

Sept. 24, 1963

T. MAIERSON

3,104,980

PRESSURE SENSITIVE RECORD AND TRANSFER SHEET MATERIAL

Filed Oct. 3, 1960

FIG. 1

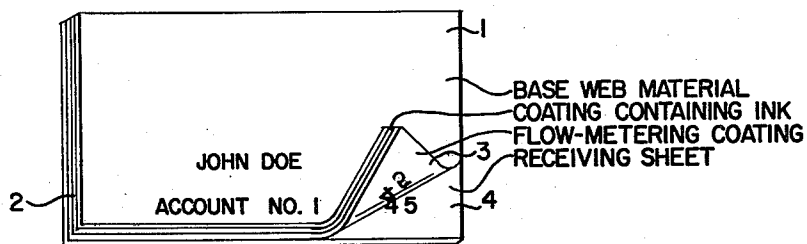


FIG. 2

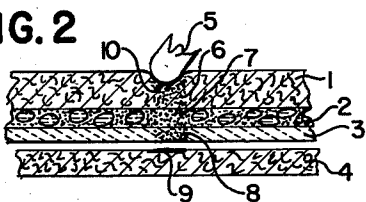


FIG. 6

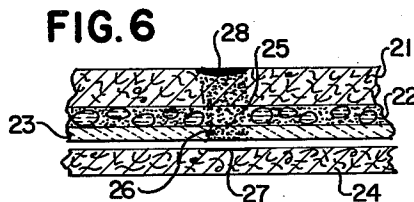


FIG. 3

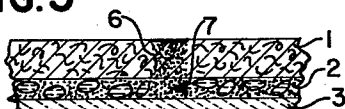


FIG. 7

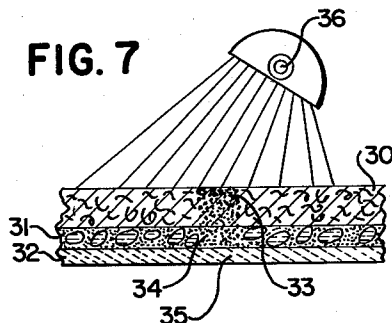


FIG. 4

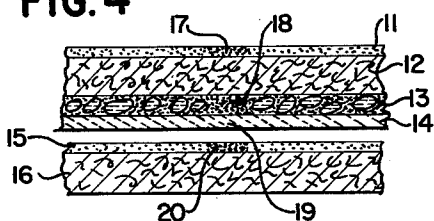
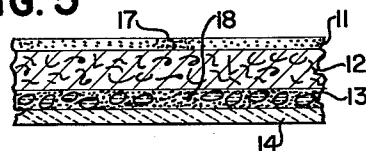


FIG. 5



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3,104,980

## PRESSURE SENSITIVE RECORD AND TRANSFER SHEET MATERIAL

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Filed Oct. 3, 1960, Ser. No. 60,078

6 Claims. (Cl. 117—36.4)

This invention relates to improved pressure-sensitive record and transfer sheet material having improved transfer characteristics, and more particularly relates to such materials which include a web base or backing material, one side of the web base having a first coating of a rupturable material containing small droplets of liquid marking material or ink carried in a low-viscosity volatile vehicle and having superposed over the first coating a second coating of flow-metering material which forms a thin layer over said first coating; the said marking material being so characterized that the application of localized pressure in a desired configuration ruptures the coating material and allows a portion of the thus-released ink to penetrate the web material to produce either a latent mark or a visible mark on the surface opposite that of the ink-coated side according to the type of ink used; and, when desired, a corresponding mark in the desired configuration may also be produced by another portion of the ink on the surface of a receiving sheet placed in pressure contact with said second or metering coating, the improvement residing in said second coating, which consists of a thin layer of material in juxtaposition with said first coating and having such composition and coated in such quantity as to selectively control or meter the amount of ink transferred from said first coating to said receiving sheet and thereby also controlling the amount of ink allowed to penetrate the ink-coated web base material so as to form a mark on the opposite side thereof.

This invention is an improvement over the record and transfer material disclosed in the commonly-assigned application for United States Letters Patent No. 52,195 filed on August 26, 1960, by Joseph A. Bakan, David J. Striley, and Theodore Maieron, now U.S. Patent No. 3,020,171, wherein a pressure-sensitive record and transfer sheet is provided which is particularly useful when used with printers for making impressions from type or from embossed identification or charge-authorizing plates, the particular advantage of so using the above novel pressure-sensitive sheet being that a single ink-containing coating on the web base material or sheet provides the means for producing two distinct marks with one and the same ink-containing coating; i.e., one mark on the surface opposite the ink coating on the web base material or sheet, the other on the surface of a receiving sheet placed in pressure contact with said ink coating. However, the invention described in the above-mentioned patent application is not limited to a two-sheet arrangement whereby the ink-coated web material serves as a transfer sheet and is used in superposed relation with a receiving sheet; the ink-coated web sheet material may be used alone as a record sheet and when thus used is equal in importance to the two-sheet arrangement.

