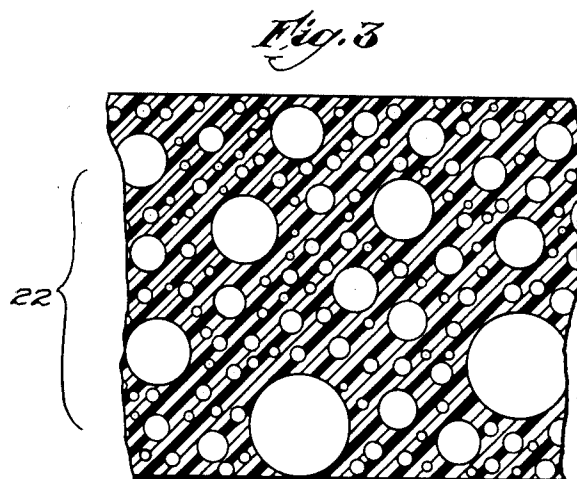
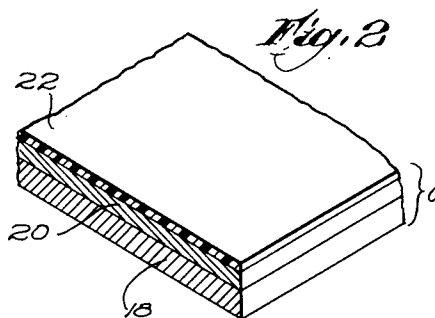
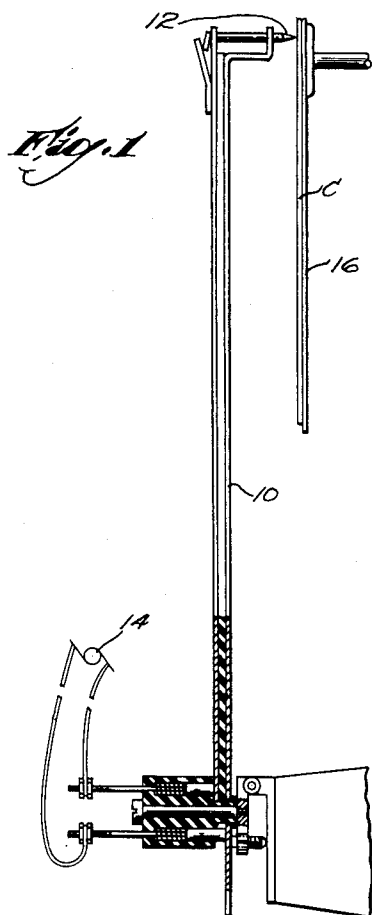


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COATED PAPER SUITABLE FOR STYLUS INSCRIPTION  
AND METHOD OF MAKING THE SAME  
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2,739,909

## COATED PAPER SUITABLE FOR STYLUS INSCRIPTION AND METHOD OF MAKING THE SAME

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This invention relates to sheet material (which usually will be paper and is so termed herein) having a coating thereon normally substantially opaque, but the physical nature of which will be so changed under the localized action of a stylus that it becomes more or less translucent, providing a conspicuously contrasting mark. The contrast arises because of the local disclosure of the contrasting color of the underlying paper, usually and conveniently due to the presence of a dark colored coating layer initially applied thereto and over which the stylus-sensitive coating is applied. The obscuring coating film is not scraped away or removed, at least to a substantial degree. The word stylus herein is used to denote any instrumentality whereby heat or pressure or both, as hereinafter explained, may be made locally effective on the obscuring coating of the paper.

