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RECORD SHEET SENSITIZED WITH SALT MODIFIED KAOLIN-PHENOLIC MATERIAL

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ABSTRACT OF THE DISCLOSURE

Paper coating compositions containing kaolin, phenolic resins, and salts of class 2B metals such as zinc chloride are disclosed. The addition of the salts enhances the color activation by kaolin-phenolic resin and the fade resistance of the colored form of normally colorless chromogenic compounds. The useful metal salts are those exhibiting a valence of 2, and in order of merit are salts of the 2B metals, i.e., zinc, cadmium, and mercury; divalent tin; the 2A metals, i.e., calcium, magnesium and strontium; and the transitional metals, e.g., manganese, cobalt and nickel. The effective metallic compounds useful in making the coating composition of this invention and in making paper coatings containing kaolin-phenolic resin are the halide, nitrate, sulfate, and acetate reaction products of metals taken from the group consisting of zinc, cadmium, mercury, calcium, magnesium, strontium, barium, manganese, cobalt, nickel, and divalent tin.

This invention relates to improvements in kaolin-phenolic sensitized record members and to record member coating compositions containing kaolin-phenolic resins and salts of class 2B metals such as zinc chloride. More specifically, this invention relates to combining kaolin-phenolic resin with certain metal salts to provide a coating combination exhibiting enhanced color and enhanced fade resistance when reacted with normally colorless chromogenic compounds to form the colored form.

This invention, when the composition is applied as a coating to paper or incorporated therein as a filler, provides a record member with a specially sensitized recording surface which also is distinguished in use for ordinary ink reception because it utilizes a paper-coating or paper-loading material, viz, kaolin clay, which is well recognized as improving the printing quality of paper.

The purpose of providing the novel sensitized record member has many facets, all contributing to the fuller commercial acceptance of color-reactant recording systems by reason of lower cost, wider utility, and better performance. Color-reactant recording systems are so called because the reactant chromogenic material content of the ink used in such systems is substantially colorless and assumes a color when applied to a specially sensitized recording surface.

A record member, as the term is used in describing this invention, consists of a base sheet or web member either of fibrous construction, such as paper, or of continuous structure, such as films of organic polymeric material, carrying the color-reactant particles in an exposed state with respect to applied ink. Particles of the coating composition of this invention are arranged in intimate juxtaposition to form an apparently unbroken ink-receptive surface, yet substantially each particle individually is available for contact with applied ink. While the record member is adapted to receive any kind of ink, whether colored or colorable, its special utility is its use with an oily ink which is normally colorless or

only slightly colored and carries in liquid solution a colorless chromogenic reactant having the property of becoming colored upon contact with an acidic composition.

During the last decade, one of the most prominent of such colorless recording systems utilized a coloring principle in which an oily ink having included therein chromogenic reactants, normally colorless, was used on an ink-receiving sheet sensitized with substantially insoluble acid-like materials of high surface activity, such as attapulgite and zeolite material. As the normally colorless chromogenic material content of inks used therewith, the most outstanding are Crystal Violet Lactone and Benzoyl Leuco Methylene Blue, both of which in the colored form have intense hues in the blue end of the visual spectrum band. Such a system is disclosed in U.S. Letters Pat. No. 2,712,507, which issued July 5, 1955, on the application of Barrett K. Green, and pertains to a construction in which the ink is applied from an over-sheet by pressure-release from microscopic capsules. This system is now in world-wide use and commands a predominant position in the field of colorless recording systems, and its continued use is expected.

As distinguished from pigment inks, the chromogenic material in the colorless ink of these systems is in the nature of a colorless dye or combination of dyes that assume, through chemical reaction, a visually distinctive color when undergoing reaction with the particulate particles on the sheet.

For most recording purposes, it is essential from a commercial standpoint that a distinctively colored mark make prompt appearance on the application of colorless ink to the recording surface to produce a visible representation of whatever is meant to be recorded, that the color be of distinctive hue but also of high intensity, and that the mark remain colored for a long period of time consistent with the objective of permanent recording. The well-known infirmities of colored dyes as regards permanence relate to light-fading, thermal fading, and molecular rearrangements and disintegrations of various kinds in which part or all of the visually perceptible color is lost.