It has been found that the dye and/or pigment distribution between the ink-coated transfer sheet and the receiving sheet of the invention described in the above-mentioned patent application may vary due to certain factors related to the characteristics of some of the ingredients thereof. For example, the porous web base material may vary greatly in porosity, wettability, and absorption characteristics and thus render accurate control of the distribution of coloring material difficult; or, again, the absorption and wettability characteristics of

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the base web material may be different from those of the receiving sheet, either by design or for reasons beyond the control of the manufacturer, and the receiving sheet may thereby receive more or less than its desired share of the released ink.

It is also noted that in the prior record and transfer sheet there is a tendency for a major portion of the ink contained in the rupturable matrix or capsules to be preferentially transferred to the receiving sheet, thus making a mark of greater intensity on the receiving sheet than on the surface of the ink-coated web base material. In the use of such sheet material, however, it is generally desirable to obtain a mark or print on the top surface of the transfer sheet which is equal in intensity and uniformity to the mark on the top surface of the receiving sheet; or, for some purposes, it may be desirable to provide a coating which is essentially impervious to ink flow and thus prevent any transfer to a receiving sheet.

The present invention provides a metering device which may be so constituted and selected as to provide an obstacle to the flow of ink, the flow being regulated by the selectively adjustable permeability of said obstacle.

In accordance with the present invention, a preferred means for efficiently metering the ink distribution between the transfer sheet and the receiving sheet is provided by the application of a novel metering coating as a thin layer or overcoating directly over the ink coating on the transfer sheet, the metering coating consisting essentially of a thin permeable layer of natural or synthetic polymer material. Preferably such materials are flexible and moderately heat resistant and possess good adhesive properties in relation to said ink coating. The material which forms the metering coating of this invention, as hereinafter specified, may be applied by conventional means as a thin film of polymer latex—i.e., an aqueous dispersion of the polymer—and then dried to provide the metering coating, or it may be applied as an aqueous or organic solvent solution of the polymer, depending on the effect desired and on the type of metering material capable of producing the desired effect.

In the record and transfer material heretofore described, wherein no flow-metering coating is employed, the flow and the distribution of ink are primarily controlled by the characteristics inherent in the materials of the ink and the transfer and receiving webs or sheets. By contrast, when the flow-metering coating in accordance with this invention is utilized, such control of ink distribution no longer resides chiefly in the web and ink characteristics, but rather becomes a function mainly of the metering coating, the permeability of which may be selectively adjusted over a wide range. Hence, an important advantage associated with the novel recording and transfer sheet material having the metering coating is that, although certain combinations of web material and ink produce poor results when used without benefit of the metering coating, these same combinations, as well as many others, provide excellent prints when the ink is metered with the metering coating, because of the wide range of ink permeabilities which may be incorporated, at will, into the metering coating. Thus, ink and web base materials of transfer and receiving sheets which were formerly incompatible may now be combined to provide desirable transfer and penetration characteristics, merely by being utilized in connection with the metering coating, which, when applied with a selected permeability, largely controls the ink distribution. The number of ink-web-base combinations which may be utilized to produce colored prints according to this invention is thus much larger than the number of useful combinations heretofore possible.

A primary object of this invention, therefore, is to pro-

vide a novel record and transfer material having a selectively permeable flow-metering coating in juxtaposition with an ink-containing coating on one side of the record and transfer sheet, the metering coating being adapted for controlling the proportion of ink distributed between the porous web material of the ink-coated record and transfer sheet and the front surface of a receiving sheet placed in pressure contact with said flow-metering coating.

It is another object of this invention to provide a flow-metering coating in contiguous relation with an ink-containing coating on one side of a record sheet, the metering coating being so constituted as to provide an essentially impervious layer over said ink-containing coating, thus providing a barrier layer which promotes the greatest possible transfer of ink to the surface of the top sheet, with a negligible amount being transferred to a supporting surface in contact therewith. This arrangement is particularly useful when only an original is required, since sheet material so constituted prevents fouling of type or pressure platen members of a printing device.

