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[54] **PRESSURE-SENSITIVE RECORDING SHEET AND METHOD OF MAKING**
11 Claims, No Drawings

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[50] **Field of Search** 117/36.2, 36.8, 36.9

[56] **References Cited**
UNITED STATES PATENTS

2,983,756	5/1961	Kranz	117/36.2
3,455,721	7/1969	Phillips et al.	117/36.2

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ABSTRACT: Record sheets having improved resistance to smudging and calender intensity for use with transfer sheets containing microscopic rupturable capsules of a colorless marking fluid are produced by coating a base sheet with a composition comprising a finely powdered oil-soluble acid-reactant polymeric material, a substantially nonreactant pigment having a relative sediment volume (RSV) in excess of 2 and a binder for said polymeric material and pigment.

PRESSURE-SENSITIVE RECORDING SHEET AND METHOD OF MAKING

FIELD OF THE INVENTION

This invention relates to the production of record sheets sensitized with finely powdered color-reactant particles. Such record sheets are for use with transfer sheets having a surface coating containing rupturable microscopic capsules of a colorless marking fluid.

DESCRIPTION OF THE PRIOR ART

Record sheets containing acid-reactant pigments such as attapulgus clay, zeolites, colloidal silica and acid-activated clays have been produced for quite some time. U.S. Pat. No. 2,699,432 issued to Marra et al. describes record sheets coated with attapulgus clay and zeolites and the process of making them. Such record sheets have had wide commercial acceptance for use in manifold assemblies in which the attapulgus clay coating is placed in contiguous relationship with a transfer sheet surface containing microscopic rupturable capsules of a colorless marking fluid. The marking fluid contains a solution of colorless color-reactant materials such as a combination of crystal violet lactone and benzoyl leuco methylene blue dissolved in an oil. Pressure contact, such as produced by pressing a typewriter key, on the manifold assembly causes the capsules to break and transfer some of the colorless marking fluid to the attapulgus clay coating where it reacts with the acid-reactant clay to give a colored mark. The crystal violet lactone reacts immediately with the clay in an acid-base reaction to form an intense blue color which fades slowly. This is followed by hydrolysis and oxidation of the benzoyl leuco methylene blue to give an intense permanent blue color. The above-described record sheets, although commercially acceptable, may show a temporary loss of color.

Recently, record sheets have been produced in which the acid-reactant pigment has been partially replaced with a finely powdered oil-soluble acid-reactant polymeric material. Such a record sheet and a process for producing it are described in British Pat. No. 1,065,587. The color-producing components of this system, crystal violet lactone in the transfer sheet and acid-reactant polymeric material in the record sheet, both are oil soluble and the color produced by reaction of the two was stated to be more permanent than that produced by using the acid-reactant pigment. However, the resistance to smudging of such sheets due to normal handling in association with capsule-containing transfer sheets is borderline when the reactant surface coating of the record sheets is 7 pounds per ream (3,300 sq. ft.) or less.

SUMMARY OF THE INVENTION

According to the present invention there is provided a record sheet of improved resistance to smudging and intense color-producing capability comprising a base sheet coated with a composition comprising an oil-soluble acid-reactant polymeric powder, a substantially nonreactant pigment having a relative sediment volume (RSV) in excess of 2 and a binder for said polymeric powder and pigment.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Among the oil-soluble acid-reactant polymeric materials useful 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, and wholly or partially hydrolyzed vinyl methyl ether-maleic anhydride copolymer which are 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 polymeric material useful in practising 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 the organic solvents used in the marking fluid and relative insolubility in aqueous media, all as described in British Pat. No. 1,065,587.

The record sheet of this invention differs from the prior art record sheets in that the pigment portion of the applied coating composition is composed of high-bulking pigments which are substantially nonreactive with the basic dyes in the colorless marking ink. In the preferred embodiment the pigment portion consists wholly of such nonreactant pigments; however, small amounts of moderately reactant pigments can be tolerated. Highly reactant pigments, such as attapulgus clay, should be omitted if excessive fading of the color is to be avoided. In any case, it is essential that loose-packing (high-bulking) pigments be used. Normal predispersed kaolin coating clays have a relative sediment volume of 1.6 to 1.8. Using high-bulking pigments or mixtures of pigments having a relative sediment volume in excess of 2 has been found to be very beneficial in improving the resistance to smudging and intensity of color over that produced by using kaolin clays. The size of the pigment particles is not critical. Pigments having a particle size of 0.1 to 5 microns equivalent spherical diameter have been successfully used.

The relative sediment volume (RSV) of a pigment is the ratio of sediment volume of an aqueous dispersion of the pigment to its actual solid volume. It is determined by placing a sample of the pigment in water in a centrifuge tube and centrifuging the slurry sample at 1,000 g. until the packed sediment volume reaches a constant value. The RSV is calculated as follows.

$$RSV = \frac{\text{Packed sediment volume} \times \text{Pigment specific gravity} \times 100}{\text{Sample weight} \times \text{Slurry percent solids}}$$

Such a test is described on page 144 of TAPPI Monograph No. 28 which is entitled *Pigmented Coating Processes*.