It is an object of this invention to overcome, as far as possible, the loss of color in the color-reactant marks which are occasioned by passage of time, by exposure to environment, or by intentional chemical or other type of degeneration.

This invention provides a novel coating composition comprising salts of Group 2B metals, at least one organic resin, and kaolin clay. The coating essentially comprises an aqueous slurry of 30% to 70% solids, by weight; the solids being a salt of a Group 2B metal, a Group 2A metal, a transitional metal, or divalent tin, a resin mixture, kaolin clay, and sufficient paper-sizing binder materials which binder materials may be used in an amount comprising up to 20% of the total solids content. Up to 15% of the total solids content may be of the metallic salts to be described, but a lesser proportion of metallic salts is satisfactory; as little as 1%, by weight, on the basis of kaolin clay operating satisfactorily.

When the chromogenic materials set forth in U.S. Pat. No. 3,455,721, issued July 15, 1969, on the application of Paul S. Phillips, Jr. et al., relating to similar record materials, are used, the reaction with the sensitizing non-chromogenic materials of this invention provides, immediately, marks having a more intense and more prolonged color persistence because this new coating composition reacts with a normally colorless or slightly colored chromogenic compound, but the color is more permanent because its colored form is substantially resistant to light fading.

Colorable by the composition of this invention are a large number of acid-colorable basic dyes which are disclosed in the application for Letters Patent in the U.S., Ser. No. 392, 404, filed Aug. 27, 1964, now abandoned by Robert E. Miller and Paul S. Phillips, Jr., such being diaryl phthalides; leucauramines; acyl auramines; γ , β -unsaturated aryl ketones; basic mono azo dyes; Rhodamine B Lactams such as N-(p-nitrophenyl) Rhodamine B Lactams; polyaryl carbinols; and 8'-methoxy benzoin-dolinspiropyrans, which may be identified as (8'-methoxy BIPS).

In general, inclusion of salts of the metals of Group 2B, Group 2A and the transitional metals in record sheet coatings compositions comprising kaolin clay and organic resins result in improved print speed, enhanced resistance to print speed, decline, greater intensity of print, enhanced resistance of print to fluorescent light fade, enhanced resistance of print to fading at elevated temperatures, and greater resistance of the record sheet material to decline caused by external contaminants such as contact with carbon paper.

There are other factors which give the novel record sheet a superiority for inks of colorless chromogenic content, and these are listed for convenience:

(1) There is no problem of the poisoning of the particulate reactants by airborne contaminants, as the reactants are not highly surface-active, as are attapulgite and zeolite particles. Record sheets made with surface-active materials normally are subject to environmental desensitization by such contaminants.

(2) The reactant particles need be supplied only in minimum calculable amounts because there is no unpredictable loss of effectiveness by environmental desensitization, to which reference was made above, and, hence, no safety factor in the way of additional material need be provided. This permits greatly reduced coating weight of sensitizing material per unit area to be used, over what has heretofore been required to insure that the commercial product has adequate storage life before it is used.

(3) Whereas in the past the practice of using surface-active minerals has resulted in serious rheological problems with aqueous coating compositions because such minerals naturally produce extraordinarily viscous slurries and because excessive amounts were used to offset air contamination, the polymeric material particles, on the other hand, have no such tendency to create extraordinary viscosity. In this respect, if air contamination is not a problem, the attapulgite, as has been used, need not be completely replaced by the acid polymeric material, and kaolin, but only in so far as is desirable to overcome any coating difficulty caused by the use of the formerly-necessary excessive quantities of attapulgite and any performance difficulty caused by fading and de-sorption.

(4) The kaolin gives the coating a superior smoothing behavior as a paper-loading agent as compared with attapulgite, and is renowned for its characteristics in providing a superior writing surface for the reception of oily inks.

(5) The kaolin and the organic polymeric materials used in practicing this invention are not particularly abrasive to paper-handling and paper-printing machinery, as has been the experience with the use of necessarily large amounts of the more abrasive attapulgite.