Further objects will become apparent from the drawing and from the following detailed description of the preferred and other embodiments of the novel record and transfer sheet embodying a flow-metering coating as contemplated in this invention. It is to be understood, however, that the flow-metering coating of this invention is useful with any and all embodiments and equivalents thereof disclosed in said co-pending patent application. accordingly, the matter disclosed therein is considered as forming part of the instant disclosure.

In the drawings:

FIG. 1 shows a two-sheet form set embodying the invention with printing marks on the top surface of a sheet coated on the opposite side with a first coating containing ink and thereover a second flow-metering coating, and shows corresponding marks on the top surface of a receiving sheet placed in contact with the coated surface.

FIG. 2 shows an enlarged cross-sectional view of one embodiment of a form set wherein the matrix coating material contains liquid droplets of colored dye and the matrix coating is overcoated with a flow-metering layer of polymeric material.

FIG. 3 shows another embodiment, similar to that of FIG. 2, except that no receiving sheet is shown as used in conjunction with the top sheet, and the metering coating is essentially impervious and serves as a barrier for the liquid colored dye.

FIG. 4 illustrates still another embodiment, in which the ink coating on the rear surface of the base sheet is overcoated with a flow-metering coating, the ink including a colorless dye which coats with a reactant coating on the top surface of the base sheet and on the surface of a copy-receiving sheet to produce a colored mark.

FIG. 5 shows a similar embodiment to that of FIG. 4, with the exception that no receiving sheet is used with the top sheet, and the metering coating is essentially impervious and serves as a barrier.

FIG. 6 is yet another embodiment, wherein the ink coating is overcoated with a flow-metering layer of polymeric material, and the ink contains a dye solution and a dispersed pigment.

FIG. 7 is a cross-sectional view of still another embodiment, which shows a base material with a first coating containing droplets of coloring material, the coloring material consisting of colorless phototropic material dissolved in a colorless volatile solvent, which material is adapted to leave a solution mark which can be developed to a colored mark by exposure to ultra-violet light, the first coating being overcoated with a second coating of flow-metering polymeric material, the formulation of which is adjustable to produce a coating of desired permeability.

In the following detailed description, it is the intention to illustrate the applicability of the flow-metering coating in novel record and transfer sheet material wherein

an ink coating on one side of a sheet is adapted to produce a colored mark on its opposite side, and also, when desired, a colored mark on the surface of a receiving sheet in contact with the ink coating. In the figures, like numerals refer to like parts.

FIG. 1 shows a plan view of a form set which consists of a top sheet 1, coated on its under side with a first coating 2, comprising a profusion of minute droplets of coloring material in a pressure-rupturable matrix and a second, or flow-metering, coating 3, of polymeric material, which top sheet is superimposed over a copy-receiving sheet 4, the flow-metering coating being in contact with said receiving sheet. The coated top sheet and receiving sheet, when pressure is applied by any suitable pressure-printing means, as, for example, when the sheets are pressed against an embossed identification plate, or printed on by another embossing element, such as a type member, a scribe, or a stylus, will produce similar sharp distinctively-colored marks when colored marking material is used, in the shape of the characters made by the printing means, on the top surface of both the top ink-coated sheet and the copy-receiving sheet. The matrix containing the droplets of coloring material may be of a continuous nature or discontinuous, such as a coating made of capsules. The flow-metering coating 3 forms a contiguous layer over the ink coating 2, and, when the top sheet is superimposed over the copy-receiving sheet 4, it acts as a sieve to control the flow of ink from the ink coating 2 to the surface of the copy-receiving sheet 4. By the application of suitable polymeric materials in proper amount, as will be specified hereinafter, the permeability or porosity of the flow-metering coating 3 may be selectively adjusted, so that the amount of ink transferred from the ink coating 3 to the copy-receiving sheet 4 may be varied over a wide range; i.e., from a very small amount up to ninety percent of the ink released by the application of printing pressure on a defined area of the ink-containing pressure-rupturable matrix.

The metering coating is also of particular value when the ink-coated sheet is to be used alone as a record sheet. For such use, the metering coating is so formulated that it forms an essentially impervious or impermeable barrier for the ink contained in the adjacent coating. The impervious coating thus substantially prevents any transfer of ink to a supporting surface. Since no ink is lost to such surface, all the released ink is available to penetrate the base web, and only a minimum amount of ink, which is just sufficient to produce a colored mark of the required intensity on the surface of the coated sheet, is required.

