Nov. 22, 1960 J. J. CLANCY ET AL **2,961,334**

POSITIVE PRINTING, PRESSURE-SENSITIVE
MATERIAL AND METHOD OF MAKING IT

Filed June 4, 1957 2 Sheets-Sheet 1

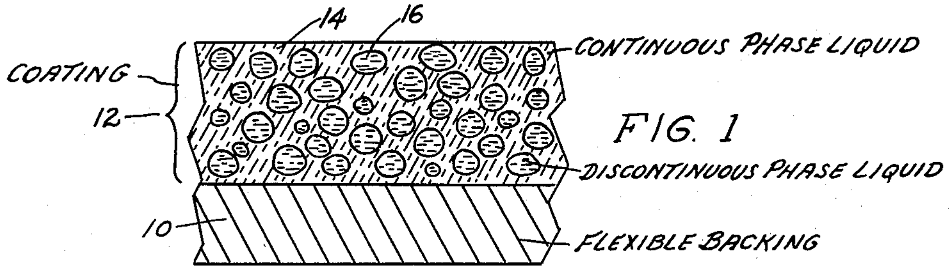

FIG. 1

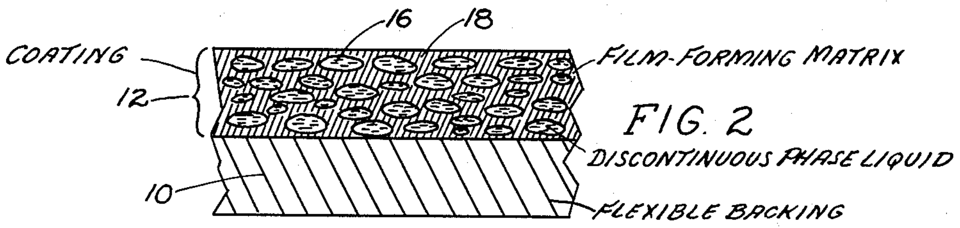

FIG. 2

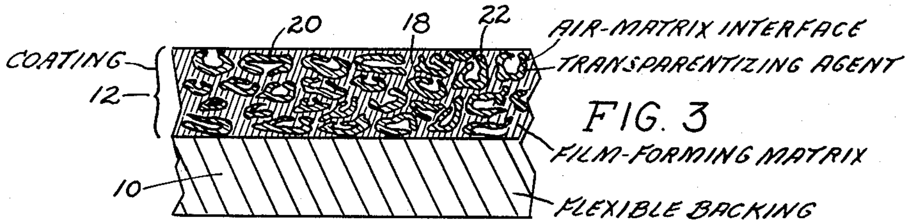

FIG. 3

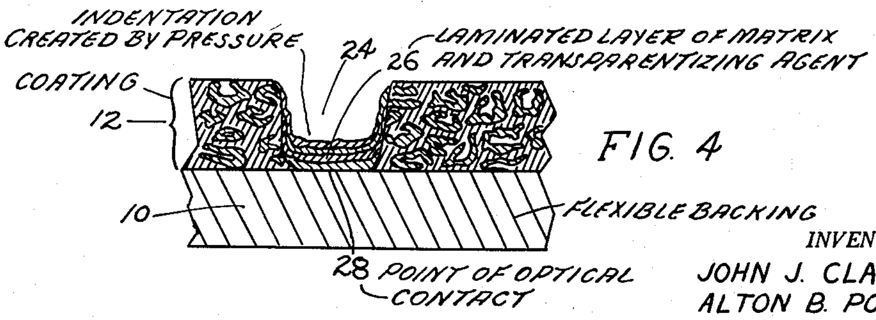

FIG. 4

INVENTORS
JOHN J. CLANCY
ALTON B. POOLE
ROBERT C. WELLS

BY Bessie A. Lepper ATTORNEY

Nov. 22, 1960 J. J. CLANCY ET AL **2,961,334**

POSITIVE PRINTING, PRESSURE-SENSITIVE
MATERIAL AND METHOD OF MAKING IT

Filed June 4, 1957 2 Sheets-Sheet 2

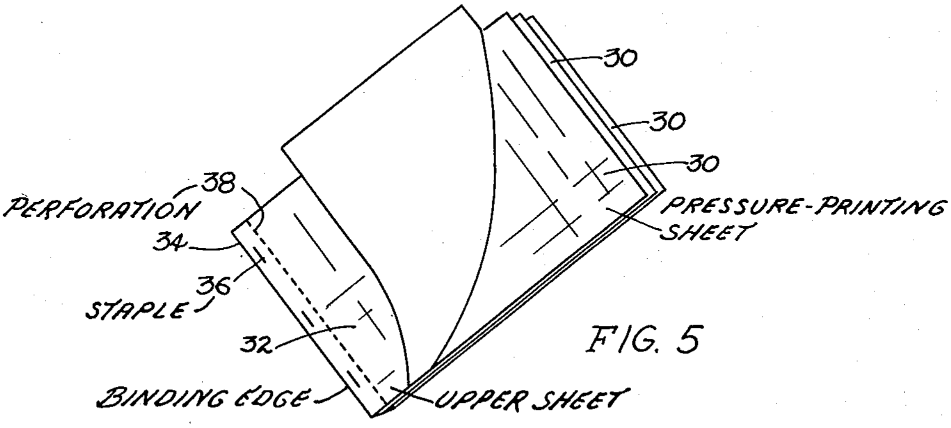

FIG. 5

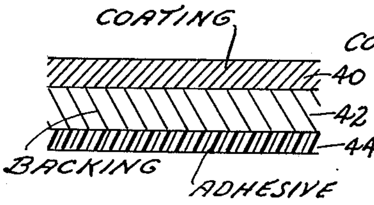

FIG. 6

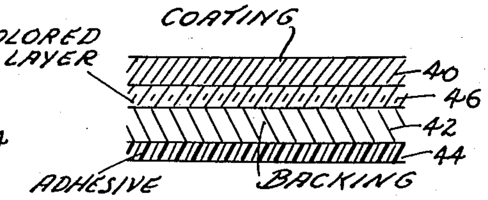

FIG. 7

INVENTORS
JOHN J. CLANCY
ALTON B. POOLE
ROBERT C. WELLS
BY Bessie A. Lepper ATTORNEY

United States Patent Office

2,961,334
Patented Nov. 22, 1960

2,961,334

POSITIVE PRINTING, PRESSURE-SENSITIVE MATERIAL AND METHOD OF MAKING IT

John J. Clancy, Westwood, Alton B. Poole, Abington, and Robert C. Wells, Arlington, Mass., assignors to Arthur D. Little, Inc., Cambridge, Mass., a corporation of Massachusetts

Filed June 4, 1957, Ser. No. 663,415

16 Claims. (Cl. 117—36)

This invention relates to a coating composition and a resulting coated product. More particularly it relates to a coating which is suitable for application to a flexible backing of a color which is in contrast with the color of the coating, and to a coating which has controllable pressure sensitivity. The coated material thereby becomes a positive pressure-printing sheet which needs only pressure to impart clearly defined marks or characters in the areas and shapes where the pressure is applied.

This application is a continuation-in-part of application Serial Number 612,520, filed September 27, 1956 in the names of John J. Clancy, David W. Lovering, and Robert C. Wells for "Opaque Coating and Composition for and Method of Making It."

In the business world, it is usually desirable to be able to make a number of copies of documents, such as accounting forms, order forms, bills of lading, bank deposit slips, sales slips, etc. In the general course of making such copies it is customary to make up sets of sheets with one-use carbon paper fixed between each consecutive sheet, or to give each but the last copy sheet a carbon backing. In the first case, carbon paper must be removed and destroyed; while in the second case, the copies have permanently affixed to the back side a waxy, usually dark colored material which can easily rub off onto objects with which it may come in contact.