(6) The invention provides an important reduction in cost of reactant materials, first, because of reduction of the amounts which it is necessary to use, and, second, because of a reduction in shipping costs of finished record material due to lighter overall weights of coating materials per unit of recording area.

(7) The novel coating composition in adequate amounts may be applied by a size-press mechanism on the paper-making machine, whereas attapulgite coatings of equivalent performance are difficult to use that way because of the high viscosities involved. The same is true of some other coating devices, such as the trailing-blade coating device.

The useful metallic salts are those exhibiting a valence of 2, and in order of merit, are salts of the Group 2B metals—zinc, cadmium, and mercury; the Group 2A elements—calcium, magnesium and strontium; the transitional metals—manganese, cobalt, and nickel, and divalent tin.

While halogen anion salts of the named metallic elements are preferred, the nitrate, sulfate, and acetate salts thereof are very effective.

Therefore, the effective metallic salts useful in making the coating composition of this invention, and in coating paper, are the halogen, nitrate, sulfate, and acetate salts of metals taken from the group consisting of zinc, cadmium, mercury, calcium, magnesium, strontium, barium, manganese, cobalt, nickel, and divalent tin.

Polymeric materials of sufficient activity in an acid sense and suitable for use in this invention have been disclosed in application for U.S. Letters Patent, Ser. No. 392,404, filed Aug. 27, 1964, by Robert E. Miller and Paul S. Phillips, Jr. The invention claimed in that application being directed to a pressure-sensitive system of one or more oil-soluble acid polymeric materials, one or more colorless color reactant materials, and capsule- or film-isolated solvent liquid situated either together on one sheet or in a couplet of sheets, all of the reactant components being soluble in the solvent.

Among the organic polymeric materials suitable for use in this invention are certain phenol-aldehyde and phenol-acetylene polymers, maleic acid-rosin resins, partially or wholly hydrolyzed styrene-maleic anhydride copolymers and ethylene-maleic anhydride copolymers, carboxy polymethylene (Carbopol 934), and wholly or partially hydrolyzed vinyl methyl ether-maleic anhydride copolymer are specified as typical of the reactive acidic polymeric materials.

Among the phenol-aldehyde polymers found useful are members of the type commonly referred to as "novolacs," which are characterized by solubility in common organic solvents and which are, in the absence of cross-linking agents, permanently fusible. Another group of useful phenol polymeric materials are alkylphenol-acetylene resins, likewise soluble in common organic solvents and possessing permanent fusibility in the absence of being treated by cross-linking materials. Generally, the phenolic polymer material useful in practicing this invention is characterized by the presence of free hydroxyl groups and the absence of groups, such as methylol, which tend to promote infusibility or cross-linking of the polymer, and by their solubility in organic solvents and relative insolubility in aqueous media.

Resoles, if they are still soluble, may be used, though subject to change in properties upon aging.

A laboratory method useful in the selection of suitable phenolic resins is a determination of the infra-red absorption pattern of a candidate material. It has been found that phenolic resins showing an absorption in the 3200-3500 cm^{-1} region (which is indicative of the free hydroxyl groups) and not having an absorption in the 1600-1700 cm^{-1} region are suitable. The latter absorption region is indicative of the desensitization of the hydroxyl groups and consequently makes such groups unavailable for reaction with the chromogenic materials to be specified.

The preparation of the phenolic polymer materials suitable for practicing this invention is described in "Industrial and Engineering Chemistry," vol. 43, pages 134 to 141, January 1951; a particular polymer thereof is described in Example 1 of U.S. Pat. No. 2,052,093, issued to Herbert Hönel on Aug. 25, 1936; and the preparation of the phenol-acetylene polymers is described in "Industrial and Engineering Chemistry," vol. 41, pages 73 to 77, January 1949.

The preparation of the maleic anhydride copolymers is described in the literature, such as, for example, one of the maleic anhydride-vinyl copolymers, as disclosed in

the publication "Vinyl and Related Polymers," by Calvin E. Schildknecht, second printing, published April 1959, by John Wiley and Sons, Incorporated. See pages 65 to 68 (styrene-maleic anhydride copolymer), pages 628 to 630 (vinyl methyl ether-maleic anhydride copolymer), and pages 530 to 531 (ethylene-maleic anhydride copolymer).

