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E. G. BOURGEOIS
METHOD OF MAKING BLUSH COATED RECORDING SHEET, COATED
SHEET AND COATING COMPOSITION
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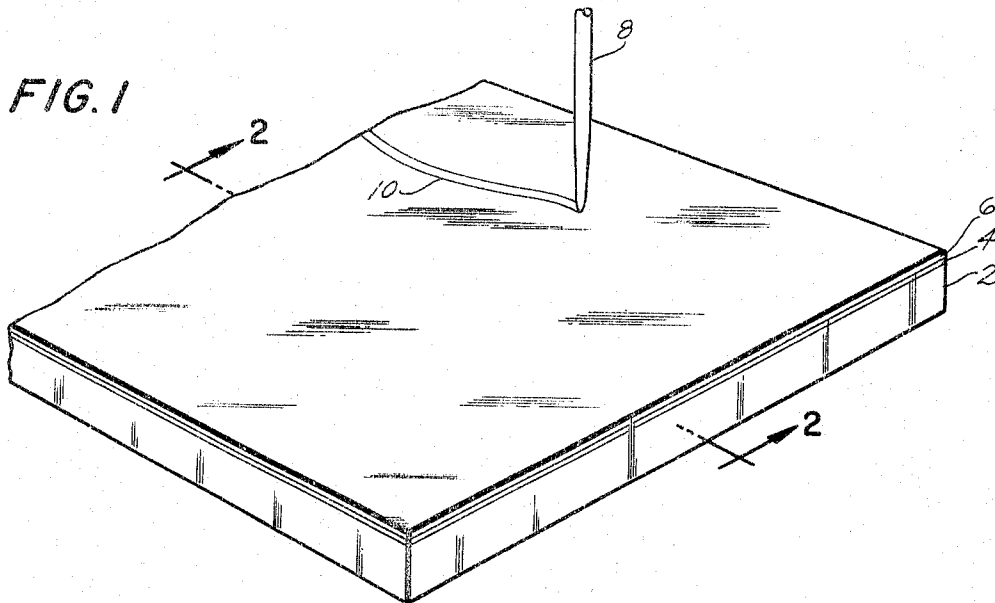


FIG. 2

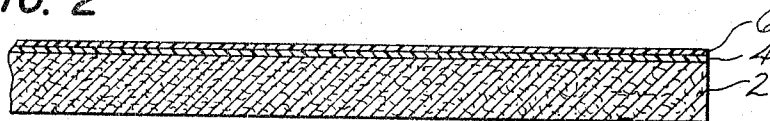
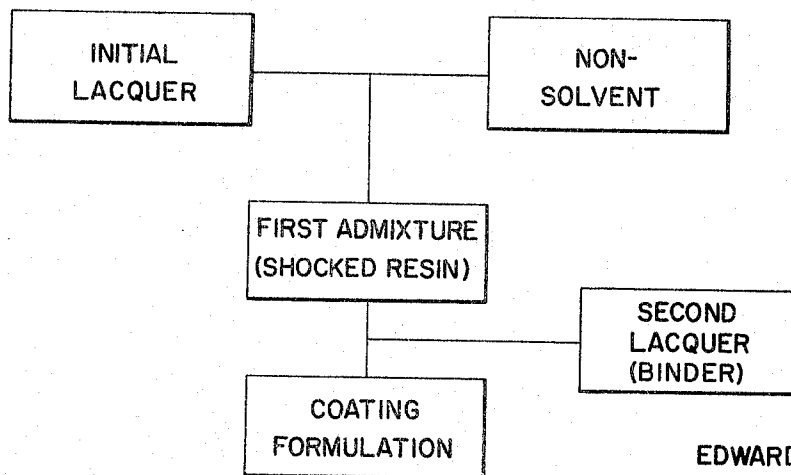


FIG. 3



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METHOD OF MAKING BLUSH COATED RECORDING SHEET, COATED SHEET AND COATING COMPOSITION

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The present invention relates to coated sheet materials and more particularly to recording sheet materials having a blushed or opaque coating thereon sensitive to heat, and to the method of making the same.

Many recording devices such as cardiographs and oscillographs employ a heated stylus and the like to scribe a line upon a length of paper which has an opaque or blushed coating thereon and which coating is rendered substantially transparent at the area wherein heat is applied to the stylus. Many blushed coatings have been proposed for this purpose including those described in United States Patents No. 2,299,991 to Kallock; No. 2,519,660 to James; No. 2,961,334 to Clancy et al.; and No. 3,031,328 to Larsen.