Pigments and pigment mixtures which have been successfully used in producing the record sheets of this invention are:

	Pigment	Trade name and source	Relative sediment volume
1	60% delaminated kaolin coating clay. 40% hydrated alumina	NuClay-Freeport Kaolin Div. (Freeport Sulfur). Hydral 705-Alcoa	2.8
2	High bulking filler clay	Hyopaque-Freeport Kaolin Div. (Freeport Sulfur).	2.4
3	Talc	Mistron Vapor-Sierra Talc Co.	3.4
4	50% Talc 50% delaminated kaolin coating clay.	Mistron Vapor-Sierra Talc Co. NuClay-Freeport Kaolin Div. (Freeport Sulfur).	2.5

All of the foregoing pigments are ordinary paper-coating pigments except item 2 which is a filler pigment. Use of these pigments in paper coatings does not present any special problems with normal coating processes, such as by roller, blade or air knife coating.

Record sheets produced in accordance with this invention have been successfully used in conjunction with transfer sheets containing an oily solution of crystal violet lactone and benzoyl leuco methylene blue or crystal violet lactone as the only chromogenic material. Generally, transfer sheets containing leuco dyes which are known to be relatively basic to the acid-reactant polymeric material can be successfully used with the record sheet of this invention.

The exact reason for the improved performance of the record sheet of this invention is not known. It is believed that the high-bulking pigments contribute to the improved smudge

resistance by better coverage of the base sheet, especially where a paper base is used. The improved intensity appears to be the result of the more porous coated surface which allows greater penetration of the colorless marking oil from the transfer sheet carrying with it the dissolved chromogenic material. Increased transfer of the marking oil has also been noted in the record sheet of this invention. A determination of the marking oil transferred under controlled pressure from the transfer sheet to a prior art record sheet containing only a low-bulking kaolin clay (RSV = 1.8) showed that 29.9 percent of the available marking oil was transferred to the record sheet, whereas a similar record sheet containing high-bulking pigments (RSV = 2.4) prepared in accordance with the instant invention showed a transfer of 52.3 percent of the available marking oil.

The base sheet for the record sheet of this invention is preferably paper, although other bases such as a plastic sheet may be used. Binders for the pigments and particulate polymeric material may be the normal paper-coating adhesives, such as starch, modified starches, synthetic latices, polyvinyl alcohol, etc., in amounts necessary for printing requirements. Defoamers, dispersing agents, lubricants and preservatives may be added to the coating composition as in normal paper-coating practices.

Calender intensity as used herein is a contrast ratio wherein the lower the numerical value, the greater the intensity of color. This value is determined by placing the coated side of a reactant paper to be tested in contact with the coated side of a standardized transfer sheet, such as is described in U.S. Pat. No. 2,711,375 granted to Robert W. Sandburg on June 21, 1955, and then passing the superimposed papers through a calender machine, the rolls of which are subjected to a known standard load. A suitable light reflectance meter is employed to obtain the percent reflectance of the printed and unprinted areas of the reactant paper after calendering. The calender intensity ratio is then calculated according to the formula:

$$\text{Calender intensity} = \frac{\text{Average painted area reflectance}}{\text{Average non-printed area reflectance}} \times 100$$

Smudge is a contrast ratio wherein the lower numerical value shows greater frictional smudge. This test is performed by placing a coated record sheet coated side down in face-to-face relationship with the coated surface of a capsule-coated transfer sheet which in turn is clamped on a stack of paper for cushioning, placing a weight on the top of the record sheet, and drawing both the record sheet and weight over the capsule-coated surface. The smudge value is determined by comparing the light reflectance reading of the record sheet surface test area with that of the untested background surface area of the record sheet and is calculated as follows.

$$\text{Smudge} = \frac{\text{Average test area reflectance}}{\text{Average background area reflectance}} \times 100$$

The following examples further illustrate the advantages of the instant invention over that of the prior art.

EXAMPLE 1

A 33 pound per ream (3,300 sq. ft.) bond paper was coated by means of an air knife with 5 dry pounds per ream of the following composition.

	Dry Parts per Weight
Hydrated alumina (Hydral 705)	20
Delaminated kaolin clay (NuClay)	43.4
Oil-soluble acid-reactant phenolic polymer	10
Styrene-butadiene latex binder	6.7
Ethoxylated starch	8.5

Included with the above composition were minor amounts of dispersants, defoamers, coating lubricants and sufficient water to bring the composition to 28 percent solids. The combined hydrated alumina and delaminated kaolin clay pigment mixture had an RSV value of 3.6.

EXAMPLE 2

A prior art record sheet was produced by coating a 33 pound per ream bond paper as in example 1 except that the coating composition did not contain any of the high-bulking pigments of this invention. Instead the pigment portion was made up of 60.2 parts of kaolin clay having an RSV value of 1.8 and a minor portion of 3.2 parts of colloidal silica.