Kaolin is generally known and used in the paper-making industry as "China Clay" and is outstandingly preferable as the particulate oil-insoluble and water-insoluble material of acid characteristics necessary to color the normally colorless compounds. A white kaolin is used, and, because of its whiteness, its plate-like particle form, which gives it unparalleled coating properties in aqueous slurries, its universal abundance in supply, its historical general usage in the paper-making and paper-converting industries and its low cost, it is an ideal material. Of course, there are many other materials of a mineral nature which can be used instead of and matched against kaolin clays as the standard of perfection. Other types of particulate and substantially colorless water- and oil-insoluble minerals of the necessary acid properties are deemed equivalents of kaolin, some being bentonites, although not so good as kaolin from a rheological standpoint.

From the foregoing choice of materials, a number of different specific compositions on a dry basis may be made, and these may then be used as desired, as being made into an aqueous slurry to be coated on a finished paper sheet, to be applied to a wet sheet of paper in the formative state in any desired manner, or made a part of the paper furnish from which a paper sheet is made, or on the other hand applied as a dispersion coating to a continuous film-like web such as synthetic organic polymeric material made into record sheets, bands, or strips, or to any record support material surface, all coming within certain limits merely set as practical and not set for any chemical or physical reason. In general, so as to be economical, the materials should be used in just sufficient quantities to make useful records for the purpose in view, and this relates to criteria of the factors of intensity, definition, color, and a great many other factors with regard to the characteristics of the base web material, the characteristics of the ink to be applied, and the environment of use, all of which come within the paper manufacturers' and printers' skill and general knowledge and are not deemed to be of inventive or operative significance, but following and employing the inventive concept. Generally, but not as a limitation in any sense, an aqueous dispersion of the particulate materials could well be from 30% to 70% water, by weight, and the remainder from 70% down to 30% being solid reactants. Amounts of paper-coating adhesives are added as is necessary to adhere the particles to the base web to which it is applied, but, of course, adhesives that have a tendency to mask the particles physically should not be used, nor should any material be used as an adhesive in great excess of actual requirements, all of such factors tending to decrease the efficient use of the associated active particles because of a limitation of the exposed surface area. Here, again, the paper makers' and printers' skill and judgment play a part.

If desired, some attapulgite or zeolite material may be used with the polymeric material and kaolin clay, and it is within contemplation that other materials of reactant nature can be employed to supplement the main pair of particulate reactants, for specific purposes. In this area of permissible substitutes or addition materials, silica gel has considerable standing because it is capable of instantaneously strongly coloring oil solutions of normally colorless chromogenic materials and is efficient oil receptor for oil-base ink. Where the particles of kaolin and acid polymeric material are slightly delayed in responsiveness because of their physical situation or condition in the support sheet, an amount of silica gel

up to equal the amount of acid polymeric material may be used for its beneficent effect in the characteristics states, but such use is not necessary to the practice of the invention in its simplest form. Silica gel is oil-insoluble but adsorbent thereof, may be finely ground, is colorless, disperses readily in water, and may be treated to increase its porosity and effectiveness as an acid. The polymeric-material-produced color of normally colorless chromogenic material is significantly more persistent than that produced by silica gel, and this must be considered in the use of the latter material.

The particle size of the reactants preferably should be from one to three microns in largest dimension, although considerable latitude at the expense of efficiency and economy is tolerable. For instance, if the grinding of materials to the most effective size is too expensive, their larger sizes are tolerable as long as sufficient color reaction per unit area of the record material is provided. On the other hand, finer grinding may result in more efficient use of materials on a weight basis, if not on a cost basis, and a lighter weight finished sheet may thereby be produced.

One of the chief considerations in selecting a preferred embodiment of the invention must be concerned with the manufacture of the record sheet, and as of now the best way to sensitize a sheet is to apply an aqueous slurry of the novel composition to a finished web of paper as it passes the coating station in a paper-making machine. Such a coating composition contains binder material and may contain defoamers and dispersing agents common to paper-coating practices, but their specification in no way is to mean a limitation of the practice of the invention in regard to either choice or necessity.