Thermo-sensitive papers of the general character referred to find an extended use in connection with recording instruments wherein a heated stylus replaces the well known ink-fed pen marking a paper chart. It has been proposed to coat chart paper with a layer of discrete crystals adapted to soften and coalesce to form a homogeneous translucent mass at the area affected by the heated stylus. It has also been proposed to use as the obscuring coating a blushed lacquer. Thus, for example, cellulose acetate may be dissolved in a solvent mixture of acetone and water and coated on a paper base. On drying the acetone evaporates more quickly, disturbing the solvent balance and causing cellulose acetate particles to precipitate out, the resultant film coating being thus "blushed" as it is termed, and in this application appearing as a white, opaque coating. Under a heated stylus the particles soften and coalesce to provide a translucent homogeneous coating of the resin at the area affected by the stylus. It is difficult to obtain uniform results in utilizing such lacquers because humidity conditions during manufacture affect the evaporation rate on which depends the final opacity and whiteness of the obscuring film. This situation imposes a severe restriction on the commercial use of blushed lacquers for this purpose.

In each of these cases the coating layer is opaque and hides the dark background beneath because it embodies a multiplicity of small particles, each homogeneous in itself, but having its own reflecting surfaces. They may be compared to the solid pigment particles in a paint to which the hiding power of the paint is due. Or we might compare them to a layer of sand grains poured over the surface and covering the same. If it were possible to visualize a sufficiently intense yet localized source of heat effective locally to fuse such grains into clear, fused-silica glass, the analogy would be complete. The coating which I am about to describe is physically quite different and operates on different principles as will appear.

The invention will be explained with the aid of illustrative examples in the accompanying specification. To this specification are annexed drawings which, as will be well understood, are of an unrealistic and diagrammatic nature, and probably will be of use chiefly as a sort of

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graphical memorandum of the subject matter for the convenience of those who may have occasion hereafter to make use of the patent. In these drawings:

Fig. 1 is a fragmentary side elevation of a recording instrument having a heated stylus;

Fig. 2 is a greatly enlarged perspective view partly in section of a small piece of a chart paper illustrative of the invention; and

Fig. 3 is a sectional view, much enlarged, schematically illustrating the physical structure of the coating layer.

In Fig. 1 I have illustrated a recording instrument having a movable arm 10 which is moved responsively to the variable condition which is being measured and which has a stylus 12 electrically heated by current supplied from the current source diagrammatically indicated at 14. The stylus is shown as making contact with a paper chart C of the type about to be described, supported on the dial plate 16.

Referring to Fig. 2, the chart paper C may embody the paper base 18 which might in itself be of a dark colored nature, but herein is shown as having a dark colored coated layer 20 applied thereto in accordance with the usual practices of the paper art. Over this is applied the coating film 22 characteristic of the invention, normally opaque, but adapted to become locally translucent under the action of the stylus to reveal the dark colored layer underneath. Reference to this coating layer 22 as a thin film refers to a coating of such thinness as is utilized in so-called coated papers. This is usually expressed in terms of pounds of coating material per ream of 3,000 square feet. The coating is ordinarily only a mil or a fraction of a mil in thickness. A coating over three mils in thickness would not be considered a thin film in this connection.

It is believed that an understanding of the invention will be facilitated by a brief sketch at this point which should not be understood as either a complete exposition thereof or as a definition of its scope, the former being provided by the specification as a whole and the latter by the annexed claims when read and understood in the light of the specification. Briefly it may be said that the film 22 consists of a heat-sensitive plastic or plastic composition which has a three-dimensional cellular structure including a multiplicity of enclosed microscopic or submicroscopic voids distributed throughout its volume beneath the outer surface thereof. The plastic, apart from these voids, is substantially continuous and homogeneous and the film as a whole is opaque because of its heterogeneous physical structure, due to such voids. Under the localized action of the stylus the plastic material is fused, that is, it softens and coalesces with attendant collapse of such voids and release of air therefrom with the resultant production of a homogeneous, relatively transparent area disclosing the underlying dark surface.