Carbon paper is the product most widely used in industry to make duplicate copies of documents. Although it has been used for many years and in great volume, carbon paper does not provide good copy quality or contrast for easy reading, particularly when more than 3 or 4 copies are required, or where the copy paper is heavy. It is not surprising, therefore, that much effort has been spent over the years in an attempt to produce an improved method for making a number of copies simultaneously either by means of writing tools or by mechanical devices.

In addition to the use of carbon paper, duplicate copies are sometimes made by using sheets of paper, the top one of which is treated on the underneath side and the second which is treated on the top side. When these surfaces are contacted and pressure is applied, chemicals contained in the two coatings will be caused to react to give a contrasting colored mark on the top of the second sheet. This system has the disadvantage of requiring surface coatings on the two faces of the two sheets which come into contact. In addition, this type of duplicating paper can prematurely develop color or can lose the colored marks already made under certain atmospheric conditions. Moreover, the number of copies which can be made by one application of pressure is limited.

In addition to the requirement for making numerous copies there are also many needs for marking papers

where duplicate copies are not particularly important, but where characteristics, such as resistance to heat, normal pressures of handling, and moisture are required. Normally, such marking papers are wax-coated with a contrasting color layer beneath the wax. However, when these materials are exposed to elevated temperatures, the wax often melts and the mark placed upon the paper is obliterated.

It would therefore be desirable to have a product which can be marked by the application of pressure only, i.e., paper or other material which would not require the deposition of ink, or carbon from carbon paper, or graphite from a pencil, for example, to make clearly defined, visible marks on it. In addition, it would also be desirable to keep the process simple by eliminating the need for chemical reactions which are difficult to control. Such a product needs no carbon paper or carbon backing on the sheet above it to make tracing copies on it, nor does it require that the two contacting surfaces each be coated with a material which will cause a chemical reaction to form a colored mark where pressure is applied. Furthermore, such a flexible material should possess good resistance to heat, to normal pressures of handling, and to moisture. Such a product would be particularly well adapted for use as marking tape which may be exposed to elevated temperatures.

Although normal duplicating methods provide for black or darkly colored tracings on a light or white colored background, it would also be desirable to have flexibility in color, both with respect to the background which in the case of the product of this invention is actually the coating on the flexible material, and with respect to the color of the tracing which is the original color of the backing material.

In order to make a flexible positive pressure-printing material of such a nature, i.e., one coated with a composition of contrasting color, it is necessary to use a coating composition which itself remains flexible after drying. This in turn means providing a coating composition with special characteristics.

It is therefore an object of this invention to provide a positive, pressure-printing material on which clearly and sharply contrasting marks or indicia may be made by application of pressure alone. Among other objects of this invention may be listed:

To provide a positive pressure-printing material which is resistant to normal pressures of handling, to heat, and to moisture;

To provide a means for making multiple copies of a document by merely applying pressure simultaneously to a number of sheets of positive pressure-printing material arranged on top of each other;

To provide a way for making multiple copies of a document which does not require the use of carbon paper, carbon backing or the necessity to effect a chemical reaction, and thereby to provide a means for making a greater number of copies and/or more distinct copies than previously possible;

To provide an opaque coating which may be applied to a flexible backing of a contrasting color and which will form an optical contact with the contrasting backing material when pressure is applied by means of a manual writing tool, or by mechanical devices using type, etc.;

To provide a material which can be marked by pressure alone and which is resistant to heat, thus making it suitable for use in labelling objects which are to be exposed to elevated temperatures;

To provide a coating composition which when deposited on a flexible backing will not detract from or lessen the flexibility of the backing; and

To provide a coating composition which will furnish the required opaque background when dried, but which contains essentially no pigment, and which at the same time scatters light to give a white or colored surface.

These and other objects will become apparent in the following discussion.

In the following description the term "positive pressure-printing material" will be used to designate the product of this invention. The application of pressure to the coated backing material causes the color of the backing material to show where the pressure was applied, thus resulting in a positive mark on the material, and giving the product the name applied hereinafter.

Other terms are used in the description which should be defined. Thus, the terms "marks" or "indicia" are used to indicate the configurations, shapes, or areas which are impressed upon the positive pressure-printing material as the result of pressure application. It is desirable that these marks or indicia have good "copy quality" which may be defined in terms of clearness or sharpness of outline and that they exhibit good "copy contrast," i.e., contrast in the colors of the background and of the marks or indicia. This contrast does not necessarily have to be between white and black, any color contrast being suitable. Finally, the term "backing" or "support" is used to designate the material on whose surface the coating is applied. It will normally be such as paper or a thin plastic film, but it need not be.

The positive pressure-printing material of this invention is comprised of a flexible backing or support on one side of which is deposited a cavernulous coating which when pressure is applied is permanently compressed and is believed to make optical contact both between the discontinuities of the coating and with the backing material at the points, lines, or areas of pressure application. Such optical contact permits the color of the backing material to show through as contrasting tracings with respect to the color of the coating.

The coating composition of this invention comprises:

(1) material capable of forming a light scattering opaque matrix hereinafter referred to as the "matrix material";

(2) material which itself is transparent or translucent and sufficiently cohesive to form the necessary permanent optical contact within the coating and with the backing on which the coating is applied, hereinafter called the "transparentizing agent";

(3) a liquid in which the matrix material is soluble or dispersible and which forms the so-called continuous phase of an emulsion;

(4) a liquid, in which the transparentizing agent is usually and preferably soluble or dispersible, which forms the so-called discontinuous phase of an emulsion;

(5) an emulsifying agent; and

(6) a water insolubilizing agent for the matrix materials.

Of these, the emulsifying agent may be eliminated under certain circumstances, and the use of the insolubilizing agent is optional and depends on the desired properties of the final coating.

A coating composition comprising an emulsion of the above listed components is applied to the surface of the backing material in such a manner as to produce throughout the final dry coating a multiplicity of air-matrix interfaces, thus causing incident light to be scattered by the coating to give a surface of high relative brightness. These air-matrix interfaces in turn are formed by applying the coating in such a manner that when it is in final dry form, the matrix material is throughout a minutely porous or cavernulous film which appears to be smooth and homogeneous to the naked eye, but which under a powerful microscope seems to include a multiplicity of air spaces, the longest dimension of which is preferably not over 5 microns. These air spaces are formed by applying the coating in the form of a continuous liquid phase in which is dispersed another liquid forming a discontinuous phase.

The transparentizing agent is believed to form an extremely thin translucent or transparent film or covering at the air-matrix interfaces. When sharp pressure is applied to the coating surface in order to make marks or indicia on the paper, it may be assumed that the matrix material is at least partially pushed aside and compressed, and that the transparentizing agent permanently welds one air-matrix interface to another and at the same time welds the now-compressed matrix material to the backing material. The optical contact thus made permits the color of the backing material to show through as a sharply defined mark which exhibits good copy quality.

The liquids of the composition are so chosen that the liquid comprising the continuous phase can be vaporized at a temperature lower than that required to vaporize the liquid forming the discontinuous phase. Inasmuch as the matrix materials suitable for the coating composition of this invention are soluble in water, water may be used to form an aqueous solution to be used as the continuous phase, thus keeping the overall costs of the coating to a minimum.

In order to render the final coating water-insensitive, a modifying agent may be added according to well-known procedures to either react with the matrix material to form an insoluble salt or to cause certain cross-linking of the matrix material molecules so as to impart water insensitivity.

The coating composition of this invention may then be described as a two-phase liquid emulsion essentially devoid of pigment, comprising an aqueous solution or dispersion of a matrix material as a continuous phase (which may or may not contain an additional modifying agent such as a water-insolubilizing agent), and a liquid having a vapor pressure greater than that of water at the drying temperature (preferably containing the transparentizing agent) as a discontinuous phase. If desired, it may also contain additional modifiers which act to render the matrix material water insoluble, or water insensitive, when the liquid phases of the coating composition have been removed to dry the matrix material. Although it is preferable to have the transparentizing agent in the discontinuous phase liquid, it is possible, under certain conditions, to introduce it in the continuous phase liquid.