EXAMPLE I

One hundred sixty (160) grams of phenol-formaldehyde resin (sold as Durez Resin 24714 by Hooker Chemical Co., New York, N.Y.), 40 grams of paraphenyl-phenol resin (sold as Varcum 523 by Reichold Chemical Co., White Plains, New York), 20 grams of gum arabic, 220 grams of water were placed in an attritor and ground for thirty minutes. One hundred forty (140) grams of a resulting dispersion was mixed with 315 grams of kaolin clay, 60 grams of calcium carbonate, 200 grams of a solution containing 20% zinc chloride by weight in water, and 150 grams of a solution containing 10% polyvinyl alcohol by weight in water.

The resulting dispersion was blended for one minute with a Dispersator, diluted to 50% solids with 165 grams of water and coated on paper with a No. 7 Meyer rod to provide a coating exhibiting a dry weight of 4 pounds per ream. (A ream of paper consisting of 500 sheets of paper exhibiting dimensions of 25 inches by 38 inches.)

The final coating composition consisted of:

	Percentage solids by weight (dry basis)
Paper coating kaolin (white) as mined in Georgia and South Carolina, United States of America, the County of Cornwall in Great Britain, Czechoslovakia, U.S.S.R., and Germany	63
Phenolic resin mixture (comprising 12.73% resin; 1.27% gum arabic)	14
Calcium carbonate	12
Zinc chloride	8
Polyvinyl alcohol	3

EXAMPLE II

Same as Example I except that the gum arabic was substituted by an anionic polymer type dispersing agent (a sulfonate of naphthalene formaldehyde), (sold as "Tamol 731" by Rohm & Haas Chemical Co., Philadelphia, Pa., U.S.A.), such that the dispersant comprised 0.38% of the coating composition and the phenolic resin mixture comprised 13.72%, by weight, of the final coating composition.

7
EXAMPLE III

Same as Example I except that 120 grams of phenol formaldehyde resin, 30 grams of paraphenyl phenol resin, 50 grams of kaolin clay and 20 grams of gum arabic were used to attain the composition of Example I.

EXAMPLE IV

	Percentage solids by weight (dry basis)
Paper coating kaolin (white) as mined in Georgia and South Carolina, United States of America, the County of Cornwall of Great Britain, Czechoslovakia, U.S.S.R., and Germany	58
Phenolic resin mixture (includes 1.27% gum arabic)	14
Calcium carbonate	12
Zinc chloride	8
Etherized starch	8

EXAMPLE V

	Percentage by weight (dry basis)
Paper coating kaolin (white)	61
Phenolic resin mixture (includes 1.27% gum arabic)	14
Calcium carbonate	12
Zinc chloride	8
Polyvinyl alcohol	5

EXAMPLE VI

	Percentage by weight (dry basis)
Paper coating kaolin (white)	63
Phenol-formaldehyde resin (includes 1.27% gum arabic)	14
Calcium carbonate	12
Zinc chloride	8
Polyvinyl alcohol	3

EXAMPLE VII

	Percentage by weight (dry basis)
Paper coating kaolin	63.0
Phenol-formaldehyde resin (includes 1.27% gum arabic)	11.2
Calcium carbonate	12.0
Paraphenyl phenol resin	2.8
Zinc chloride	8.0
Polyvinyl alcohol	3.0

EXAMPLE VIII

	Percentage by weight (dry basis)
Paper coating kaolin	66
Phenolic resin mixture (includes 1.27% gum arabic)	14
Calcium carbonate	12
Zinc chloride	5
Polyvinyl alcohol	3

EXAMPLE IX

	Percentage by weight (dry basis)
Kaolin	60
Phenolic resin mixture (includes 1.27% gum arabic)	14
Calcium carbonate	12
Zinc chloride	11
Polyvinyl alcohol	3

EXAMPLE X

	Percentage by weight (dry basis)
Kaolin	56
Phenolic resin mixture (includes 1.27% gum arabic)	14
Calcium carbonate	12
Zinc chloride	15
Polyvinyl chloride	3