Such a film may be prepared and applied to the paper base by applying thereto an emulsion of the water-in-oil-type, wherein a film-forming plastic is the continuous phase and the dispersed phase is present in the form of multitudinous droplets, at least almost all of which are of microscopic or submicroscopic dimensions, and by drying the film in such manner that the dispersed phase is evaporated without essential disruption or substantial collapse of the cellular structure of the continuous phase. While the gelation of the plastic film and the evaporation of the water therefrom may to a certain extent be simultaneous, in general they occur in substantial sequence in that order, in that the plastic layer first attains such a degree of semi-solidity as to be effective to trap the dispersed water droplets. The water is then evaporated by diffusion through the rigid, or substantially rigid, cellular walls of the plastic and is replaced by air forming the

voids already referred to. Thus, referring to Fig. 3, this might be considered a schematic view of an emulsion with the sectioned portion representing the continuous phase and the unsectioned circles the droplets of the dispersed phase. It is to be assumed that the physical structure of the emulsion will not be exactly reproduced during drying. There will be a certain shrinkage of the plastic layer. Certain of the droplets may merge and some may escape from the mass, but in general the solidified layer will reproduce in substantial degree in solid form the structure of the emulsion and the sectioned portion in Fig. 3 represents the cellular layer of rigidified plastic and the unsectioned areas the multiplicity of included air-containing voids. It may be desirable to recall at this point that the vertical width shown in Fig. 3 represents a dimension which in practice may be only a fraction of a mil.

The cellular character of the coating layer 22 and the presence thereon of the isolated voids may be strikingly demonstrated by submerging the paper in a solvent for the resinous material. A substantial ebullition of bubbles through the solvent is noted as the layer is dissolved. This would not be the case if the material were merely porous with open pores defined by a multiplicity of aggregated particles, since there the solvent would enter these pores and displace the air therefrom in major degree as the material was lowered into the solvent.

As has already been explained, under the stylus the film of resinous material is caused locally to coalesce into a homogeneous mass with collapse of the voids at the areas affected and release of air therefrom. Such coalescence is dependent upon heat, pressure and time. In practical applications the time interval will usually be brief. The heat should not be enough to ignite the chart or otherwise impair its integrity. In the case of recording instruments the pressure involved is light. If a localized beam of radiant heat were used the pressure factor would be zero. If the cellular coating were sufficiently plastic it might be termed pressure-sensitive and would be adapted for inscription at room temperature by pressure alone. In this case the heat factor is the normal ambient temperature, as will be apparent when we consider the fact that we would not expect satisfactory results from the same pressure at sub-zero temperatures when the film had thereby been substantially increased in rigidity.

The continuous phase of the emulsion may be termed a lacquer in that it is a film-forming material dissolved in a solvent adapted, on normal evaporation of such solvent, to dry down as a continuous layer. In the present instance the solvent is characterized by insolubility in water. The dispersed phase is aqueous, either water, a water-soluble liquid or a water-dissolved solid, incompatible with the ingredients of the continuous phase, both film-former and solvent, or a combination of water with such liquid or solid. The formation of an emulsion is aided by the addition of an emulsifying assistant suitable for water-in-oil dispersions, such as are known to the art, among which may be instanced stearyl dimethyl benzyl ammonium chloride, available under the commercial name "Triton K-60," aromatic polyglycol ethers, such as that available under the commercial name "Antarox A-200" or sorbitan trioleate, available under the commercial name "Span 85." These emulsifiers are soluble in the lacquer solvent, which may be benzene, toluene, chloroform or any other meeting the requirements outlined above. Ethyl cellulose has been found excellent for use as film-former, because of its range of heat-sensitivity, as well as because of its compatibility with many substances capable of modifying the desired coating. Such modification may involve providing a lower softening temperature of the coating which may be achieved by adding a plasticizer to the film-former. In addition to compatibility with the resin, the plasticizer should be incompatible with the dispersed phase. Tricresyl phosphate, dioctyl phthalate and castor oil are examples of plasti-

cizers which fill these requirements and which I have successfully used. Other additives, which are known to enhance gloss and hardness of ethyl cellulose coatings, may be used to advantage. For example, I have obtained such results by incorporating a chlorinated diphenyl resin commercially known as "Aroclor 5460" in proportions ranging from 0 to 75% by weight of ethyl cellulose. Coumarone-indene resins are also useful as resin extenders.