One embodiment of a form set consisting of a combination of sheets is shown in FIG. 2. In this arrangement, a top sheet 1, of opaque porous material, is provided with a first coating 2, of a pressure-rupturable matrix containing minute droplets of liquid colored dye material, and a novel second coating 3, of flow-metering polymeric material, which coated top sheet is superimposed over a receiving sheet 4. The top sheet must ordinarily be sufficiently opaque to mask the colored coating and be of such color as to provide good contrast with the colored dye which is to make the colored mark thereon. As will be described later, the invention also has application when used with transparent or translucent sheet material, so long as the coloring material is originally colorless, such as dyes which become colored on contact with particles which react as acids toward the dye, as well as with colorless phototropic dyes which develop characteristic color when exposed to electromagnetic radiation. In use, when pressure is applied to the top sheet 1 by an element, such as the stylus 5, the pressure ruptures the matrix material in the defined area 7 and thereby releases the colored ink contained in said matrix coating, which ink is so constituted and provided in such quantity that it penetrates the base sheet 1 in

the pressure area 6 to form a colored mark on the opposite surface of the sheet, as at 10. A portion of the colored ink released by rupture of the matrix coating in the area 7 permeates through the microscopic pores of the novel polymeric flow-metering coating, as in the area 8, and is thereby transferred to the surface of the receiving sheet 4 to produce a colored mark 9. The ink, as will be specified later, contains a high proportion of volatile low-viscosity solvent which causes rapid drying and minimizes lateral bleed of the ink in the base sheet, so that a clearly-defined colored mark appears on the surface of the two sheets.

FIG. 3 shows substantially the same arrangement as that shown in FIG. 2, except that the copy-receiving sheet is not used. Here, the ink-coated sheet is used alone as a record member, without any of its transfer features being utilized, the print appearing only on the top of the ink-coated sheet. In this arrangement, the polymeric flow-metering coating may advantageously be so constituted and coated in such amount as to provide an essentially impermeable or impervious barrier to the flow of ink.

The liquid droplets of color-containing, quick-drying, low-viscosity marking material, or ink, which enable the two prints to be obtained, may be applied to the record and transfer sheet by any suitable coating means which can entrap and retain the liquid droplets. Brushing, rolling, and spraying may be utilized; however, conventional coating techniques particularly suitable for forming thin uniform coating films, such as the use of an air knife, an equalizer rod such as a Baker applicator, or a reverse roller, are the preferred coating means. Similarly, the polymeric material may be applied by the foregoing conventional coating methods. A preferred ink coating arrangement consists of minute pressure-rupturable capsules distributed in profusion in a binder, as shown in United States Patent No. 2,712,507, which issued to Barrett K. Green on July 5, 1955, but in which the capsules entrap and retain a color-containing, quick-drying, low-viscosity marking material, the capsule size and the coating weight being so adjusted in relation to the base web material as to enable prints of the desired density to be made on the web sheets. Capsules containing such high-volatility, low-viscosity marking liquids for coating transfer sheet material in accordance with this invention may preferably be made by the methods disclosed in United States Letters Patent No. 2,800,457, which issued to Barrett K. Green and Lowell Schleicher on July 23, 1957, and No. 2,800,458, which issued to Barrett K. Green on July 23, 1957, also. Another coating arrangement which is also suitable, but which is different from the above-described coating, is disclosed in United States Letters Patent No. 2,374,862, which issued to Barrett K. Green on May 1, 1945, and in which the coating consists of a continuous polymer film which contains the liquid marking material as droplet inclusions which escape when the matrix is locally ruptured.

FIG. 4 is an enlarged cross-sectional view of another arrangement embodying the invention. In this arrangement, the top sheet 12 has coated on its bottom surface a first coating 13, containing encapsulated droplets of colorless marking material, such as crystal violet lactone, dissolved in a volatile solvent, and a second, or flow-metering, coating 14, of polymeric material, in contiguous relation with the first coating, and has on its top surface a reactive coating 11, such as attapulgitic clay particles, which reacts with said colorless marking material to produce distinctively-colored marks. This doubly-coated sheet, when superimposed on a receiving sheet 16 coated with reactive material 15, is also capable of developing a mark on the receiving sheet when wet with the colorless marking material. As in the arrangement of FIG. 2, pressure applied at the point 17 ruptures the coating at 18, thereby allowing a portion of the therein-contained colorless marking material to penetrate through

the web and react with the reactive coating 11 to produce a mark 17 on the surface of the top sheet. Simultaneously, a portion of the colorless marking material released by rupture of the matrix coating in the area 18 permeates through the microscopic pores of the novel polymeric flow-metering coating, as in the area 19, and is thereby transferred to the surface of the reactive coating 15 on the receiving sheet 16 to produce a colored mark 20.

FIG. 5 is a cross-sectional view of an arrangement similar to that shown in FIG. 4, but in which the arrangement is used only as a record member, without a coated receiving sheet. In this arrangement, the novel flow-metering coating 14 may be so formulated as to be essentially impermeable to the flow of ink.