It is an object of the present invention to provide a recording sheet for marking by a stylus and the like having a blushed coating which is relatively facile and economical to produce and which has readily controllable and highly desirable opacity coupled with facile convertability to the desired transparency and resistance to pressure defacing.

It is also an object to provide a simple and readily controlled method for making the coating materials for such recording sheet and for making the final recording sheet.

Other objects and advantages will be readily apparent from the following detailed description and claims and the attached drawing wherein:

FIGURE 1 is a fragmentary perspective view to a greatly enlarged scale of a recording sheet embodying the present invention with a fragmentarily illustrated stylus tracing a line thereon;

FIGURE 2 is a sectional view of the recording sheet along the line 2-2 of FIGURE 1; and

FIGURE 3 is a diagrammatic view of the process of making the coating formulation of the present invention.

It has now been found that the foregoing and related objects may be readily attained by use of a coating formulation which is prepared by admixing a lacquer consisting essentially of cellulose ester resin dissolved in an organic solvent therefor to provide a resin solution, with an organic liquid which is a non-solvent for the resin in an amount sufficient to shock a portion of the resin into resin particles within a matrix of the resin solution. This admixture is then admixed with a second lacquer consisting essentially of cellulose ester resin dissolved in an organic solvent therefor to provide a second admixture with the minute resin particles distributed throughout a resin solution of desired bonding power formed thereby. This coating formulation may then be applied to the surface of sheet material to provide a coating thereon wherein the resin particles are distributed in a matrix formed by the resin solution and provide a blushed or opaque appearance.

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Upon application of a heated stylus and the like to the blushed coating, the blushed appearance is eliminated from the heated area and a clear appearance is obtained to expose the substrate or sheet material under the coating. As is well known, the sheet material may have a coloring agent incorporated within the body thereof or a separate colored coating may be applied to the surface thereof to underlie the blushed coating. In either case, the color of the sheet material (or its colored coating) is exposed when the heated stylus renders the blushed coating clear.

The theory of operation is not fully understood. However, it is believed that the organic non-solvent disturbs the solvent balance of the original lacquer and shocks or precipitates a portion of the resin. Upon initial addition of the non-solvent, a gelatinous flocculate is formed which is dispersed to produce an apparently clear solution by rapid agitation. It is considered that the non-solvent is absorbed into the shocked resin and that the flocculate is dispersed by agitation into very minute or microscopic particles which are in colloidal solution and do not interfere with the clarity of the liquid admixture although some loss in clarity will often be encountered as the result of flattening agents and other components of the lacquers. Indicative of this state is the loss of blushing power which occurs when an excessive amount of the second lacquer is utilized, presumably due to re-solution of the shocked resin particles. Additionally, the admixture is stable at room temperature for extended periods.

The first admixture thus produced has inferior bonding power and is further mixed with a second lacquer (which may be the same as the first in formulation) to provide a matrix of the desired bonding power. When the second admixture is applied to the surface of the sheet material, the coating develops a blushed or opaque appearance which is presumably due to the suspension of the shocked resin particles within the substantially clear matrix formed by the resin solution. Upon application of heat, the shocked resin particles apparently are fused with the resin of the matrix to provide a clear, continuous film.

Upon testing of the coating by immersion in solvent, no bubbling was observed indicating the absence of discontinuities or voids within the coating as contrasted with results obtained by similar testing of other coatings which rely upon voids produced by differential evaporation of water or non-solvents. Furthermore, the blushed appearance is not appreciably affected by application of pressure without heat as in the case of pressure-sensitive, void-containing coatings.

Although many water-insoluble resins have been utilized for making coatings including cellulose esters, cellulose ethers such as ethyl cellulose, polyethyl and polymethyl methacrylates and vinyl polymers such as vinyl chloride-acetate copolymer, only cellulose esters have proven successfully adaptable to the present invention. Nitrocellulose is preferred since it has been continuously effective due to its susceptibility to being shocked into minute resin particles within the resin solution.

Among the solvents commonly employed for cellulose esters are methyl acetate, ethyl acetate, amyl acetate, acetone, methanol, ethanol and butanol. Toluol and xylol are often employed as diluents. Ethyl acetate in

combination with butyl alcohol and/or toluol has found widespread acceptance in the manufacture of nitrocellulose lacquers. Generally, the cellulose ester will constitute about 3 to 25 percent by weight of the total lacquer formulation.

Other components may be added to the resin solution formed by the cellulose ester and its solvent to provide improved or desirable properties thereto. Plasticizers such as blown castor oil and fatty acids and their salts and esters are desirably included. Other resins may be included to improve hardness and resistance to scuffing such as polystyrene solutions which improve scuff resistance and urea-formaldehyde solutions which improve hardness. Generally, these resins should be incorporated in the second lacquer or admixture to avoid possible interference with the shocking of the cellulose ester.