Satisfactory white coating are obtained when the evaporation of the dispersed phase occurs essentially after the evaporation of the lacquer solvent, i. e. after gelation of the lacquer film. When a solvent of relatively low evaporation rate is used, such as toluene or even xylene, it may be advantageous to retard the evaporation rate of the water or other components of the dispersed phase. This can be effected by adding to water numerous water-soluble substances, for example salts such as sodium acetate or lead acetate, but especially polyvalent alcohols, such as ethylene glycol or glycerol. Such alcohols are insoluble in the lacquer solvent and incompatible with the film-formers.

Emulsions thus formed are applied to a suitable base paper previously coated with a black or dark-colored base coating as known in the art. The emulsion is applied at such a rate as to form a thin coating (3 to 5 pounds, or even less, per ream of paper). It is possible in accordance with the invention to provide coatings of such order of weight having, when coated over a black backing a whiteness, measured by a photometer as high as 86% of a magnesium carbonate standard.

One of the important features of this invention is the wide range over which the ratio of lacquer solution to dispersed phase may be varied in a "water-in-oil" emulsion. While in a blushed lacquer the ratio of solvent to water is limited by the water tolerance of the lacquer (in the vicinity of 30 parts water to 100 parts lacquer solution), it is possible in the emulsion system to increase the water (dispersed phase) to lacquer ratio to 150:100 if desired. It is thus possible to alter at will the characteristics of the emulsion and of the heat-sensitive coating, which may be prepared from the emulsion.

More specifically, the dispersed phase determines the degree of aeration of the final coating in two ways, (1) the water to lacquer ratio as indicated in the previous paragraph and (2) the particle size of the dispersion which may be reduced by such mechanical means as a pass through a homogenizer. Such homogenization renders the emulsion more stable and thus improves the degree of aeration of the solidified coating resultant from evaporation of the dispersed phase. This degree of aeration determines the whiteness of the final coating. Aeration is also manifested by a measurable increase in apparent volume of the coating.

An important practical advantage of these coatings is that the degree of aeration can be controlled, as I have outlined, by the amount of the dispersed phase and the nature of the dispersion. Aerated resins of determined physical properties are reproducible to a degree practically impossible with blushed lacquers of the prior art, which depend on such outside factors as temperature and relative humidity.

I shall next give numerous examples which will further elucidate the nature of the invention and in the light of which and of the explanations already given and to be given those skilled in the art will be enabled, without experimentation of an inventive character, to apply the principles of the invention to the selection and compounding of other specific ingredients.

Ethyl cellulose is a very desirable plastic for use as the solid portion of the cellular film. The first eight examples now to be given illustrate the use of this material in various ways. In all these cases the uniformity

and stability of the emulsions are enhanced by passing them through a homogenizer.

#### Example 1

41.25 grams of ethyl cellulose, grade N-100 are dissolved in 650 cc. of toluene under stirring. Grade N-100 identifies a resin, a 5% solution of which in a solvent consisting of 80 parts toluene and 20 parts ethanol has a viscosity of 93.5 centipoises. As emulsifier, 1.9 grams of "Triton K-60" are added. Under constant high-speed stirring, 92 cc. of distilled water are added dropwise or in the form of a fine spray at a rate slow enough to permit uniform emulsification. This emulsion produces a photometer reading of 73% when applied and dried as a coating of 6.0 pounds per ream. The apparent density of the coating is measured to be 0.39.

#### Example 2

This differs from Example 1 in the amount of water used to form the dispersed phase, 184 cc. of water, or twice as much as in Example 1. This emulsion produces a photometer reading of 80% when applied and dried as a coating of 4.0 pounds per ream. That is, the coating is lighter in Example 1, but the whiteness is superior. The apparent density of the coating is measured to be 0.16.