FIG. 6 is an enlarged cross-sectional view of yet another arrangement. In this arrangement, the top sheet 21 has coated on its bottom surface a first coating 22, containing liquid inclusions of coloring material comprising a colored dye and a finely-divided pigment which may be of a different color, and, as a flow-metering polymeric coating, a second coating 23 in contiguous relation with said first ink coating. This doubly-coated sheet is superimposed over an uncoated receiving sheet 24. Pressure applied to the surface of the top sheet 21, as at 28, ruptures the coating in the area 25 and thus releases the liquid coloring material, so that a portion of the colored dye marking material contained therein will permeate the paper to produce a distinctively colored mark at 28 on the top of the sheet, the color of the mark being that of the colored dye, most of the pigment being filtered out by the web material. The polymeric flow-metering coating 23 is so constituted as to provide a selectively permeable barrier, so that a selected amount of the colored pigment which was contained in the ink marking material, together with a portion of the colored dye, is transferred to the receiving sheet 24 to produce a distinctively colored mark 27 thereon, the color of the mark so produced being a color corresponding to the composite color of the dye and the pigment.

The arrangement in FIG. 7 is similar to that in FIG. 3, except that a colorless phototropic (often designated "photochromic") dye, which may be distinctively colored by exposure to radiant energy, is used instead of a colored dye. In this arrangement, the top sheet 30 is coated with a first coating 31, containing droplets of a solution of a phototropic dye, such as 1,3,3-trimethyl-6'-nitro-spiro-(2'H-1'-benzopyran-2,2'-indoline) or similar dyes, as disclosed in United States Letters Patent No. 2,953,454, which issued to Elliot Berman on September 20, 1960, the droplets being entrapped in a rupturable matrix. As in the other arrangements, pressure applied over the area 34 ruptures the coating in that area, so that the liquid potentially-colorable material migrates to the surface of the sheet 30. The colorless mark is converted to a distinctively-colored mark 33 when irradiated with ultraviolet light 36. The flow-metering coating 32 may be so constituted that the area 35 may be made essentially impermeable to the passage of ink, or it may be adjusted to pass any desired proportion of ink within the range of about 0% to 90% of the ink released in the area 34. Except with essentially impermeable polymeric coatings, a similar mark, activatable and colorable by irradiation, may be transferred to a receiving sheet placed in pressure contact with the flow-metering coating 32.

As mentioned above, a number of polymeric film-forming compositions may be utilized in making the metering coating of this invention. Some polymeric materials may be applied as aqueous dispersions or solutions, whereas others are conveniently applied as organic solvent solutions.

The following examples will further illustrate certain desirable embodiments of polymeric flow-metering coating compositions, but are not to be construed as limiting

the invention to those illustrated. All proportional parts are given by weight unless otherwise specified.

#### Example 1

The preferred metering coating composition consists of an aqueous solution of a polymer prepared as follows:

40 parts of styrene maleic anhydride copolymer (sold under the name designation of Lytron 820 by Monsanto Chemical Company, Springfield, Massachusetts, United States of America, and having a specific viscosity of 3.3 to 4.3 cps. as a 5% solution of ammonia at pH 8) is dissolved completely in 300 parts of water while the mixture is heated to a temperature of 175 to 180 degrees Fahrenheit. The solution is then adjusted to pH 8 with 20% LiOH solution and the following plasticizer added in the amount indicated: 16 parts of polyethylene glycol monolaurate 400 (sold by Glyco Chemicals, 417 Fifth Avenue, New York N.Y., United States of America).

The coating composition may be prepared with or without plasticizer; however, coatings with plasticizer are more flexible and exhibit less curl and are thus to be preferred.

Instead of the plasticizer mentioned, others, such as Carbowax 300, a polyethylene glycol sold by Union Carbide Chemicals Company, Cincinnati 6, Ohio, United States of America, may be utilized. The water-soluble polymer compositions of this example are generally coated in an amount of one pound per ream (25 inches x 38 inches x 500 sheets). More or less may be coated, however, depending on the coating permeability desired in the dried coating.

Similarly, other water-soluble film-forming polymers which produce suitable coatings are, for example, Hydroxyethylcellulose, sold by Union Carbide Chemicals Company, Cincinnati, Ohio, United States of America; Carboxymethyl cellulose, sold by Hercules Powder Company, Wilmington 99, Delaware, United States of America; modified starch, such as Penford Gum, an etherized starch sold by Penick & Ford, Cedar Rapids, Iowa, United States of America; and oxidized starch such as Stayco M Starch, sold by Staley Starch Company, Box 151, Decatur, Illinois, United States of America.