Various non-solvents for cellulose esters are known including aromatic hydrocarbon liquids such as benzene, toluene and xylene; aliphatic hydrocarbon liquids such as hexane and heptane; and mixtures thereof such as commercially available petroleum solvents. The mixtures have proven satisfactory and petroleum solvents sold by Esso Company under the trademark Varsol with kauri-butanol values of about 35 to 55 have been employed. Varsol No. 2 has been particularly effective and is described by the manufacturer as containing 30.4 percent aromatics, 0.5 percent olefins and 69.1 percent saturated aliphatics with a kauri-butanol value of 45.0. As will be apparent, the non-solvent should be miscible with the solvent system of the lacquer.

The amount of organic non-solvent should be sufficient to shock out the desired amount of resin but well below that to totally unbalance the lacquer solvent and thus precipitate all of the resin. Generally, the amount should be that sufficient to produce an appreciable flocculate which is almost gel-like and which may be broken up and apparently dissolved by rapid agitation.

As a specific example of a formulation and ratio, in use of nitrocellulose lacquers a weight ratio of the petroleum solvent Varsol No. 2 of Esso to resin in the first lacquer of about 1.1 to 3.3:1 has been utilized with optimum results at a ratio of about 2.2:1. However, the ratio of non-solvent to resin for various combinations may be readily determined by visual observation in tests with various admixtures. If too much non-solvent is employed, an excessive amount of resin will be shocked and the matrix of resin solution will provide insufficient bonding power to the substrate and significant powdering will be readily apparent. If too little is employed, the opacity will be greatly reduced and the shocked resin will tend to redissolve excessively in the second lacquer.

In applying the second admixture, the viscosity may require adjustment for the particular apparatus employed. Various noninterfering thinners may be added such as methyl ethyl ketone as is conventional in lacquer coating of sheet materials.

The second admixture may be applied to the substrate in any conventional manner such as by wire coating, knife coating and reverse roll coating. The wet coating should have a thickness of about 0.006 to 0.015 inch to provide a dry coating thickness of about 0.001 to 0.004 inch with the desired opacity since the solids content of the admixture will generally be about 10 to 30 percent. Preferably, a solids content of about 15 to 20 percent is employed to provide a wet coating of about 0.007 to 0.010 inch which will yield a dry coating of highly satisfactory opacity at relatively low cost.

Various sheet materials may be employed for the substrate including paper, glassine and films of synthetic plastic which will not be excessively attacked by the organic solvents in the coating compositions. As previously stated, the substrate should be differentially colored either by incorporation of a coloring agent within the body of the sheet material or by a separate colored coating upon the surface as by printing, laminating or coating with a

separate formulation. In this manner, the blushed coating which is substantially white in appearance will be readily differentiated from the underlying substrate which is exposed when the coating is rendered transparent by the stylus. Carbon-impregnated paper has proven highly desirable because of the apparent sensitivity of the resultant sheet material coupled with greater resistance to excessively wide fusing of the coating when the stylus moves slowly.

Generally, the substrates should be sheet material of about 15 to 30 pounds basis weight (24 in. x 36 in. sheets) to provide satisfactory strength and flexibility commensurate with economy. Preferably, paper having a carbon black additive to the beater furnish or black glassine are employed at a basis weight of about 23 to 26 pounds.

After the sheet material has been coated, the coating is allowed to dry by evaporation of volatile components. Although this may be effected at room temperature, generally it is desirable to employ low elevated temperatures on the order of 110 to 130° Fahrenheit to accelerate the process, conveniently in a forced air oven.

The recording paper may be printed with lines or other indicia if so desired so long as the ink does not appreciably attack the blushed coating such as by use of hydrocarbons as the carrier. As a specific example of a suitable ink, inks sold by Gotham Ink Company of Long Island City, N.Y., under the designation Zyroto have been highly satisfactory and are described as hydrocarbon soluble inks.

Turning now to the attached drawing, FIGURES 1 and 2 illustrate a recording sheet material embodying the present invention and comprised of a paper substrate 2, a colored layer 4 provided by a separate lacquer or a laminate, and the blushed coating 6 which is of sufficient opacity to mask the colored layer 4. When the heated stylus 8 contacts and applies heat to the blushed coating 6, the area of the coating 6 thereabout is rendered transparent to expose the colored layer 4 thereunder and provide a line tracing of the stylus path as indicated by the numeral 10.