#### Example 3

This is like Example 1 except a still larger amount of water is used, 504 cc. This emulsion produces a photometer reading of 71% when applied and dried as a coating of 2.2 pounds per ream. The apparent density of the coating is measured to be 0.08.

#### Example 4

This example illustrates the use of a less volatile solvent for the resin and an evaporation retarder for the aqueous constituent. If the resin solvent is less readily driven off the continuous resin phase does not pass over into the solid form so rapidly and it might be possible for much of the water to evaporate before it was trapped, with resultant collapse to a considerable degree of the cellular structure and the production of a coating of poor hiding power. This may be avoided by the addition to the water phase of an ingredient retarding its evaporation that is, providing a decreased vapor pressure of the dispersed phase. This is the specific example.

41.25 grams of ethyl cellulose, grade N-100, are dissolved in 650 cc. of xylene under stirring. As emulsifier, 1.9 grams of "Triton K-60" are added. Under constant high-speed stirring, a mixture of 378 grams of ethylene glycol and 126 cc. of distilled water are added dropwise or in the form of a fine spray at a rate slow enough to permit uniform emulsification. This emulsion produces a photometer reading of 71% when applied and dried as a coating of 2.2 pounds per ream.

#### Example 5

This example as contrasted with Example 2 illustrates the use of a smaller amount of resin of greater molecular weight and hence greater viscosity, whereby a lower proportion of solids may be utilized to provide a coating of acceptable whiteness and opacity. Ethyl cellulose of grade N-300, having a viscosity of 319.7 centipoises as contrasted with 93.5 for grade N-100 previously referred to, is used.

24.5 grams of ethyl cellulose, grade N-300, are dissolved in 650 cc. of toluene under stirring. As emulsifier, 1.9 grams of "Antarox A-200" are added. Under constant high-speed stirring, 229 cc. of distilled water are added dropwise or in the form of a fine spray at a rate slow enough to permit uniform emulsification. This emulsion produces a photometer reading of 69% when applied and dried as a coating of 2.8 pounds per ream.

#### Example 6

This example, as contrasted with Example 2, illustrates

the addition of a plasticizer in order to reduce the softening temperature of the coating and increase its heat sensitivity.

41.25 grams of ethyl cellulose, grade N-100, are dissolved in 650 cc. of toluene under stirring. As plasticizer, 20.62 grams of tricresyl phosphate, available under the commercial name "Lindol," and as emulsifier, 1.9 grams of "Antarox A-200" are added. Under constant stirring, 229 cc. of distilled water are added dropwise or in the form of a fine spray at a rate slow enough to permit uniform emulsification. This emulsion produces a photometer reading of 70% when applied and dried as a coating of 4.9 pounds per ream.

#### Examples 7 and 8

Examples 7 and 8 are examples in which a mixture of resinous plastics is utilized as the lacquer base, or otherwise expressed, ethyl cellulose as used in the previous examples is modified by added resins. In these instances coatings of improved gloss and hardness and a superior degree of whiteness are provided for.

#### Example 7

41.25 grams of ethyl cellulose, grade N-100, are dissolved in 650 cc. of toluene under stirring. As resin modifier 10.25 grams of "Aroclor 5460" and as emulsifier, 1.9 grams of "Antarox A-200" are added. Under constant stirring, 229 cc. of distilled water are added dropwise or in the form of a fine spray at a rate slow enough to permit uniform emulsification. This emulsion produces a photometer reading of 83% when applied and dried as a coating of 5.4 pounds per ream.

#### Example 8

41.25 grams of ethyl cellulose, grade N-100, are dissolved in 650 cc. of toluene under stirring. As resin modifier, 41.25 grams of a coumarine-indene resin and as emulsifier, 1.9 grams of "Antarox A-200" are added. Under constant stirring, 620 cc. of water are added dropwise or in the form of a fine spray at a rate slow enough to permit uniform emulsification. This emulsion produces a photometer reading of 82% when applied and dried as a coating of 5.8 pounds per ream.