#### Example 2

This example illustrates the preparation of a composition which is coated as an aqueous dispersion of polymer. To obtain this coating, disperse

10 parts of Rhoplex (trademark designation of polyacrylic resin sold by Rohm & Haas Company, Washington Square, Philadelphia 5, Pennsylvania, United States of America) in  
40 parts of water.

When this composition is coated on sheet material, it forms a discontinuous film of closely-packed minute resin particles, the close arrangement and density of the particles providing the desired screening or metering action. The porosity of the film is adjusted by varying the coating weight.

Another polymer dispersion or latex which produces similar results is an aqueous dispersion of Acrysol, a trademark designation of an alkali soluble acrylic polymer also sold by Rohm & Haas Company. It is also possible to apply the Acrysol polymer as a continuous film if the polymer dispersion is first made alkaline by the addition of a base, such as NaOH, to about pH 8. By so doing, the polymer is dissolved by the base, and the polymer may then be coated as in Example 1 as an aqueous polymer solution.

#### Example 3

This example illustrates a coating composition in which the polymer is dissolved in an organic solvent. To make this coating material, dissolve

10 parts of Amberol resin (trademark designation of

solvent and oil soluble phenol-formaldehyde and maleic glyceride resins sold by Rohm & Haas Company) in

90 parts of toluene.

For Amberol resin there may be substituted other organic solvent soluble resins such as, for example, polyacrylic ester polymers sold under the trademark "acryloid" by Rohm & Haas Company at the address mentioned above. When desired, plasticizers are added to impart flexibility to the polymer coating.

Any one of the above-described flow-metering coating compositions may be coated as a thin, smooth layer over the rupturable ink coatings by well-known coating techniques such as the conventional methods described above.

The compositions defined in the above examples may be used in any amount required to produce the desired result, depending on the coating porosity necessary to provide the desired amount of metering. The amount required to provide an essentially impermeable polymer coating, or the amount that will permit the transfer of any amount from 0% to 90% of the coated ink, may readily be determined from results obtained with test coatings. Generally, the metering coating compositions of Examples 1, 2, and 3 are applied in an amount to provide from 0.75 pound to 4 pounds per ream of 25" x 38" x 500 sheets, and preferably at the rate of one pound per ream of 25" x 38" x 500 sheets.

The following preferred specific embodiment is intended to further illustrate the practice and principles of the novel polymeric metering coating when it is used for its intended purpose as an ink flow distribution control and metering element, wherein the element forms an overcoating layer over an ink coating distributed on one side of a preferred form of record and transfer sheet material. All parts and proportions are given by weight.

In making the preferred form of record and transfer sheet having on one side an ink coating in contiguous relation with the novel polymeric flow-metering coating, a sheet of sulfite manifold paper, nine pounds per ream of 25" x 38" x 500 sheets, is first coated with a liquid dispersion of solid-walled capsules, each capsule being pressure-rupturable by pressures normally encountered in printing and marking operations, and each capsule containing an ink wherein the vehicle comprises a high-volatility, low-viscosity solvent. The capsule dispersion is made, in an aqueous medium, in the manner to be described.

An internal phase of an intended emulsion is first prepared by mixing the following ingredients, in parts by weight:

193 parts of perchlorethylene and 64.5 parts of 2-50-W High Flash Naphtha (coal tar distillate with distillation range of 158 degrees centigrade to 190 degrees centigrade, specific gravity of .881, and a flash point of 105 degrees centigrade, sold by Neville Chemical Company, Neville Island, Pittsburgh, Pennsylvania, United States of America),

heating the mixture to 150 degrees Fahrenheit, and dissolving therein

7.7 parts of Hysol Blue B200% [1,4-bis (n-butylamino) anthraquinone dye, sold by Patent Chemicals Incorporated, Paterson, New Jersey, United States of America, and having the following structure]:

and  
5.1 parts of Oil Brown DN (brown azo dye sold by National Aniline Division of Allied Chemical and Dye Corporation, Chicago, Illinois, United States of America).

A mixture of the following ingredients, in parts by weight, is then prepared:

(1) 93.25 parts of 11%, by weight, aqueous gum arabic solution;  
(2) 21 parts of a 2%, by weight, aqueous solution ad-

justed to pH 9, of a copolymer of polyethylene-maleic-anhydride having a specific viscosity of .6 as a 1% solution in dimethyl formamide at 25 degrees centigrade as obtained by Ostwald method "B." (This polymer is sold under the trade designation DX843-21 by Monsanto Chemical Company, St. Louis, Missouri, United States of America.)