The calender intensity of the resultant prior art sheet was 53 and the smudge resistance was 80 as compared to the calender intensity of 39.5 and smudge resistance of 92.2 of the record sheet produced in example 1.

EXAMPLE 3

Example 1 was repeated except that no oil-soluble acid-reacting phenolic resin was added to the composition. The calender intensity was 97 after 10 minutes (100 would show no color at all), and aging for several months did not show any perceptible color change. It is apparent from this test that, as used in the coating composition, the pigments used are substantially nonreactive to either crystal violet lactone or benzoyl leuco methylene blue.

EXAMPLES 4–10

A series of record sheets were prepared in which the following compositions, listed as dry parts by weight, with minor amounts of dispersants, lubricants and sufficient water to make the composition coatable were applied and dried on a bond paper.

Examples	4[1]	5	6	7	8	9	10
High bulk kaolin clay		60	60				
Hydrated alumina				40	40		
Talc						60	60
Delaminated kaolin clay	60			20	20		
Colloidal silica	3	3	3	3	3	3	3
Styrene-butadiene latex	6.5	6.5	6.5	6.5	6.5	6.5	6.5
Ethoxylated starch	9.5	9.5	9.5	9.5	9.5	9.5	9.5
Phenolic polymer	12.0	12.0	12.0	12.0	12.0	12.0	12.0
RSV of pigment portion	1.8	2.4	2.4	3.0	3.0	3.4	3.4
Coat weight applied	6.0	4.0	6.0	4.0	6.0	5.0	6.0
Calendar intensity	63.3	40.9	43.8	42.2	41.1	46.5	59.9
Smudge	82.0	86.4	89.9	86.7	89.7	84.9	87.8

[1] Prior art.

As can be seen by the comparison above, greatly improved resistance to smudging and intensity of color (calender intensity) are obtained when using the pigment mixtures having RSV values in excess of 2. It would be possible in view of the above results to substantially reduce the coat weight of the record sheets and still have as good or slightly better performance than was previously obtained in record sheets prepared before the instant invention. Thus, it can be seen that in comparison with prior art record sheets, the basis weight of the coated record sheet can be reduced or the strength of the record sheet may be increased if they are produced according to this invention.

The amount of oil-soluble acid-reactant polymeric material of the coating may vary greatly, the preferred amount being 5 percent to 15 percent of the total coating solids. In comparison with the prior art practices, a more efficient use of the expensive polymeric material is possible in the record sheets produced according to this invention.

It is intended that the present invention includes all modifications and equivalents which fall within the scope of the invention as defined by the appended claims.

What is claimed is:

1. A record sheet for use in producing a colored mark by pressure contact with a surface comprising pressure rupturable capsules containing a colorless marking oil, comprising a coating on a base sheet, said coating consisting essentially of 5 to 15 percent by weight of a finely powdered oil-soluble acid-reactant polymeric powder capable of producing a color when contacted by said colorless marking oil, a nonreactant pigment having an RSV value in excess of 2, said nonreactant pigment producing substantially no color in contact with said colorless marking oil, and sufficient binder for said oil-soluble acid-reactant polymeric powder and said pigment to produce a coated sheet satisfactory for printing.

2. A record sheet according to claim 1 in which the polymeric powder is an oil-soluble acid-reactant phenolic polymer powder.

3. A record sheet according to claim 1 in which the nonreactant pigment is selected from the group consisting of hydrated alumina, high-bulking filler clay and talc pigments and mixtures thereof.

4. A record sheet according to claim 3 in which the nonreactant pigment additionally contains a nonreactant kaolin coating clay.

5. A record sheet according to claim 1 in which the nonreactant pigment is hydrated alumina.

6. A record sheet according to claim 5 in which the nonreactant pigment additionally contains a nonreactant kaolin coating clay.

7. A record sheet according to claim 1 in which the nonreactant pigment is talc.

8. A record sheet according to claim 1 in which the nonreactant pigment is a high-bulking filler clay.

9. A record sheet according to claim 1 in which the coating contains approximately 3 percent by weight of colloidal silica.

10. A record sheet according to claim 1 in which the base sheet is paper.

11. A method of producing a record sheet for use in producing a colored mark by pressure contact with a surface comprising pressure rupturable capsules containing a colorless marking oil, comprising the steps of applying to a base sheet an aqueous coating composition consisting essentially of 5 to 15 percent by weight of solids of a finely powdered oil-soluble acid-reactant polymeric powder capable of producing a color when contacted by said colorless marking oil, a nonreactant pigment having an RSV value in excess of 2, said nonreactant pigment producing substantially no color in contact with said colorless marking oil, and sufficient binder for said oil-soluble acid-reactant polymeric powder and said pigment to produce a coated sheet satisfactory for printing, and drying said applied coating composition.

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