I have given a series of examples in which ethyl cellulose is used as the resin. I will here give other examples involving the use of other thermoplastic polymer materials. These have been selected as a typical cross-section of high polymer thermoplastic resins. I shall give only a single example for each resin, as the possibilities of variation will be apparent from the examples already given.

#### Example 9

40 grams of polystyrene are dissolved in 200 cc. of benzene under stirring. As emulsifier, 2 grams of sorbitan sesquioleate, available under the commercial name "Arlacel C," are added. Under constant stirring, 100 cc. of water are added dropwise or in the form of a fine spray at a rate slow enough to permit uniform emulsification. This emulsion produces a photometer reading of 74% when applied and dried as a coating of 5.8 pounds per ream.

#### Example 10

8 grams of polyvinylchloride-acetate (commercial grade VYHH of Carbide and Carbon Chemicals Corporation) are dissolved in 60 cc. of propylene dichloride under stirring. As emulsifier, 0.5 gram of "Arlacel C" are added. Under constant stirring, 30 cc. of water are added at a rate slow enough to permit uniform emulsification. This emulsion produces a photometer reading of 69% when applied and dried as a coating of 5.9 pounds per ream.

#### Example 11

25 grams of polymethyl methacrylate, having a molecular weight of 31,600 or more and a flow temperature (Max.) of 138° C. are dissolved in a mixture of 100 cc.

of toluene and 50 cc. of methylene dichloride. As emulsifier, 2 grams of "Arlacel C" are added. Under constant stirring, 75 cc. of water are added at a rate slow enough to permit uniform emulsification. This emulsion produces a photometer reading of 82% when applied and dried as a coating of 10.5 pounds per ream.

#### Example 12

25 grams of nitrocellulose, of a grade having a viscosity of 5-6.5 seconds in a solution of 12.2% concentration, are dissolved in 200 cc. of n-butyl acetate. As emulsifier, 2 grams of an anhydrous aliphatic polyethylene glycol amide, available under the commercial name "Antarox G-100," are added. Under constant stirring, 200 cc. of water are added at a rate slow enough to permit uniform emulsification. This emulsion produces a photometer reading of 77% when applied and dried as a coating of 4.3 pounds per ream.

#### Example 13

10 grams of cellulose acetate of a grade having a low acetyl value and an Eastman viscosity of 2-5 seconds are dissolved in a mixture of 100 cc. of methylene dichloride and 10 cc. of iso-octyl alcohol under stirring. As emulsifier, 1.5 grams of "Antarox G-100" are added. Under constant stirring, 55 cc. of water are added at a rate slow enough to permit uniform emulsification. This emulsion produces a photometer reading of 77% when applied and dried as a coating of 5.5 pounds per ream.

#### Example 14

I shall now discuss in connection with a specific example, the use of a low polymer resin, not because the example provides a particularly advantageous application of the principles of the invention, but because of the light it sheds on such principles. By way of example I have chosen a coumarone-indene resin having a melting point of about 150° C. of a type known by the commercial designation "Nevindene R-3." This resin being of low molecular weight has a rather low viscosity, also it tends to be brittle, a property also inherent in resinous materials of low molecular weight. In accordance with the invention, as already explained, entrapment of the water droplets and resultant whiteness in the solidified layer are achieved by postponing substantial evaporation of the water until a certain degree of viscosity or rigidity has developed in the continuous phase, due to solvent evaporation. Thus in a resin of low molecular weight such as the coumarone-indene resin referred to, this rigidity is reached only at a more advanced degree of solvent evaporation as compared with the higher molecular weight materials. Therefore to insure retention of water droplets sufficient for desired whiteness a solvent of high volatility should be chosen. Thus a solution of coumarone-indene resin "Nevindene R-3" in toluene, emulsified with an equal volume of water by means of an emulsifier "Arlacel C" did not produce a satisfactory coating, apparently because the relatively high-boiling toluene maintained the lacquer component sufficiently soft or fluid to permit the water of the dispersed phase to escape to the air. The same materials, utilizing benzene as a solvent, on the other hand produced a moderately good coating when utilized in a relatively thick layer. Thus a coating of 22½ pounds per ream gave a photometer reading of 52%. That is, as compared with Example 1, about four times as much coating material was required to provide a reflectance value only about two-thirds as great.