In addition to the modifying agent used to render the final coating water insensitive, it may be desirable or necessary in accordance with known practices to use a solubilizing agent to aid in putting the matrix material into an aqueous solution and to add an emulsifying agent to disperse the discontinuous phase liquid in the aqueous matrix solution or dispersion.

It is important to note that the final opaque coating of this invention is to be distinguished from coatings which contain discrete and normally unbroken bubbles, small enveloped liquid particles, or flakes; from blushed coatings, such as are heat- and pressure-sensitive; from an ordinary sizing compound which in itself scatters very little light; and from pure wax coatings; or from pressure-resistant coatings which are included in our Serial Number 612,520.

The coating composition and the positive pressure-printing material of this invention will be more fully described in the following discussion and with reference to the accompanying drawings in which

Fig. 1 is a greatly enlarged cross-sectional representation of a backing material covered on one side with the coating of this invention after it has been applied, but before any appreciable amount of either liquid has been expelled;

Fig. 2 is the same coated background after the matrix solvent or liquid of the continuous phase is driven off, but before the final drying is accomplished;

Fig. 3 is the same coated background material after drying is completed;

Fig. 4 is a diagrammatic representation of the coated background material of Fig. 3 showing how an applied pressure forms the required optical contact;

Fig. 5 illustrates a manifold of sheets of the positive pressure-printing material of this invention;

Fig. 6 is a cross-sectional representation of one form of a marking tape made in accordance with this invention; and

Fig. 7 is a cross-sectional representation of another form of a marking tape made in accordance with this invention.

The multitudinous, minute air-matrix interfaces which provide the uniformly cavernulous basic structure of the final coating of this invention are formed by first expelling or driving off the liquid of the continuous phase to leave the matrix which contains minute pockets of the liquid of the discontinuous phase. The discontinuous phase liquid is then driven off from the minute pockets to form a structure containing the air-matrix interfaces. At the same time at which the liquid of the discontinuous phase is driven off, the transparentizing agent is believed to precipitate or crystallize on at least a portion of the matrix that defines the discontinuities of the cavernulous film. This coating is in itself transparent or at least translucent and may be of no more than molecular thickness. This mechanism requires that the liquids forming the two phases are immiscible, and that the liquid of the continuous phase is a solvent for the matrix material (in which the term solvent may refer to the continuous phase of a colloidal solution), and is preferably a non-solvent for the transparentizing agent. The liquid of the discontinuous phase is preferably a solvent for the transparentizing agent and essentially a non-solvent for the matrix material.

Due to the nature of the matrix material and to the manner in which the transparentizing agent is applied, and to the fact that the matrix material itself is a light-scattering material, there are no distinct flakes or scales formed as in a process where flakes are added to an adhesive material and actually attached to the surface to be coated, such as, for example, in U.S. Patent No. 1,922,548. In fact when the coating of our invention is thoroughly dry, it is glossy and smooth to the touch. Scraping lightly with a knife-edge or the back of a fingernail, for example, raises no particles and leaves no traces. This film, in fact, can best be characterized as being very much like a white cellophane or a glossy white paper. Photographs made by the electron microscope show little pockets elliptical in cross-section and shape, one to two microns long and about one-half micron wide or high. Most of these pockets appear to be ruptured, presumably as a result of expelling the liquid of the discontinuous phase in proper sequence.

The mechanism of the formation of the air-matrix interfaces and of the role of the transparentizing agent may be explained, in a much simplified manner, with references to Figs. 1 through 4 in which like numbers refer to like elements.

In these figures backing **10**, such as a colored tissue paper, is coated with a layer of coating composition **12** formulated in accordance with this invention. In Fig. 1 coating composition **12** is made up of the continuous phase **14**, for example, an aqueous dispersion of casein as the matrix material, and minute globules or pockets **16** of the liquid of the discontinuous phase such as xylene containing paraffin, for example, as the transparentizing agent dissolved therein.

In Fig. 2, wherein a large portion of the matrix material solvent (which is the liquid of the continuous phase) has been driven off, the coating comprises the matrix **18** and minute pockets **16** of the liquid of the discontinuous phase. It is believed that after the liquid of the continuous phase is driven off, some shrinking of the coating takes place and the globules **16** probably assume an ellipsoid-like shape. Finally, when the liquid in the globules **16** of Fig. 2 is driven off, there remains the air-matrix interfaces **20** which are coated with a translucent or transparent coating **22** of the transparentizing agent, which probably has precipitated or crystallized out of the discontinuous phase liquid. These air-matrix interfaces serve to scatter incident light to produce the opaque coating of this invention. These interfaces **20** generally vary in maximum dimension from about one-half to one micron high or thick and from about one-half to five microns long, depending upon the conditions under which the coating was formed. It is preferable that no appreciable number of air-matrix interfaces have a maximum dimension of more than five microns.

In Fig. 4 there is a diagrammatic representation of what is believed takes place when pressure is applied by means of a writing tool, or type face, to the coated material of Fig. 3. The indentation made by the marking tool is represented as **24**. Pressure applied to the composition **12** pushes some of the matrix aside and forces the coating down toward the backing material **10**, thus laminating multiple thin layers of matrix and transparentizing agent until this welded area occupies a very thin section **26** which basically outlines the mark made by the pressing tool and which forms optical contact at point **28** with backing **10**. Thus, when light strikes the coated material it is scattered by the air-matrix interfaces which have not been disturbed by the pressure making tool so that the background material is the color of the coating, usually white, while the points or lines where pressure has been applied show up as the color of the contrasting backing material **10** by reason of the fact that the backing material shows through. Thus, there is in effect the making of marks or indicia of a contrasting color upon a pleasing white background which is formed by the coating material.

From the above description of what is believed to be the mechanism by which the positive pressure-printing material of this invention achieves good, clear copy, it may be seen that it would be advantageous to have a coating composition, the pressure-sensitivity of which may be varied according to the type of pressure to be applied and the number of copies which may be desired from one pressure application. For example, positive pressure-printing material which is to be typed or printed upon need not be as pressure-sensitive as that which is to be written on by pencil, pen, or the like. Likewise, if few copies are to be made, the material need not be as pressure-sensitive as in the case where a number of copies are desirable. In the following detailed description of this invention a number of ways of controlling the degree of pressure sensitivity of the coating will be presented and then summarized.

The components making up the coating composition of this invention may now be further described and defined.

The matrix-forming material

The matrix material of the coating of this invention may be any of the water-soluble or water-dispersible film-forming materials which will adhere tightly to the background area to be covered and which will scatter light at its air interfaces to give a bright, continuous surface. Generally, the materials which are suitable to form matrices may be defined as those materials which assume colloidal dimensions when peptized.

Many natural and synthetic materials are suitable as matrix materials, among which may be listed casein, bentonite (a clay which swells in water), polyvinyl alcohol, methyl cellulose, alpha protein, animal glue, modified starches, sodium silicate, shellac, natural rubber, and the synthetic rubbers such as acrylonitrile-butadiene copolymers and butadiene-styrene copolymers.

In the case of matrix materials which are elastic in nature such as the natural and synthetic rubbers, it is desirable to include at least a small percentage by weight of matrix materials which are non-elastic in nature. This is due to the fact that the elastic matrix materials have a tendency to expand and then to subsequently shrink when the liquid of the discontinuous phase is driven off, rather than to break and maintain the required air-matrix interfaces. Of course, compatible mixtures of any two or more of the above listed matrix materials may be used.