8
EXAMPLE XI

	Percentage by weight (dry basis)
Paper coating kaolin	75
5 Phenolic resin mixture (includes 1.27% gum arabic)	14
Calcium carbonate	0
Zinc chloride	8
Polyvinyl alcohol	3

EXAMPLE XII

	Percentage by weight (dry basis)
Paper coating kaolin	69
Phenolic resin mixture (includes 1.27% gum arabic)	14
Calcium carbonate	6
Zinc chloride	8
Polyvinyl alcohol	3

EXAMPLE XIII

	Percentage by weight (dry basis)
Paper coating kaolin (white)	57
Phenolic resin mixture (includes 1.27% gum arabic)	14
Calcium carbonate	18
25 Zinc chloride	8
Polyvinyl alcohol	3

Percentage range of components (by weight on a dry basis)

Kaolin clay (white)	30-80
Polymeric material	5-20
Salt of a metal selected from the group consisting of: zinc, cadmium, mercury, calcium, magnesium, strontium, manganese, cobalt and nickel	1-15

The following table expresses the improvement experienced in using the composition of Example I over the coating compositions of the prior art in terms of decline in light reflectance of prints made by applying a standard Crystal Violet Lactone colorless ink by calendar action, the standard being "Attasorb." The numbers represent relative reflectance in an opacimeter. The lower the reflectance value, the better the color.

	Zinc chloride modified	Phenolic kaolin modified	Standard Attasorb
Unexposed:			
Calendar Int., 15 sec.	49	57	55.
Calendar Int., 30 sec.	40	51	53.
Calendar Int., 1 min.	38	49	52.
Calendar Int., 3 min.	35	44	52.
Exposed to 120° F. oven, 72 hrs.:			
Calendar Int., 15 sec.	51	65	60.
Calendar Int., 13 sec.	41	60	58.
Calendar Int., 1 min.	37	53	56.
Calendar Int., 3 min.	35	46	56.
Frictional smudge, 10 min.	93	89	93.
Mullensmudge, 72 hrs.	82	88	86.
55 Fluorescent light fade	Delta 18	Delta 20	Delta 19.
Fluorescent light decline	Delta 0	Delta 2	Delta 0.
120° F. circulating oven fade	Delta 2	Delta 12	Delta 14.
120° F. circulating oven decline	Delta 0	Delta 2	Delta 10.
Multiple copy (6 part)	(1)	(2)	Standard.
Carbon compatibility decline	Delta 3	Delta 14	Delta 12.

¹ Better than standard.

² Equal to standard.

It will be apparent that the ratio of the solids content of kaolin clay to polymeric material content to the compositions may vary greatly. The examples pertain especially to coatings for paper. In filling paper furnish with these reactant materials, only such quantitative amounts should be used that will insure reaction with the ink and integrity of the paper web, such being determined empirically by the paper maker.

For coating non-fibrous web material, the application should be less wet, as there ordinarily will be no drying of the coating by absorption.

What is claimed is:

1. A sheet of record material sensitized with a coating to produce color on contact with basic, acid-colorable,

colorless chromogenic material, said coating comprising kaolin clay, at least one oil-soluble acidic organic polymeric material, a binder, and a salt selected from the group consisting of the halogen, nitrate, sulfate, and acetate salts of metals selected from the group consisting of zinc, cadmium, mercury, calcium, magnesium, strontium, barium, manganese, cobalt, nickel, and divalent tin, wherein the kaolin clay constitutes from 30% to 80% of the weight of the coating on a dry basis, the polymeric material constitutes from 5% to 20% of the weight of the coating on a dry basis, and the metallic salt constitutes 1% to 15% of the weight of the coating on a dry basis.

2. The sheet of record material of claim 1 wherein the polymeric material is a phenolic polymer.

3. The sheet of record material of claim 1 wherein the salt is a halogen salt.

4. The sheet of record material of claim 1 wherein the salt is a nitrate salt.

5. The sheet of record material of claim 1 wherein the salt is a sulfate salt.

6. The sheet of record material of claim 1 wherein the salt is an acetate.

7. The sheet of claim 1 wherein the record material is a paper sheet.

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