The qualities of such lower polymer coatings, however, may be substantially improved by incorporating therewith a proportion of high polymer material. This is an example wherein the lacquer base is a plastic composition involving more than one resin, the resins having different names. Thus, a similar emulsion utilizing as the lacquer base 97% coumarone-indene resin and 3% ethyl cellulose and laid down as a coating of 11.2 pounds per ream,

gave a photometer reading of 54%. That is, equally good reflectance was obtained with about half the material as compared with the unmodified resin. An increase in the proportion of high polymer resin used, for instance say 10% of ethyl cellulose, results in a further improvement. Example 8, given above, is an example wherein 50% of coumarone-indene resin is combined with 50% ethyl cellulose and the low viscosity resin in that case acts as a useful modifier of the ethyl cellulose to afford highly desirable physical properties.

#### Example 15

I shall next give an example of a coating which may be considered pressure-sensitive rather than heat-sensitive, that is, it will yield an inscription under moderate pressure at room temperatures. It will be understood that for practical purposes the coating should be such as to resist smudging during handling. Thermoplastic materials of relatively low molecular weight will tend to be more pressure-sensitive than homologues of higher molecular weight, and moreover, the incorporation of plasticizers to enhance pressure sensitivity is facilitated in materials of lower molecular weight because of improved compatibility of such plasticizers therewith in comparison with the homologues of the former of higher molecular weight. Guided by these considerations the specific example hereinafter set forth utilizes ethyl cellulose grade N-10, having in solution form as previously described a viscosity of 9.3 centipoises, substantially lower than grades N-100 and N-300 which have been referred to in preceding examples.

The specific data follows. 10 grams of ethyl cellulose grade N-10 are dissolved in 75 cc. of benzene under stirring. As plasticizer 5 grams of tricresyl phosphate, and as emulsifier 0.5 gram of "Antarox A-200" are added. Under constant stirring 75 cc. of water are added at a rate slow enough to permit uniform emulsification. This emulsion produces a photometer reading of 70% when applied and dried as a coating of 4.9 pounds per ream.

As a measure of its sensitivity to pressure a sapphire stylus having a top rounded to the curvature of  $\frac{1}{16}$  of an inch radius was pressed thereagainst with the force of one ounce. The coating became transparent under this pressure, providing a clear marking.

It is apparent from the examples given that many different components may be utilized in the manufacture of coatings under the invention. Also new synthetic resins and polymers are constantly being developed and made commercially available, many of which undoubtedly will be found adaptable as components of such coatings. It is therefore not only impossible to attempt a comprehensive catalog of useful components, but to attempt to apprehend or describe the invention in its broader aspects in terms of the chemical names of the components used would be misleading. The invention is not chemical but physical, being characterized by the physical form of the completed coating and the individual composition of any ingredients is important only in the sense that the individual properties of the elements of any mechanical assemblage are important to their proper combination and coaction. To formulate a specific recipe for a composition comparable to those in the examples given will call for a certain familiarity of the physical properties of resins and other materials and their relative compatibility but the office of the chemist writing such a recipe would be like that of a mechanical engineer who prescribes in the construction of a machine the proper materials and the proper dimensions therefor. One skilled in the art, from his knowledge of the materials available, will know or deduce with confidence their applicability for the purposes of the invention or, otherwise, and in the case of novel materials routine tests, not of an inventive nature, will provide reliable data.