It is well known that casein or alpha protein, or mixtures of these, can be put into a water solution only with the aid of a solubilizing agent which is alkaline in nature and results in the formation of a water-soluble salt of the proteins. Such solubilizing agents include, but are not limited to, ammonium hydroxide, sodium hydroxide, sodium tetraborate (borax), sodium carbonate and trisodium phosphate. Any of the known solubilizing agents for casein may be used in the process of formulating the coating of this invention.

When the matrix material components of the coating is a mixture of casein or alpha protein and a water-soluble synthetic matrix material, separate solutions of these are prepared. The synthetic materials are put into solution by any appropriate procedure. Thus, for example, polyvinyl alcohol may be mixed by sifting the powder into water which is being stirred very rapidly, preferably rapidly enough to form a vortex. The polyvinyl alcohol powder is introduced into the vortex and stirring is continued (usually for about 10 minutes) until the powder is completely wetted and dispersed. The dispersion is then heated to a temperature of 195° F. until the polyvinyl alcohol has all gone into solution. After cooling, the polyvinyl alcohol solution may be mixed with a casein or an alpha protein solution. Similarly a modified starch (e.g., a hydroxyethyl ether derivative of corn starch) may be put into a water solution.

If the matrix material is sensitive to water, as casein is known to be, it may be rendered insensitive by converting it to a water insoluble condition in the final coating by the addition of any suitable water-insolubilizing agent known in the art. In the case of casein this may be conveniently done by adding to the casein solution an inorganic metal salt which is appreciably soluble in water and which forms an insoluble derivative with casein. Such an inorganic metal salt is zinc sulphate. The resulting coating then comprises the water-insoluble zinc salt of casein making the final coating practically water insoluble. Casein, alpha protein, glue or the matrix mixtures containing one or a combination of these may also be modified by reacting with other metallic ions such as copper, aluminum or chromium to form water-insoluble products.

The amount of modifying agent to be added is based upon the assumption that a reaction takes place between the modifier and casein (or alpha protein) as indicated below, using zinc sulphate and ammonium caseinate as examples of the reaction. The ammonium caseinate was, of course, formed when ammonium ions were introduced to aid in solubilizing the casein.

$$ZnSO_4+2NH_4\text{ (Caseinate)}\rightarrow Zn\text{ (Caseinate)}+(NH_4)_2SO_4$$

Another type of water-insolubilizing agent which can be used is exemplified by the addition of an aldehyde to a coating formulation containing casein or other protein material to react with the protein present through the amino group to form an insoluble cross-linked product. The reaction with an aldehyde may take place before the protein-bearing coating is applied by adding the aldehyde to the liquid, or after application to the area to be covered by exposing the applied coating to aldehyde vapors, for example formaldehyde.

Generally the ratio of matrix material to the liquid of the discontinuous phase will range from about 1:5 to 1:25. The actual ratio will depend upon the characteristics of the final coating desired. As a rule the more liquid used with respect to the matrix material, the higher the brightness in the final coating and the more sensitive the coating will be to pressure.

In preparing the matrix dispersion, it has been desirable to formulate solutions having from about 5 to 20% solids content by weight.

The following examples (I–III) illustrate the use of three different matrix materials and typical formulations of coating compositions in accordance with this invention. These examples show the use of a protein-containing material (casein), a natural occurring hydrophilic clay (bentonite), and a synthetic material (methyl cellulose or Methocel).

EXAMPLE I

To 10 pounds of water (the continuous-phase liquid) was slowly added 3.8 pounds of casein (matrix material) with stirring, and the resulting mixture was permitted to stand for about 20 minutes until the casein particles were wetted and swollen by the water. An additional 9.2 pounds of water was added and the mixture was heated to about 160° F. To this heated mixture was added 1.52 pounds of ammonium hydroxide (28% NH_4OH) as the solubilizing agent, and the batch was stirred continuously until the casein was completely peptized. Care was exercised not to overheat the casein solution, and as soon as all the casein had been peptized the solution was allowed to cool to room temperature. In a separate vessel 0.4 pound of zinc sulfate (insolubilizing agent for the matrix material) was dissolved in 1.8 pounds of water and the resulting solution was added with constant stirring to the cooled casein solution. To this completed solution were added 10.7 pounds of water and 10.7 pounds of 28% NH_4OH.

In a separate mixing vessel 1.8 pounds of stearic acid (emulsifying agent) was added to 58.2 pounds of xylene (discontinuous-phase liquid) along with 2.7 pounds of a paraffin having a melting point of about 128° F. as the transparentizing agent. The xylene was heated to about 160° F. and maintained at that temperature until the stearic acid and the paraffinic were completely in solution. This solution of stearic acid and paraffin in xylene was added to the warmed casein solution (120° F.) while the latter was being stirred rapidly. Stirring was continued until the emulsion had been formed. In this formulation the paraffin i.e., the transparentizing agent, was present in a concentration equivalent to about 71% of the weight of the matrix material (solid basis).

This coating composition had a viscosity of approximately 2900 centipoises. It was applied at a temperature of approximately 85° F. by means of a coating roller to a number of samples of 10-pound tissue paper, the tissue being black or brightly colored such as red, blue, green, etc. The coated paper was then dried in a stream of air heated to 100° F. to form the multitudinous air-casein interfaces required in the coating. The final coated tissue was pure white on the coated side and was relatively smooth.

A sheet of uncoated tissue and 15 sheets of the material coated as described above were placed contiguously in an electric typewriter and the top uncoated tissue was typed upon. The resulting 15 copies were all legible, the last copy having better definition and contrast than normally associated with the sixth or seventh carbon copy when conventional one-use carbon paper and tissue paper of the same basis weight are used.

EXAMPLE II

Approximately 2.4 pounds of bentonite (sodium montmorillonite) was stirred into about 21.6 pounds of water.

The mixture was permitted to stand until the bentonite had been swelled and completely peptized. Into this was added 10.8 pounds of ammonium hydroxide (28% NH_4OH). In a separate vessel 3 pounds of paraffin (melting point about 128° F.) along with 2.15 pounds of stearic acid, was dissolved in 65 pounds of xylene heated to about 140° F. The two solutions were rapidly mixed at a temperature of 120° F., the xylene solution being poured slowly into the rapidly stirred bentonite solution. In this formulation the paraffin was present in a concentration equivalent to about 125% of the weight of the bentonite (solid basis). This high percentage of paraffin was found to be advantageous in the case of the bentonite to make the final coating sufficiently water insensitive.

The resulting emulsion had a viscosity of about 1000 centipoises and was applied to 10-pound tissue paper by means of a paper-coating roller. The drying of this coating was accomplished in the same manner as that described for Example I and the final coating created a bright white surface which was not overly waxy-like. When pressure was applied through an original, uncoated sheet by either a hand-held instrument such as a pen or pencil, or by type face to the white surface, there resulted a clear, well defined tracing in the color of the tissue paper backing on the coated sheet. In addition to producing good copy quality, the final coating of this example exhibited good water and heat resistance.

EXAMPLE III

A dispersion of matrix material was made up by wetting 1.75 pounds of methyl cellulose in 17.5 pounds of hot water. When the methyl cellulose had been completely wetted, an additional 21.9 pounds of cold water was added along with 17.5 pounds of ammonia (28% NH_4OH). In a separate vessel the transparentizing agent and the emulsifying agent were put into solution with the discontinuous phase liquid by adding 2.65 pounds of stearic acid and 1.1 pounds of paraffin (melting point 128° F.) to 15.7 pounds of Stoddard solvent (mineral spirits having a boiling fraction ranging from 310 to 375° F.). The matrix dispersion was then stirred rapidly and into it was added the discontinuous phase liquid solution until a good emulsion had been formed. To this emulsion was then added 21.9 pounds of water to adjust it to the proper viscosity. This composition was used in coating tissue paper as described in Example I and the final coating on the tissue paper showed good copy quality when pressure was applied by typing or printing. It showed fair copy quality when pressure was applied by means of a pencil. This is attributed to the fact that the coating was less sensitive to pressure than that made with casein as the matrix material, for example.

