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MOISTURE-SENSITIVE PAPER AND THE MANUFACTURE THEREOF

Francis L. Simons, Montclair, N. J., assignor to George La Monte & Son, Nutley, N. J., a corporation of New Jersey

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1

This invention relates to coated products and the manufacture thereof.

It is a purpose of this invention to provide a coating for paper or other article, which coating is sensitive to moisture, namely, has the capacity to reveal by development of color change application of moisture thereto. It is a further purpose of this invention to provide a coating of the character aforesaid wherein the developed color change persists after the moisture that effects the color change has evaporated from the coating.

The present invention is of particular value in affording a unique type of paper that is sensitive to the application of moisture. Thus paper embodying the present invention is highly effective in preventing the transmission of messages written on paper with so-called "invisible" or "sympathetic" ink materials, namely, inks in the form of aqueous solution that, when applied to paper, have little or no visibility, but which, by suitable treatment such as application of heat, exposure to suitable chemical reagents, etc., developed sufficient color to permit visual detection of the writing or other legend inscribed thereon. Tea, milk, and lemon juice, for example, are readily available for use as "invisible" ink in the manner referred to. The transmission of normally non-detectable messages, can readily be accomplished using ordinary writing paper or other paper. However, if the paper of the present invention is utilized for any such purpose, the paper develops a pronounced color wherever the "invisible" ink is applied, so that the message intended to be non-discernible becomes most apparent. Moreover, the developed color persists even after the "invisible" ink dries out so that a permanent visual record of the inscribed legend is made.

The safety-paper of this invention is also of utility in revealing attempted alterations of ink legends inscribed thereon by the employment of a chemical ink eradicator such as a chlorine bleach solution or a potassium permanganate solution. Heretofore chemicals have been incorporated in safety paper which chemicals, when subjected to a bleach, for example, develop a stain, e. g., brown, due to the action of the chlorine bleach. Such materials, being sensitive to only certain particular types of chemical reaction, have limited utility, however, in evidencing use

2

of different types of chemical ink eradicators. By way of contrast, the safety-paper of this invention is sensitive merely to the moisture in chemical ink eradicators and for this reason it is immaterial whether one type of ink eradicator or another is applied, and it is obvious that a wider field of protection is available than is possible with one of the chemically reactive safety chemicals heretofore incorporated in safety-paper.

Another possible use of the moisture-sensitive paper of this invention is in the taking of fingerprints quickly and without messiness. If the fingers are moistened, even only slightly, the moisture on the fingers will cause color to develop on the paper in the distinguishing fingerprint patterns and the fingerprints will remain permanently upon the paper. The developed color of the dyestuff does not come off on the fingers and the operation can be carried out without the messiness usually incident to taking fingerprints and also much more rapidly.

While the coating of this invention is of particular value as applied to paper, it is apparent that it will exhibit its unique properties when carried by the surface of any other articles regardless of the material used, e. g., cardboard, cloth, wood, metal, etc.

In order to afford an understanding of the practice of this invention, the invention is described hereinbelow in connection with a preferred illustrative embodiment. According to this embodiment, there is applied to paper (or other article) a dyestuff that has been substantially decolorized by means of an alkaline earth hydroxide but that, after application in a decolorized condition as a coating, has the property of having its color restored upon moistening the coating. Preferably, the decolorized dyestuff is applied to the paper in admixture with a conventional paper coating composition containing a finely-divided solid water-insoluble filler and a binder for the filler which binds the filler to the paper as a coherent coating suitable for the writing or printing of legends or other indicia thereon.

