 20 parts of 35 percent aqueous sodium silicate, 200 parts of 5 percent aqueous poly(vinyl alcohol) solution and sufficient water to give a final solids content of 30 percent. The paper-coating slurry of this example was

coated as in Example 1 onto bond paper stock at 2.0 pounds per ream. The so-coated sheets were then over-printed with a benzene solution containing one percent zinc as the naphthenate salt, to give a CVL-metal salt coated CF sheet which readily gave satisfactory prints when written on with a 20 percent solution of paraphenyl-phenol-formaldehyde resin in dioctyl phthalate. The resin solution was supplied either by pen or from an overlying CB sheet having resin solution droplets encapsulated and coated thereon.

Equivalent CVL-metal salt coated CF sheets were also obtained by grinding similar quantities of CVL and zinc acetylacetonate together and coating the resulting powder on paper sheets from an aqueous slurry with cooked starch binder material. However the rate of color-development of pressure prints made on the latter sheets is considerably less than that on the over-printed type.

EXAMPLE 4

Metal salt-CVL transfer (CB) sheets.—A solution of CVL (1.5 percent) and zinc naphthenate 2-ethylhexanoate (4.3 percent) in dioctyl phthalate was encapsu'ated according to the procedure taught and claimed in U.S. Pat. No. 3,533,958 which issued on Oct. 13, 1970, on application of I. L. Yurkowitz. The resulting microcapsules were coated onto bond paper sheets at a weight of 2.5 pounds/specified ream using the following slurry:

	Parts (dry)	Parts (wet)
Microcapsules	38	130
Alpha cellulose floc fibers	16	16
Cooked starch binder	8	40
Water		192

The resulting transfer sheet gave good, fade-resistant prints on novolak resin-containing receiving sheets made according to the previously mentioned patent of Phillips and Hein.

What is claimed is:

1. A pressure-sensitive record sheet material comprising supporting web material having adhesively bound on at least one surface thereof at least three color-forming reactants, one of which is an acid-colorable, colorless, chromogenic dye-precursor material, a second of which is an oil-soluble phenol-formaldehyde novolak resin and a third of which is an oil-soluble water-insoluble metal salt, and oily solvent droplets capable of dissolving said color-forming reactants in mutual solution, wherein said oily solvent droplets are held in a contained condition by hydrophilic organic polymeric film material, isolated from at least one of said color-forming reactants, provided that when the oily solvent droplets are not isolated from said resin material, said droplets are isolated from said other color-forming reactants.

2. The record sheet material of claim 1 wherein the chromogenic dye-precursor material comprises Crystal Violet lactone, the novolak resin is a para-phenylphenol-formaldehyde resin, the metal of the metal salt is zinc(II), and at least one of the color-forming reactants is dissolved in the oily solvent droplets.

3. The record sheet material of claim 2 wherein the zinc(II) salt has an anion selected from the group consisting of acetylacetonate, hexafluoroacetylacetonate, benzoate, naphthenate, salicylate, 2-ethylhexanoate, abietate, oleate and palmitate.

4. The record sheet material of claim 3 wherein the metal salt is zinc(II) naphthenate.

5. The record sheet material of claim 3 wherein the metal salt is zinc(II) 2-ethylhexanoate.

6. The record sheet material of claim 3 wherein the Crystal Violet lactone and the zinc(II) salt are dissolved in the oily solvent droplets.

7. A pressure-sensitive record sheet material comprising supporting web material having adhesively bound on a surface thereof oil-soluble phenol-formaldehyde novolak resin material, microscopic droplets of oil, an oil-soluble water-insoluble metal salt and a substantially colorless acid-colorable chromogenic dye-precursor material, wherein said oil droplets are held in an isolated and contained condition by hydrophilic, organic, polymeric, film material, and wherein said resin material is present on said web material as a particulate coating or a solution residue coating.

8. The record sheet material of claim 7 wherein said chromogenic dye-precursor material is Crystal Violet lactone and said metal salt is a zinc(II) salt selected from the group consisting of acetylacetonate, caprylate, laurate, 2-ethylhexanoate, oleate, abietate and naphthenate and wherein said dye-precursor material and said metal salt are dissolved together in said oil droplets.

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