The transparentizing agent

The transparentizing agent should be a material which in itself is transparent or at least translucent when deposited in the form of a thin film. It should possess certain characteristics which enable it to provide the necessary optical contact believed to be required in the mechanism described above. It is preferable, moreover, that it be of such a nature that it can be added with the discontinuous phase of the emulsion.

The transparentizing agent may be a liquid, paste or solid so long as it provides the necessary optical contact. In order to provide this necessary optical contact, the transparentizing agent should be cohesive, i.e., it should be capable of uniting layers or particles of itself as well as layers or particles of the matrix material with itself. The requirement for cohesion is illustrated in Fig. 4 in which the laminated layer **26** of transparentizing agent and matrix material is shown. The transparentizing agent should also be capable of wetting the matrix material, a property which contributes to its cohesiveness. In order to form the necessary indentation **24** (see Fig. 4) which apparently requires some local displacement of the matrix material and the transparentizing agent, the transparentizing agent should be plastically deformable or flowable to a degree to permit such localized displacement. Moreover, to achieve the maximum effect in contrasts and good clear copy, the transparentizing agent should be at least translucent when deposited in a thin film and it should have a refractive index of the same order as the matrix material to prevent the formation of scattering interfaces in the final copy. It appears from the mechanism which has been postulated for the action of the transparentizing agent that it should possess all, or most, of these characteristics to achieve the optical contact believed to be necessary.

In addition to achieving optical contact, the transparentizing agent, for practical reasons, is preferably one which will not migrate either into the backing material, the matrix material, or to the surface of the coating. Although migration does not at first materially reduce the performance of the final product (i.e., the positive pressure-printing material) it can shorten its useful life if migration is excessive.

The transparentizing agent will normally be water insoluble but soluble or dispersible in the discontinuous phase liquid. It is therefore preferably introduced by dissolving or dispersing it in the discontinuous phase liquid. Those transparentizing agents which are insoluble in water appear to contribute to making the final coating more water insensitive.

A large number of transparentizing agents have been used in the practice of this invention. This can be seen in the following example which contains a tabulation of the results from a large number of different coating formulations prepared in accordance with the practice of this invention. Each coating composition was made up in the manner described in Example IV. A basic casein dispersion was used to form the continuous phase of the emulsion. Xylene was used as the discontinuous phase liquid and different transparentizing agents were used in the formulation.

EXAMPLE IV

A basic casein dispersion in water was made by slowly adding 3.8 pounds of casein to 10 pounds of water with stirring. The resulting mixture was permitted to stand for about 20 minutes until the casein particles were wetted and swollen by the water. An additional 9.2 pounds of water was added and the mixture was heated to about 160° F. To this heated mixture was added 1.52 pounds of ammonium hydroxide (28% NH_4OH) and the batch was stirred continuously until the casein was completely peptized. Care was exercised not to overheat the casein solution, and as soon as all the casein had been peptized the solution was allowed to cool to room temperature. In a separate vessel 0.4 pound of zinc sulfate was dissolved in 1.8 pounds of water and the resulting solution was added with constant stirring to the cooled casein solution. To this completed solution was added 10.7 pounds of water and 10.7 pounds of 28% NH_4OH.

In a separate mixing vessel 57 pounds of xylene (xylene to casein ratio of 15 to 1) was warmed to about 160° F. and sufficient stearic acid and transparentizing agent were added to give the weight percents of solids in the final coating indicated in the tabulation below. The mixture was maintained at this temperature until the stearic acid and transparentizing agent had gone into solution. This solution of stearic acid and paraffin in xylene was then added to the warmed casein solution (at about 120° F.) while the latter was being stirred rapidly. Stirring was continued until the emulsion had been formed.

These coating compositions were applied at a temperature of about 85° F. by means of a coating roller to samples of 10-pound tissue paper and dried as in Example I.

The results, in terms of final coating performance, are tabulated below for the different transparentizing agents used in the above basic formulation. The final coating performance is based upon the contrast and definition, or copy quality, of marks and indicia placed on the positive pressure-printing material thus made. These results are rated on the basis of copy quality obtained when pressure was applied by typing and by writing with pencil or pen on an uncoated top sheet having a number of sheets of the positive pressure-printing paper placed directly under it.

Transparentizing Agent	Physical Form of Transparentizing Agent	Solids Content of Final Coating			Quality of Reproduction	
		Wt. Percent Trans. Agent	Wt. Percent Stearic Acid	Wt. Percent Casein	Pencil	Typewriter
Stearic Acid	Solid		21	79	Fair	Fair.
Do	do		50	50	Good	Good.
Polyamide [1]	Viscous liquid	39	13	48	do	Do.
Paraplex G-20 (Alkyd-type polyester)	Grease-like	39	13	48	do	Do.
Hycar Liquid 1312 [2]	Very viscous liquid	17	17	66	Fair	Poor.
		39	13	48	Fair-Good	Poor-Fair.
		54	10	36	Good	Fair.
Silicone Fluid [3] (Viscasil, 10,000)	Liquid (10,000 cps.)	39	13	48	do	Do.
Pale Oil 1000	Liquid	39	13	48	do	Do.
Lanolin, anhydrous	Petrolatum like	39	13	48	Fair-Good	Poor-Fair.
Blown Soya Bean Oil	Viscous Liquid	17	17	66	Fair	Fair.
	do	39	13	48	do	Poor-Fair.
Paraffin, M.P., 128° F	Solid	47	21	32	Good	Very Good.
	do	26	26	48	do	Do.
	do	35	35	27	do	Do.
	do	33	21	46	do	Do.
	do	71	10	19	Fair	Fair to Good.
Mineral Oil	Liquid	33	21	46	Poor-Fair	Fair.
Stearamide Type Wax	Solid	33	21	46	Fair	Do.
Polyethylene	do	33	21	46	do	Do.
Polyglycol Mol. Wt. 4000	do	33	21	46	do	Fair-Good.
Glyceryl Monostearate	do	33	21	46	Good	Good.
Petrolatum	Paste	33	21	46	Fair	Fair.
Oxidized Microcrystalline	Solid	33	21	46	Good	Good.

[1] Polymerization product of dimerized linoleic acid and aliphatic polyamines.
[2] Butadiene-acrylonitrile copolymer.
[3] General Electric Company "Viscasil 10,000."

It will be seen from the tabulation that a number of materials possessing the characteristics discussed make satisfactory transparentizing agents. The final choice will be at least partly determined with respect to the pressure sensitivity desired in the final coating. Of the transparentizing agents listed above, and for which specific examples are given in the tabulation, the hydrocarbon wax having a melting point of about 128–130° F. is preferred for the practice of this invention.

The amount of transparentizing agent will be determined by the degree of sharpness or definition required in the final tracing on the positive pressure-printing material of this invention. Because of the role of the transparentizing agent as a coating for the matrix interfaces, the amount of transparentizing agent will depend primarily on the amount and type of matrix material present in the final coating.

It has been found that the amount of transparentizing agent may vary from about 10 to 300% of the weight of the matrix solids present. A preferred range is from about 30 to 75% of the weight of the matrix material. If too little transparentizing agent is present, the desired effect obtainable from the transparentizing agent is not fully realized while if too much of the transparentizing agent is used, the final coating takes on the characteristics of a wax rather than a coating suitable for a positive pressure-printing material. As exemplified in Example III, it may be desirable to determine the amount of transparentizing agent with respect to the matrix materials used. For example, in the case of the bentonite it was desirable to use more transparentizing agent since it also served in the role of a water-insensitizing agent.