A preferred typical dye for use according to this invention is sodium salt of dibenzyldiethyldiaminotriphenylcarbinol disulphonic acid anhydride ($C_{37}H_{35}N_2O_6S_2Na$) (Color Index No. 666 of

the Color Index of the Society of Dyers and Colourists). This dye is normally of a pronounced green color and is commonly designated as Acid Green LX. However, it may be decolorized by mixing therewith in an equeous medium an alkaline-earth hydroxide, preferably calcium hydroxide or slaked lime. However, other alkaline-earth hydoxides may be used such as barium, strontium and magnesium hydoxides. The extent of the decolorization depends upon the amount of the calcium hydroxide mixed with the dye. Ordinarily, however, in the case of calcium hydroxide, the ratio by dry weight of the hydrated lime to the dyestuff will range from about 1 to 1 at the one extreme to about 5 to 1 at the other extreme. Where substantially complete decolorization of the dyestuff is desired, at least about 2 parts by dry weight of the calcium hydroxide to about 1 parts by dry weight of the dyestuff is employed. The composition above described can be applied to any desired carrying body such as paper, cardboard, cloth, metal, etc., and when spread as a coating and dried, the resulting coating will lack the normal color characteristics of the dyestuff. Thus, if the composition is applied as a coating to ordinary white paper, the coating will dry out white or with a slight greenish-gray tint. However, after the coating has been applied and dried, it is sensitive to moisture, for wherever moisture is applied, the pronounced green color of the dyestuff will be developed and evidence very prominently any area that has been moistened.

Of course, a dried coating consisting merely of dyestuff and calcium hydroxide would chalk off, and it is readily understood the coating can be caused to adhere to the coated surface by use of a suitable binder which may be any conventional binder such as casein, glue, starch, or the like. Moreover, in order to better carry the decolorized dyestuff in a substantial coating, it is preferable as aforesaid to incorporate with the binder, decolorized dyestuff, and calcium hydroxide (or the equivalent) a finely-divided solid water-insoluble filler material which may be, for example, any of the fillers commonly used in coatings for paper such as clay, calcium carbonate, etc.

In any specific case for determining the amounts of dyestuff and alkaline earth hydroxide for use in the coating composition, one can first determine the amount of dyestuff that is adapted to afford the color intensity desired for the coating composition when the color of the dyestuff is developed, and then employ an amount of alkaline earth hydroxide that brings about the desired degree of decolorization of the dyestuff. There is no sharply defined upper limit as to amount of alkaline earth hydroxide relative to dyestuff that may be employed, although, when the amount of alkaline earth hydroxide is increased beyond the amount indicated above as preferable, such large amount retards the rate of development of the color of the decolorized dyestuff upon moistening and tends to make the coating material brittle. At the lower extreme, the limits are somewhat more significant, but here again there is no sharp transition point and the amount of alkaline earth hydroxide used depends upon the completeness of the decolorization that is desired. When barium hydroxide is used, it is necessary to use somewhat more of the barium hydroxide in relation to dye than when calcium hydroxide is employed. For example, whereas it is ordinarily desirable to employ two parts by weight of calcium hydroxide to each part by weight of dyestuff, it is necessary to employ four or even five parts of barium hydroxide for each part of the dyestuff to obtain an equivalent amount of decolorization.

The following is a typical example of a preferred embodiment of this invention, the composition of the coating being (dry weight):

	Pounds
Casein	56
Clay	240
Calcium carbonate	160
Hydrated lime	5
Dye (sodium salt of dibenzyldiethyldiamino-triphenyl-carbinol disulphonic acid anhydride)	1¾