The method of making the formulation of the present invention is diagrammatically illustrated in FIGURE 3. The initial lacquer is admixed with non-solvent for the resin of the lacquer to provide the first admixture wherein resin particles are shocked out of the resin solution and are then suspended therein by vigorous agitation, presumably in colloidal solution. This first admixture is then admixed with a second lacquer to produce a final admixture or coating formulation of desired bonding power.

Illustrative of the efficacy of the present invention are the following specific examples:

Example one

A first lacquer formulation was prepared by admixing two nitrocellulose lacquers. One lacquer was nitrocellulose resin dissolved in ethyl acetate and butyl alcohol with toluol as a diluent using blown castor oil and zinc stearate as plasticizers and flattening agents. This lacquer was commercially sold by Athol Lacquer Company under the designation Sealer 3040 and contained about 28 percent solids. Thirty parts by weight of this composition contained about 2.02 parts nitrocellulose, 4.73 parts stearates and plasticizers, 8.85 parts solvents and 14.4 parts diluents. The 30 parts by weight of this lacquer were admixed with 10 parts by weight of another nitrocellulose lacquer containing nitrocellulose dissolved in ethyl acetate and toluol in a 70:30 admixture with a solids content of about 25 percent. This lacquer is commercially sold by Raffi and Swanson under the designation "Cotton Solution No. 6727 (½ Second)."

The resultant first lacquer formulation was then admixed with 10 parts by weight of a petroleum solvent containing aliphatics and about 30.4 percent aromatics with a kauri-butanol value of 45 (sold commercially as Varsol No. 2 by Esso). A gelatinous flocculate was

produced and intensive agitation for thirty minutes with a Lightning Mixer (1750 r.p.m.) broke up the flocculate and resulted in a cloudy solution (due to the zinc stearate).

This admixture was then admixed with 4 parts of nitrocellulose lacquer, 5 parts of polystyrene solution and 4 parts of urea-formaldehyde solution (added in that order) with rapid agitation following each addition. The added nitrocellulose lacquer is commercially sold by Athol Lacquer under the designation "201-6" and contains 28 percent solids. The composition contains about 0.227 part by weight cellulose nitrate, 0.613 part by weight stearates and plasticizers, 1.2 parts solvent and 1.96 parts diluent. The polystyrene solution contains 24 percent solids and is commercially sold by Resyn Corporation under the designation "Resipol 130." The urea-formaldehyde solution contains 40 percent solids and is sold commercially by Reichold Chemicals under the designation "Beckamine P-817." This admixture was then thinned with 20 parts of methyl ethyl ketone to provide final coating composition which was slightly cloudy.

The coating composition was then applied to a substrate of black glassine by a wire rod to provide a wet coating of about 0.009 inch. This was dried in a forced air oven at about 125° Fahrenheit to yield an even blushed coating which concealed the color of the underlying substrate and was highly resistant to scuffing. Upon tracing by a heated stylus, the coating was readily rendered transparent to expose the color of the substrate, and no resin pickup upon the stylus was observable.

Similar properties and conditions prevailed when the coating was applied to a paper substrate having carbon black incorporated in the beater furnished to impart a black color thereto.

Example two

Thirty parts of a nitrocellulose lacquer was admixed with 10 parts of petroleum solvent containing about 30.4 percent aromatics (Varsol No. 2, Esso). The nitrocellulose lacquer is sold commercially by Raffi and Swanson under the designation "Sealer 4767" and is said to contain 21 percent solids broken down as 35.5 percent nitrocellulose, 47.5 percent Cellolyn 104, 5.0 percent zinc stearate and 12.0 percent blown castor oil; the solvent consists of 13 percent ethyl acetate, 20.0 percent butyl acetate, 2.5 percent ethyl alcohol, 3.0 percent butyl alcohol and 61.5 percent toluol. A gelatinous flocculate was produced which was dispersed to form a clear solution by rapid agitation in a Lightning Mixer at about 1750 r.p.m. for one-half hour.

This admixture was then admixed with 8 parts by weight of a second nitrocellulose lacquer commercially sold by Raffi and Swanson under the designation "Cotton Solution No. 6727 (½ Second)." The manufacturer describes the composition as 25.0 percent nitrocellulose dissolved in a solvent system consisting of 70.0 percent ethyl acetate and 30.0 percent toluol. After the lacquer had been thoroughly admixed for about one-half hour in the Lightning Mixer, 2 parts by weight of 50 percent by weight Gum Damar solution (using 40 percent toluol, 60 percent alcohol) were admixed therewith for another one-half hour to provide the coating composition.