The range of the transparentizing agent is shown below in Examples V and VI in which hydrocarbon wax with a melting point of about 128° F. was used in a basic formulation with varying amounts of transparentizing agent as illustrated in these examples.

EXAMPLE V

A dispersion of casein was prepared as described in Example I and a solution of xylene, stearic acid, and paraffin was prepared also as in Example I, except that 0.65 pound of paraffin was substituted for the 2.7 pounds of paraffin used in that example. This formualtion gave a concentration of paraffin equivalent to about 17% of the weight of the casein present. Samples of 10-pound tissue paper were coated with this composition, dried as described in Example I, and tested for good copy quality. Although pressure applied by means of a pen, pencil, or the face of a typewriter key gave good copy, it was not as satisfactory as far as optical contact achieved as was the composition of Example I, in which the paraffin was present in about 71% of the weight of the solid casein.

EXAMPLE VI

A matrix dispersion was prepared as described in Example I and a xylene solution of stearic acid and paraffin was prepared as given also in Example I, except that 3.3 pounds of paraffin was substituted for the 2.7 pounds. This paraffin was equivalent to about 87% of the solid weight of the casein. The coating composition was prepared, applied, and dried in the same manner as described in Example I. The final dried surface gave good copy quality, excellent water and heat resistance without showing any strong tendency towards being waxy.

In addition to using a material which serves only as a transparentizing agent, it should be pointed out that the emulsifying agent, if present, can also serve as a transparentizing agent. The quantity of emulsifying agent thus serving in an alternate role is in addition to the quantity of the transparentizing agent specified.

Emulsifying agent

The emulsifying agent has a dual role in the coating composition of this invention. It acts both as an aid in forming the desired emulsion and also as a transparentizing agent.

In the mixing of the coating composition of this invention a thorough dispersing of one liquid in another is required to form the necessary emulsion and it is desirable under some conditions to add an emulsifying agent such as those commonly used to prepare emulsions. Such emulsifying agents may be one of the appropriate soaps which may be defined as salts of a strong base such as ammonium hydroxide, or sodium hydroxide, and of a fatty acid such as stearic, palmitic, or lauric. The soap used as an emulsifying agent should be one which is a solid at room temperature in the final form which appears in the coating. The emulsifying agent can be omitted provided it is not essential to the making of the emulsion, but it is preferable to have one, inasmuch as it serves also as a transparentizing agent.

The emulsifying agent may be formed in situ by reaction between the fatty acid and an alkali metal ion furnished for example from an excess of a solubilizing agent used in connection with the matrix material. Thus, if a stearic or palmitic acid is added to a coating mixture containing an excess of ammonium ions, ammonium stearate or ammonium palmate is formed and serves as the emulsifying agent.

The amount of emulsifying agent used will be determined first by the quantity required to produce a good emulsion of the continuous phase and discontinuous phase liquids, and secondly by the amount desirable to contribute to the effect of the transparentizing agent. Thus, if no emulsifying agent is required to form the necessary emulsion and no additional transparentizing effect is required, no emulsifying agent need be added. However, if an emulsifying agent is required to form the emulsion and/or is required in the role of a transparentizing agent, then the amount of emulsifying agent may be as high as about four times the weight of the matrix material solids present in the continuous phase portion of the emulsion. The incorporation of large quantities of emulsifying agent into the formulation may require an increase in the amount of discontinuous phase liquid. Generally, the desired amount of emulsifying agent used will vary from about 3 to 10 percent of the weight of the discontinuous phase liquid containing the emulsifying agent in solution.

The following examples illustrate the types of emulsifying agents which are satisfactory for the process of this invention.

EXAMPLE VII

A casein dispersion was first formed by mixing 14.1 pounds of casein, 73.2 pounds of water, and 5.7 pounds of ammonia (28% NH_4OH). After the casein had been solubilized, 1.4 pounds of $ZnSO_4$, dissolved in 5.6 pounds of water, was added to the casein dispersion. The dispersion was otherwise made up in the manner described in Example I. To twenty-five parts by weight of this dispersion was added 10 parts by weight of water to dilute it to the proper consistency. In a separate vessel 5.4 pounds of stearic acid, and 2.5 pounds of paraffin (melting point 128° F.) were dissolved in 54 pounds of warm xylene and the mixture was stirred until complete solution had been obtained. To the 25 parts by weight of the casein solution, now containing the additional 10 parts by weight of water, was added 7.5 parts by weight ammonia (28% NH_4OH) with stirring. Then, one-half of the xylene solution was added to the casein dispersion with rapid stirring, an additional 7.5 parts by weight of ammonia was added and finally the remaining portion of the xylene was added and stirred to form the desired emulsion. The resulting coating composition was coated on 10-pound black tissue in the manner described in Example I and the coating composition dried in the manner described also in Example I. It was possible to make 10 duplicate copies by marking on an uncoated sheet having under it 10 sheets of the coated material when pressure was applied to the top uncoated sheet by a pencil. With this material it was possible to make up to some 25 copies by use of a typewriter.

EXAMPLE VIII

A coating composition was made up exactly as described in Example VII except that an equal weight of palmitic acid was substituted for the stearic acid of Example VII. The performance of the coating when applied to tissue paper was similar to that achieved by the coating composition containing stearic acid as an emulsifying agent.

EXAMPLE IX

The stearic acid in the coating composition of Example VII was replaced by an equal weight of lauric acid and the coating composition treated and handled in the same manner as in Example VII. The resulting coating composition was not as satisfactory as that obtained in Example VII in that the whiteness of the coating produced was inferior.

EXAMPLE X

The stearic acid in Example VII was replaced with an equal weight of oleic acid. The resulting coating composition which was mixed, applied and dried as in Example VII, was not found to be as satisfactory because the oleic acid present as an emulsifier was not a solid at room temperatures. This, in turn, caused the oleic acid to migrate into the pores of the tissue paper.

Continuous-phase liquid

Liquids suitable for the continuous phase of the emulsion forming the coating of this invention should be solvents for the matrix material and preferably nonsolvent for the transparentizing agent. Liquids other than water may be used to form the continous phase, but water is preferred for practical and economical reasons. It should be noted that the use of a water-soluble matrix material, and hence of an aqueous solution as a continuous phase, means that the cost of the coating composition of this invention can be materially reduced below the cost of an oil-base paint or a coating using an organic vehicle to form the continuous phase.

Discontinuous-phase liquid

The liquid forming the discontinuous phase must have a vapor pressure less than that of the liquid forming the continuous phase, i.e., usually less than that of water at the drying temperature, but for practical purposes it should have a boiling point not above 325° F. Such liquids include, but are not limited to, xylene, kerosene, mineral spirits, high-flash naphthas, ketones (such as butyl methyl ketone and amyl ethyl ketone), paraffin hydrocarbons such as octane, and the higher boiling acetates such as butyl acetate or amyl acetate.

The choice of the liquid forming the discontinuous phase will have some influence on the pressure sensitivity of the final coating. Thus, if a liquid is used for the discontinuous phase which has a relatively high vapor pressure, i.e., fairly close but somewhat below that of water, some of the discontinuous phase liquid will pass off from the coating simultaneously with the water leaving less of the discontinuous phase liquid within the matrix thus forming smaller globules of the liquid which in turn means less distortion of the matrix to form the air-matrix interfaces. The final result of using a high vapor phase liquid means a strong matrix and hence a more pressure-resistant final coating.

The final choice of the liquid for the discontinuous phase may also require the consideration of such points as that which will give the brightest coating for a given weight per unit area of surface for a specific film-forming material; that which will prove to be the most compatible with other components such as the binder, the emulsifying agent, and any dye or dyes added; and that which will meet certain other requirements such as toxicity, inflammability, adaptability to production procedures, cost, and the like.