(3) 21 parts of a 2%, by weight, aqueous solution adjusted to pH 9, of the same copolymer as in (2) above, but having a specific viscosity of 1.0 when measured as described therein. (This polymer is sold under the trade designation of DX843-31 by Monsanto Chemical Company, of St. Louis, Missouri, United States of America.)

(4) 1240 parts of dilution water.

After the temperature of the mixture is adjusted to 100 degrees Fahrenheit, there is added to the mixture an emulsion prepared by emulsifying 129 parts of the above specified internal phase in a mixture of 155 parts of water and 93.25 parts of an 11%, by weight, aqueous gelatin (isoelectric point at pH 8.9) solution, the emulsification being preferably carried out in a colloid mill until the dispersed phase has attained a size range of from about 10 to 15 microns. The resulting dispersion is slowly cooled to 80 degrees Fahrenheit, the cooling rate being so controlled that the temperature is lowered 20 degrees Fahrenheit for every 1½ hours of cooling. Upon reaching 80 degrees Fahrenheit, the dispersion is cooled rapidly to a temperature of 50 degrees. Coacervation of the colloidal polymer material is initiated during the cooling phase and progressively continues throughout the cooling period. Coacervation is a separation out of the aqueous mixture of a colloid-rich phase, which deposits on the individual dispersed droplets of organic solvent containing ink. When the chilled dispersion has attained a temperature of 50 degrees Fahrenheit, the pH is lowered to 4.5 by the addition of 14% acetic acid. During this pH adjusting phase, the coacervation, which was initiated during the cooling phase, is finally completed. At this point, each of the ink droplets is coated with a gelled wall of complex polymer material formed by the interaction of colloid polymer material deposited on the ink droplets during the period of coacervation. The capsule walls so formed may then be hardened so as to become substantially water-insoluble and able to withstand drying temperatures which before such treatment would have softened them. The hardening is achieved by adding to the dispersion, while stirring, 5.2 parts of glutaraldehyde. The hardened capsule dispersion is stirred overnight and allowed to settle overnight, and the supernatant liquid is siphoned off. The capsules are then redispersed in an equal volume of fresh water and again allowed to settle overnight. A capsule dispersion of suitable viscosity for coating was obtained by removing supernatant liquid sufficient to terminate with a dispersion containing about 25% solids. This dispersion of capsules is coated with an air knife on 13 pounds per ream of 17" x 22" x 500 sheets sulfite manifold paper at a rate sufficient to provide a coating weight of ten pounds per ream of 25" x 38" x 500 sheets.

After the coating is dried by known procedures, the ink-coated sheet is then coated with the novel polymeric flow-metering coating. The preferred polymeric metering composition of Example 1 is coated with an air knife as a thin layer which is applied directly over the first applied ink-containing capsule coating in an amount to provide about one pound per ream of 500 sheets x 25" x 38". Upon drying of the second coating, the record and transfer sheet so produced will function in the manner hereinbefore described, wherein the second or flow-metering coating, having a selected ink permeability, controls the flow and distribution of ink in the web base material and to a receiving sheet.

Application of the novel flow-metering coating is not

limited to use with the above preferred record and transfer sheet having the specified ink coating, but, rather, it is to be understood that the novel coating may be used with any one of the ink coatings shown in the various arrangements illustrated and disclosed in the beforementioned co-pending patent application.

Although a wide variety of porous web materials may be used as the base sheet material, paper is preferred, since it provides a uniform fiber structure and thus promotes, through capillary or wetting action, even and homogeneous penetration of the porous web by the ink. Instead of paper, there may be substituted such materials as cellulose, degenerated cellulose, fibrous cellulose acetate, and suitably woven fabric derived from cotton, wool, or similar fibers, and equivalents thereof.

To produce desirable prints, it is generally advisable to adjust the coating weight of ink per unit area and the size of the liquid entity which is entrapped to the particular requirements of the selected web base material.

The porosity, wettability, thickness, and density of the porous web are of primary importance in the determination of suitable coating weight and ink droplet size.

Coating weights for the ink coating may vary from one to fifty pounds per ream of 25" x 38" x 500 sheets, and the capsule or droplet size may vary from five to five hundred microns. With normal-weight typewriting paper, coating weights of from five to fifteen pounds per ream and preferably five to ten pounds per ream of capsules ranging in size up to forty microns, preferably five to thirty microns, give excellent results.