I am aware that the invention may be embodied in other specific forms without departing from the spirit or

essential attributes thereof, and I therefore desire the present embodiment to be considered in all respects as illustrative and not restrictive, as is in fact clear in several matters from the description itself. Reference is to be had to the appended claims to indicate those principles of the invention exemplified by the particular embodiment described and which I desire to secure by Letters Patent.

I claim:

1. Recording material suitable for receiving inscriptions from a stylus comprising a backing an adherent obscuring film covering its surface which film consists of thermoplastic resinous material and has a three-dimensional cellular structure including a multiplicity of discrete microscopic or sub-microscopic enclosed voids beneath the outer surface thereof and distributed throughout the volume of the film in a major proportion of its thickness, the resinous film apart from said voids therein being substantially continuous and homogeneous, the film being normally opaque throughout its area because of its heterogeneous physical structure due to the inclusion of such voids, but adapted for local coalescence under the stylus to permit release of air from said voids and collapse thereof with resultant production of a homogeneous, relatively transparent area disclosing the underlying surface.

2. Recording material as defined in claim 1, wherein the resinous material consists essentially of ethyl cellulose.

3. Recording material as defined in claim 2, wherein a compatible resin is admixed with the ethyl cellulose to harden the film.

4. Recording material as defined in claim 1, wherein the resinous material consists essentially of polystyrene resin.

5. Recording material as defined in claim 1, wherein the resinous material consists essentially of polyvinyl resin.

6. Recording material as defined in claim 5, wherein the resinous material consists essentially of polyvinyl chloride acetate.

7. Recording material as defined in claim 1, wherein the resinous material consists essentially of acrylate polymer.

8. Recording material as defined in claim 7, wherein the resinous material consists essentially of methyl methacrylate.

9. Recording material as defined in claim 1, wherein the resinous material consists essentially of cellulose ester.

10. A method of preparing recording material suitable for receiving inscriptions from a stylus and comprising a supporting backing having an obscuring film covering its surface: the method comprising dissolving in a volatile solvent therefor a thermoplastic, film-forming, resinous material which in the form of a solid film is at least slowly pervious to the vapor of the liquid hereinafter referred to, and softenable under the heat and pressure of the stylus;

emulsifying in said solution as a continuous phase a volatile liquid which is a non-solvent for the resinous material and is substantially incompatible with the solution, the liquid being present in significant quantity to provide as a dispersed phase multitudinous microscopic or sub-microscopic droplets uniformly distributed at random throughout the volume of the continuous phase; depositing a film of the emulsion as a continuous superficial coating extending over the area of the backing, gelling the resinous material by substantial evaporation of its solvent and in substantial sequence to such gelling evaporating the dispersed droplets by diffusion through the essentially undisturbed and uncollapsed walls of the microscopically cellular structure provided by such gelled resinous material.

11. The method of claim 10 when an ingredient insoluble in the volatile solvent and incompatible with the resinous material is added to the volatile liquid to decrease the vapor pressure thereof.

12. Recording material suitable for receiving inscriptions by the application of heat thereto in a delimited portion of its area corresponding in form to a significant mark, said recording material comprising a backing and an adherent obscuring film of less than fifteen pounds per ream covering its surface which film consists of thermoplastic resinous material and has a three-dimensional cellular structure including a multiplicity of discrete microscopic or submicroscopic enclosed voids beneath the outer surface thereof and distributed throughout the volume of the film in a major proportion of its thickness, the resinous film apart from said voids therein being substantially continuous and homogeneous, the film being normally opaque throughout its area because of its heterogeneous physical structure due to the inclusion of said voids and having a reflectance value greater than 65%, the film being adapted for local coalescence under application of heat thereto in such a delimited portion of its area to permit the release of air from the voids at said portion with collapse of said voids and resultant production of a homogeneous, relatively transparent mark visibly contrasting with the adjacent unaltered film surface.

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