The amount of discontinuous phase liquid with relation to the amount of continuous phase liquid may vary within the limits which may be used to form the type of emulsion required, normally an oil-in-water emulsion. The limits on such liquid ratios are well known or can easily be determined. Within these physical limitations for obtaining the emulsion, the amount of discontinuous phase liquid may be varied in accordance with the amount of emulsifying agent added. Thus, depending on the solubility of the emulsifying agent in the discontinuous phase liquid, it may be desirable to use more discontinuous phase liquid when the larger quantities of emulsifying agent are used.

The amount of discontinuous phase liquid may also be expressed in terms of the weight ratio of discontinuous liquid to matrix material in the coating composition, i.e., in the emulsion. As noted above in connection with the matrix material, this weight ratio may vary from about 5:1 to 25:1. Generally, the less discontinuous liquid present with respect to the amount of matrix material, the more pressure it will require to mark the final positive, pressure-printing material. This is due to relatively large amounts of casein solids in the coating which make the coating hard and hence difficult to break down the porous, cavernulous structure. Where relatively large quantities of discontinuous phase liquid, with respect to matrix material, are used, the final structure of the coating is very porous and requires relatively little pressure to mark. This means that under some circumstances, positive pressure-printing material having a very porous coating may be subject to unwanted marks brought about in handling etc. The preferred range of 15:1 offers a compromise between good copy quality and freedom from such unwanted marks.

Of the discontinuous phase liquids listed above, the preferred liquid is xylene, a liquid which has been illustrated in Examples I and II, and Examples III through X. Example IV illustrates the use of Stoddard solvent with mineral spirits of a boiling fraction from about 310 to 375° F.

The use of kerosene is illustrated in the example below.

EXAMPLE XI

The xylene of Example I was replaced with a petroleum fraction boiling between 153 and 200° C., i.e., normally called kerosene. The formulation otherwise was the same as that described for Example I and the resulting coating was equally satisfactory.

Although it will ordinarily be desirable to use a composition which will give a white coating on a contrasting dark-supporting sheet, it may be desirable to use a colored coating and hence have a colored background. The essentially non-pigmented coating of this invention may be made in any desired color by adding one or more dyes to the coating composition. The dyes may be either of the oil-soluble or water-soluble type added to the appropriate phase of the coating composition depending upon the effects desired.

The examples given above have illustrated in detail the steps in the process of mixing the coating composition of this invention. The process may be described generally as comprising the steps of forming a solution or dispersion of the matrix material in the continuous phase liquid, adding a portion of a strong base if it is to be used to form the emulsifying agent in situ, adding additional continuous phase liquid, preparing a solution of the transparentizing agent and the emulsifying agent (or the fatty acid portion of the emulsifying agent) in the discontinuous phase liquid, adding about one-half of the solution to the dispersion of the matrix material in the continuous phase liquid with very rapid stirring, and finally adding the remaining portion of the strong base and the solution of the emulsifying agent and transparentizing agent in the discontinuous phase liquid. If a coating composition of low viscosity is required, additional continuous phase liquid may be added at the end of the mixing to adjust the viscosity.

The viscosity of the coating composition just prior to application can be controlled by the amount of continuous phase and discontinuous phase liquid used and, as noted above, the viscosity may be finally reduced if necessary by adding the necessary quantity of continuous phase liquid.

Viscosities of a wide range have been successfully used, the practical upper limit being about 2960 centipoises while the practical lower limit is about 400 to 600 centipoises. The optimum viscosity will be determined by such factors as (1) the method used to coat or apply the coating composition, (2) the mobility of the matrix material, and (3) the type of backing used to which the coating is applied. For example, it would be desirable when using a knife coater to employ a coating of relatively high viscosity, while when a reverse-roll is used, coating compositions of lower viscosities would be desirable. As another example, where casein is the matrix material it is desirable to have a composition of relatively high viscosity since the casein has a tendency to be fairly mobile and to work into the fibers of the backing, thus, acting as a saturant rather than as a coating. Finally, the viscosity should be adjusted with relation to the porosity of the paper and the absorbing rate of the paper. Papers which do not absorb easily can tolerate coating compositions of lower viscosity.

Once the coating composition has been thoroughly mixed, it may be applied to the supporting material by any well-known technique such as rolling, brushing, spraying, printing, and the like. Although the coating may be dried by atmospheric action only, it is more practical to dry it by passing a warm stream of air at about 100° F. over the coating or over the uncoated side of the backing material. Other suitable drying techniques may of course be used.

The thickness of the coating when first applied will range from about 8–10 mils. When drying has been completed, the final coating thickness will range from between about 0.2 and 0.5 mil.

The coating composition of this invention may be deposited on a variety of backing or supporting materials. However, where the purpose is to produce a positive pressure-printing material and achieve production of a number of copies without the use of any carbon paper or carbon backing, it is necessary to deposit the coating on relatively thin backing material. If the final copies are to be colored tracings on a white background, a white coating will be used over a dark colored backing, e.g., black, red, green, blue, etc. To obtain good clear copy it is desirable to use a backing which is fairly highly colored.

The backing is, of course, not limited to tissue paper but may be any material or surface on which it is desired to make tracings, etc. Where marking tape for example, is to be made it would be advantageous to use a material which has an adhesive on one side.

Although it has been found that the coating composition of this invention when applied to a colored tissue gives good clear copy even when it is the twenty-fifth copy, it has been found that the quality and clarity of the copy may be improved by exposing the sheet after pressure application to a very brief heating up to temperatures at or below which the wax and the coating composition will melt and flow appreciably. Once paper, to which pressure had been applied and the tracing has been made, has been heated the coating becomes practically completely water-insensitive and heat-insensitive.

It will be noted from the above description that there are a number of ways in which the pressure sensitivity of the coating composition of this invention, and hence the resulting positive pressure-printing material, may be controlled. These may be summarized as follows:

(1) The choice of transparentizing agent: in general

if the transparentizing agent is a relatively hard wax-like material the final coating will be less pressure sensitive;

(2) The amount of transparentizing agent and/or emulsifying agent which may serve as a transparentizing agent: the greater the ratio of transparentizing agent and emulsifying agent to the amount of matrix material the more pressure sensitive is the final coating;

(3) The vapor pressure of the liquid forming the discontinuous phase: the higher the vapor pressure, i.e., the closer it approaches the vapor pressure of the continuous phase liquid, the less pressure sensitive the final coating will be;

(4) The formation of insoluble material such as sodium caseinate which tends to make the coating less pressure-sensitive;

(5) The ratio of the binder to the amount of liquid forming the discontinuous phase: the higher the ratio the more sensitive it is to pressure; and

(6) The control of the moisture content of the liquid which in turn is related to the transparentizing agent chosen and the amount used.

These factors may be so adjusted as to give a final coating, the pressure sensitivity of which may vary over a wide range. The actual pressure sensitivity of the final coating will be, of course, dictated by the application to which it is put. For example if the coating is for a positive pressure-printing duplicating paper which is to be used in multiple sheets for making many duplicate copies the coating should be relatively sensitive to pressure. Likewise, if the pressure is to be applied by hand tools such as pencils or pens, the coating should be more pressure sensitive than if pressure is to be applied by mechanical devices using type. On the other hand, where the coating is to be applied to marking tapes where duplicates are not required, a lesser degree of pressure sensitivity is required because more handling, etc., may be involved.

This invention contemplates the binding of a number of sheets of forms, pads, or stacks of sheets suitable for making multiple copies by means of applying pressure to the top sheet without the use of any carbon backing or interleaving carbon paper. It has been shown for example that it is possible when pressure is applied by means of a typewriter to make up to 25 duplicate copies with this type of paper.