As described in the above-mentioned co-pending patent application, the ink which is coated on the record and transfer sheet contains high-volatility, low-viscosity solvents, such as tetrachloroethylene, toluene, hexane, ortho-, meta-, and para-diethylbenzene, trichloroethylene, and the xylenes. Low-volatility solvents may be mixed with any combination of the preceding high-volatility solvents, so long as the latter is present in a major amount. It is generally desirable to formulate the ink to a viscosity of between .3 and 20 centipoises, and preferably between .4 and 2.5 centipoises.

Other marking materials or inks which are also useful with this invention include colored dyes and pigments and colorless color-forming dyes used alone or in combination with colored dyes. Typical colored dyes are, for example, Hysol Blue B 200% (1,4-bis [N-butylamino] anthraquinone), Hysol Blue SS (a 50:50 mixture of 1,4-bis [n-butylamino] anthraquinone and 1-N-methylamino-4N-isopropylamino anthraquinone), both dyes sold by Patent Chemicals Incorporated, of Paterson, New Jersey, United States of America, Oil Black BT (Colour Index No. 26150), Oil Soluble Nigrosine, Azo Blue Black, Sudan II, Sudan III, and other similar dyes. As colorless color-forming dyes there may be mentioned Crystal Violet Lactone, Benzoyl Leuco Methylene Blue, and N-(2,5-dichlorophenyl) Leucauramine, which become colored when adsorbed by acid clay or like acid complex aluminates. Such dyes are disclosed in United States Letters Patent Nos. 2,646,367; 2,714,074; Re. 23,024; and 2,828,341.

Dyes which are colorable to a distinctive color by exposure to electromagnetic radiation and which are useful in certain arrangements as specified herein are such as those described in United States Letters Patent No. 2,953,454, which issued to Elliot Berman on September 20, 1960, and in commonly-assigned application for United States Letters Patent filed by Elliot Berman on July 14, 1959, Serial No. 827,420, now U.S. Patent No. 3,024,362.

Pigments which may constitute a portion of the ink are inorganic or organic pigments such as carbon black, titania, phthalocyanine blue, methyl violet, and similar well-known ink pigments. Such pigments may vary in size from a few millimicrons to several microns, depend-

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ing on the intended application, on the permeability of the novel metering coating, and on the print color desired.

The invention has been described in terms of specific embodiments and examples; however, it is to be understood that the invention is broad in scope and is not to be interpreted as limited to such examples and embodiments.

What is claimed is:

1. A pressure-sensitive record and transfer material consisting of a porous web base having a first coating and a second coating superposed one over the other on one side of said base, the first coating being pressure-rupturable and containing a profusion of encapsulated liquid droplets of ink, which ink contains coloring material in a volatile vehicle capable of readily penetrating and wetting the web material, said second coating overlapping the first coating and consisting of a selectively-permeable polymeric flow-metering material selected from the group consisting of:

(a) styrene-maleic anhydride copolymer

(b) polyacrylic acid

(c) basic salts of polyacrylic acid, and

(d) oil-soluble phenol formaldehyde resin coated in an amount from about 0.75 to 4 pounds per ream of said base.

2. The pressure-sensitive record and transfer material of claim 1 wherein the coloring material consists of an ink containing colorless color-reactant material.

3. The pressure-sensitive record and transfer material of claim 1 wherein the coloring material consists of an

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ink containing a colored dye and a colorless color-reactant dye.

4. The pressure-sensitive record and transfer material of claim 1 wherein the coloring material consists of an ink containing a soluble colored dye and a dispersed finely-divided colored pigment.

5. The pressure-sensitive record and transfer material of claim 1 wherein the coloring material consists of an ink containing a dissolved colorless color-forming phototropic dye.

6. The pressure-sensitive record and transfer material of claim 1 wherein the coloring material consists of an ink containing dissolved colorless color-forming phototropic dye and finely-divided colored pigment.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

|           |              |                |
|-----------|--------------|----------------|
| 972,742   | West         | Oct. 11, 1910  |
| 1,732,187 | Pelton       | Oct. 15, 1929  |
| 1,796,956 | Neidich      | Mar. 17, 1931  |
| 2,163,601 | Humes        | June 27, 1939  |
| 2,213,645 | Antrim       | Sept. 3, 1940  |
| 2,654,673 | Steinhardt   | Oct. 6, 1953   |
| 2,730,456 | Green et al. | Jan. 10, 1956  |
| 2,790,742 | Wharton      | Apr. 30, 1957  |
| 2,800,458 | Green        | July 23, 1957  |
| 2,932,582 | Pesa et al.  | Apr. 12, 1960  |
| 2,939,009 | Tien         | May 31, 1960   |
| 2,953,454 | Berman       | Sept. 20, 1960 |
| 3,020,171 | Bakan et al. | Feb. 6, 1962   |