A black chart paper substrate was provided by printing chart paper with a black ink coating provided by a nitrocellulose black ink dissolved in a solvent in a ratio of 1:1. The black ink is sold commercially by Raffi and Swanson under the designation "4000-98" and the solvent was 70.0 percent ethyl acetate and 30.0 percent toluol. To the black printed surface was applied the coating formulation by reverse roll coating apparatus to provide a dry coating of about 0.003 inch which concealed the color of the substrate and which exhibited a high degree of scuff-resistance. Upon application of a heated stylus, the coating was rendered transparent to

expose the color of the substrate, and little resin pickup on the stylus was observed.

Thus, it can be seen from the foregoing specific examples and detailed description that the present invention provides a recording paper or sheet with an effective and desirable blushed coating with relative economy and ease. The coating has a high degree of opacity, highly desirable scuff-resistance and low tendency toward stylus pickup.

Having thus described the invention, I claim:

1. In the method of making a recording sheet for marking by a heated stylus and the like, the steps comprising: admixing a lacquer consisting essentially of cellulose ester in a solvent therefor providing a resin solution with an organic liquid which is a non-solvent for said cellulose ester and in a sufficient amount to shock only a portion of said cellulose ester into resin particles within a matrix of said resin solution and form a gelatinous flocculate which is dispersible by agitation into an apparently clear solution; thereafter admixing said first-mentioned admixture with a second lacquer consisting essentially of cellulose ester in a solvent therefor to provide a second admixture which comprises shocked minute resin particles distributed throughout a resin solution of desired bonding power and which blushes upon evaporation of the solvent therein; and applying said second admixture to the surface of sheet material to provide a blushed coating thereon.

2. The method of claim 1 wherein said cellulose ester in said first and second lacquers is nitrocellulose.

3. The method of claim 1 wherein said organic non-solvent contains aromatic hydrocarbons.

4. The method of claim 2 wherein said organic non-solvent contains aliphatic and aromatic hydrocarbons and has a kauri-butanol value of about 35 to 55.

5. The method of claim 1 wherein said sheet material has a colored coating on said surface to which said second admixture is applied.

6. The method of claim 1 wherein said sheet material has a coloring agent incorporated therein.

7. A coating composition for producing blushed coatings upon sheet material for inscribing by a heated stylus and the like formed by the steps of admixing a lacquer consisting essentially of cellulose ester in a solvent therefor providing a resin solution with an organic liquid which is a non-solvent for said cellulose ester and in a sufficient amount to shock only a portion of said cellulose ester into resin particles within a matrix of said resin solution and form a gelatinous flocculate which is dispersible by agitation into an apparently clear solution; and thereafter admixing said first-mentioned admixture with a second lacquer consisting of said first-mentioned admixture with a second lacquer consisting essentially of cellulose ester in a solvent therefor to provide a second admixture which comprises shocked minute resin particles distributed throughout a resin solution of desired bonding power and which blushes upon evaporation of the solvent therein.

8. The coating composition of claim 7 wherein said cellulose ester is nitrocellulose.

9. The coating composition of claim 7 wherein said non-solvent contains aromatic hydrocarbons.

10. The coating composition of claim 7 wherein said non-solvent contains aliphatic and aromatic hydrocarbons and has a kauri-butanol value of about 35 to 55.

11. A recording sheet for marking by a heated stylus and the like having a substrate of sheet material and a blushed coating on one surface thereof formed by the steps of admixing a lacquer consisting essentially of cellulose ester in a solvent therefor providing a resin solution with an organic liquid which is a non-solvent for said cellulose ester and in a sufficient amount to shock only a portion of said cellulose ester into resin particles within a matrix of said resin solution and form a gelatinous flocculate

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culate which is dispersible by agitation into an apparently clear solution; thereafter admixing said first-mentioned admixture with a second lacquer consisting essentially of cellulose ester in a solvent therefor to provide a second admixture which comprises shocked minute resin particles distributed throughout a resin solution of desired bonding power and which blushes upon evaporation of the solvent therein; and applying said second admixture to the surface of sheet material to provide a blushed coating thereon.

12. The recording sheet of claim 11 wherein said cellulose ester is nitrocellulose.

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References Cited by the Examiner

UNITED STATES PATENTS

2,299,991	10/1942	Kallock	117—36.7
2,519,660	8/1950	James	117—36.7
2,961,334	11/1960	Clancy et al.	117—36.7
3,020,172	2/1962	Mohnhaupt	117—36.7
3,031,328	4/1962	Larsen	117—36.7
3,180,752	4/1964	Bollinger et al.	117—36.7
3,181,965	5/1965	Michelotti	117—36.7
3,228,785	1/1966	Growald et al.	117—36.7

MURRAY KATZ, *Primary Examiner.*