A typical such manifold is illustrated in Fig. 5. Sheets of positive pressure-printing material **30** are bound to an uncoated upper sheet **32** at one edge **34** by means of any suitable device such as staples **36**. The sheet may have perforations **38** for easy separation. The sheets **30** may, of course, be white coating on different colored backgrounds so that copies can be made with tracings in different colors. This is often useful in business forms where it is necessary to sort out copies for various uses. In addition to using coated sheets which give a variety of colored tracings, it is also possible to selectively coat portions of these sheets so that when pressure is applied to the top sheet, selective marking on the subsequent sheets is achieved.

This invention also contemplates the making of marking tapes by depositing the coating composition of this invention on a suitable flexible backing which is coated with an adhesive on the side not containing the coating composition. Two such marking tapes are illustrated in Figs. 6 and 7. In Fig. 6 the coating composition of this invention **40** is applied to backing **42** which has a layer of adhesive **44** on the other side. This arrangement is suitable if backing **42** is of a color which exhibits sufficient contrast to coating **40** to give a good mark. If backing **42** is not highly colored or is transparent, then it will be desirable to interpose a colored layer **46** (Fig. 7) to give well defined marks.

It will be seen from the above description that by the process of this invention it is possible to prepare a positive pressure-printing material which can be marked on by means of application of pressure only, i.e., paper or other material which does not require the deposition of ink or the use of carbon paper or carbon backing. The use of such paper in making up business forms such as bank deposit slips, bills of lading, sales slips, and the like would achieve economic advantages as well as eliminate the use of carbon paper or carbon backing. Furthermore, the positive pressure-printing duplicating material of this invention is such that it does not detract from the flexibility of the original backing or support, e.g., paper, and at the same time possesses good resistance to heat, normal pressures of handling, and to moisture.

We claim:

1. A coating composition capable of forming a thin, opaque, essentially non-pigmented film on a surface, said composition consisting essentially of an oil-in-water emulsion, the continuous phase of said emulsion being water containing a film-forming matrix material which acquires colloidal dimensions when peptized, and the discontinuous phase of said emulsion being an organic liquid which is a non-solvent for said matrix material, immiscible with water and having a boiling point above water and containing dissolved therein a plastically deformable transparentizing agent which is a cohesive, highly viscous to solid material, the weight ratio of said matrix material to said discontinuous liquid ranging from about 1:5 to about 1:25, and said transparentizing agent being present in an amount equivalent to from about 10 to 300% of the weight of said matrix material.

2. A coating composition in accordance with claim 1 wherein said discontinuous phase liquid is xylene.

3. A coating composition in accordance with claim 1 wherein said matrix-forming material is casein.

4. A coating composition in accordance with claim 1 wherein said transparentizing agent is a paraffin wax melting at about 130° F.

5. A coating composition capable of forming a thin, opaque, essentially non-pigmented film on a surface, said composition consisting essentially of an oil-in-water emulsion, the continuous phase of said emulsion being water containing a film-forming matrix material which acquires colloidal dimensions when peptized, and the discontinuous phase of said emulsion being an organic liquid which is a non-solvent for said matrix material, immiscible with water and having a boiling point above water and containing dissolved therein an emulsifying agent and a plastically deformable transparentizing agent which is a cohesive, highly viscous to solid material, said emulsifying agent being one which is solid when said coating composition forms said film and which is present in an amount ranging from about 3 to 10% by weight of said discontinuous phase liquid, the weight ratio of said matrix material to said discontinuous liquid ranging from about 1:5 to about 1:25, and said transparentizing agent being present in an amount equivalent to from about 10 to 300% of the weight of said matrix material.

6. A coating composition in accordance with claim 5 wherein said emulsifying agent is stearic acid.

7. A coating composition in accordance with claim 5 wherein said transparentizing agent and said emulsifying agent are the same.

8. A coating composition capable of forming a thin, opaque, essentially non-pigmented film on a surface, said composition consisting essentially on an oil-in-water emulsion, the continuous phase of said emulsion being water containing a film-forming matrix material which acquires colloidal dimensions when peptized, and an insolubilizing agent for said matrix material whereby said matrix material becomes substantially water insoluble upon formation of said film, and the discontinuous phase of said emulsion being an organic liquid which is a non-solvent for said matrix material, immiscible with water and having a boiling point above water and containing dissolved therein a plastically deformable transparentizing

agent which is a cohesive, highly viscous to solid material; the weight ratio of said matrix material to said discontinuous liquid ranging from about 1:5 to about 1:25, and said transparentizing agent being present in an amount equivalent to from about 10 to 300% of the weight of said matrix material.

9. A positive, pressure-printing material comprising a flexible backing having deposited on one side thereof a coating characterized by being a matrix of a film-forming material having uniformly distributed throughout its entire volume, multitudinous, minute air-matrix interfaces varying in maximum dimensions from about one-half to one micron with no appreciable number exceeding five microns providing a uniform cavernulous structure and containing a plastically deformable transparentizing agent present in an amount equivalent to from about 10 to about 300% of the weight of said matrix, said agent being further characterized as a cohesive, highly viscous to solid material, said film-forming material being a water swellable material which acquires colloidal dimensions when peptized.

10. A pressure-printing material in accordance with claim 9 wherein said coating is white and said backing is of a color which forms a sharp color contrast with said white coating.

11. A pressure-printing material in accordance with claim 9 wherein said backing is tissue-weight paper.

12. A manifold of flexible sheets joined in superimposed arrangement and suitable for simultaneously making a number of copies by application of pressure alone to the top sheet of said manifold, comprising a plurality of sheets of a flexible material, each sheet under the top sheet consisting essentially of a flexible colored backing having deposited on the top side thereof a coating characterized by being of a color which contrasts with the color of said backing, said coating being a matrix of a film-forming material having distributed throughout its entire volume, multitudinous, minute air-matrix interfaces varying in maximum dimensions from about one-half to one micron with no appreciable number exceeding five microns providing a uniform cavernulous structure and containing a plastically deformable transparentizing agent present in an amount equivalent to from about 10 to about 300% of the weight of said matrix and being further characterized as a cohesive, highly viscous to solid material, said film-forming material being a water swellable material which acquires colloidal dimensions when peptized.

13. A manifold in accordance with claim 12 wherein selected areas of said sheets are coated with said coating.

14. Process for coating a substrate area with a coating composition to form a pressure-sensitive positive printing marking surface, comprising the steps of preparing a dispersion of a matrix material in water, preparing a solution of a transparentizing agent in an organic liquid immiscible with water and having a boiling point above that of water but below about 350° F., rapidly stirring said dispersion and simultaneously adding said solution to form an oil-in-water emulsion, depositing said coating composition on said flexible backing material, expelling first a major portion of said water and forming in the resulting film of said matrix material a multiplicity of small pockets of said organic liquid, and then expelling said organic liquid thereby to form multitudinous air-matrix interfaces while simultaneously precipitating out said transparentizing agent in said air-matrix interfaces uniformly distributed throughout the volume of said film and which range in maximum dimensions from about one-half to one micron with no appreciable number exceeding five microns, whereby said film becomes opaque and light scattering; said transparentizing agent being a plastically deformable, cohesive, highly viscous to solid material.

15. Process in accordance with claim 14 wherein said drying steps comprise exposing said coating to a warm air stream.

16. Process in accordance with claim 14 further characterized by the step of introducing an emulsifying agent into said discontinuous phase liquid.

References Cited in the file of this patent

UNITED STATES PATENTS

1,783,442	Mayer et al.	Dec. 2, 1930
2,299,694	Green	Oct. 20, 1942
2,299,991	Kallock	Oct. 27, 1942
2,306,525	Cummings	Dec. 29, 1942
2,310,795	La Piana	Feb. 9, 1943
2,374,862	Green	Mar. 1, 1945
2,519,660	James	Aug. 22, 1950
2,648,924	Brewster	Aug. 18, 1953
2,655,453	Sandberg	Oct. 13, 1953
2,710,263	Clark et al.	June 7, 1955
2,739,909	Rosenthal	Mar. 27, 1956