In preparing the coating composition, the casein may first be dissolved in ammonia, borax, sodium hydroxide, triethanolamine, sodium silicate, or other alkali adapted to render the casein soluble in water. The clay and calcium carbonate are then added to produce a slurry suitable for application as a coating, e. g., the water content may be sufficient to provide 100 gallons of the slurry. The hydrated lime is then added to the slurry, e. g., as a slurry in about two gallons of water. Lastly, the dyestuff is added in the form of a solution in about 3 gallons of water. If desired, a small amount of a defoaming agent, e. g., about ½ to 1 quart of pine oil emulsion, may be incorporated to improve spreading quality and prevent foam. Usually, when a dye having high tinctorial power is incorporated in the relative proportions above mentioned, one would expect the slurry to become highly colored; but, due to the decolorizing action of the hydrated lime, the added dyestuff is substantially completely decolorized. The composition is then ready for application to a surface to be coated and may, for example, be applied to the surface of paper by any conventional coating method, the coating being applied at the rate of about two to about five pounds per 100 square feet of surface coated. The coating as applied is then permitted to dry, e. g., when applied to paper may be dried as by use of a conventional festoon dryer. Coated paper can then be super-calendered in the usual manner and the product will have the appearance and texture of high grade paper of the coated type. The degree of finish or gloss may be whatever is desired, although I prefer a dull or so-called eggshell finish as being easier to write upon. During the drying step, some color may appear briefly but the color disappears during drying. The color of the coating will be white or may have a slightly grayish-green cast. However, if, after the coating has been produced and dried, moisture is applied thereto, the coating, wherever the moisture is applied, becomes colored with the normal color of the dyestuff, namely, the dyestuff is caused to occur in its non-decolorized condition. Moreover, when the moisture applied to the coating dries out, the coating remains colored wherever the moisture had been applied thereto.

An alternative method of making up the coating composition above described consists in mixing the casein initially with the hydrated lime, the hydrated lime being used instead of the ammonia, borax, etc., as an alkali for dissolving the casein. The remainder of the procedure above described is then followed except that no further separate addition of lime is necessary. It may be mentioned, however, that, in order to facilitate

solution of the casein, it may be desirable to employ a slightly greater proportion of hydrated lime than in the specific exemplary formula set forth above.

In connection with the foregoing, it may be pointed out that, in the formulation of the coating composition, there is very great latitude in selection of ingredients other than the dyestuff and the decolorizing agent therefor. Thus the nature of the filler material is optional since the filler is merely used to provide bulk and thickness to the coating and merely exercises a physical effect in the coating. In the coating of paper to provide a moisture-sensitive coating, it is, of course, preferable to employ the mineral fillers (either natural or artificially produced) that are commonly used in the paper-making art, such as clays, calcium carbonate (precipitated chalk), a mixture of precipitated calcium sulphate and aluminum hydroxide, a mixture of precipitated barium sulphate and aluminum hydroxide, titanium dioxide, zinc sulphide, asbestine, lithopone, etc. In addition to the foregoing, other fillers may be used, even an organic filler such as wood flour. As aforesaid, the filler can be omitted entirely but preferably is present in addition to the dyestuff and decolorizing agent. Preferably, the coating composition contains an amount by weight of finely-divided solid water-insoluble filler that is at least about 100 times the weight of the dyestuff. Moreover, it is preferable to have present in the slurry that is applied as a coating at least about 3 pounds of alkaline earth hydroxide per 100 gallons of the slurry, or 3 pounds of alkaline earth hydroxide per 275 pounds of other solids (dry weight) in the coating composition. Preferably, also, the coating composition contains about 1.25 to 4 parts of binder for each 10 parts of solids (including hydrated lime or other alkaline earth hydroxide). The filler materal is ordinarily white or nearly white in color, but this is not essential provided the color of the filler is not inconsistent with detection of the development of color of the dyestuff upon application of moisture. When filler is used in the proportions above mentioned, it is generally desirable to apply the coating composition at the rate of about two to about five pounds per 100 square feet. In the usual case, it is desirable to apply the coating material as a relatively heavy coating so that the color reaction that is developed by the application of moisture will be as vivid as possible, and for this reason application of the coating material at the rate of at least about three pounds per 100 square feet is preferable.

With regard to the binder material, other binder materials than casein obviously can be employed. Thus glue or starch may be employed. However, such binders being somewhat weaker in bonding strength than casein should be used in somewhat greater amount. For example, in the specific formula above given, the amount of glue or starch preferably is about two or three times the amount of casein. Moreover, when an adhesive such as glue or starch is employed, it is not necessary to treat the binder material with an alkaline material to render it soluble. In the case of starch, the amount of water in the coating composition may be somewhat greater than with other binders in order to provide a composition of suitable spreadability. Shellac may be used as a binder, together with a little borax, ammonia, or other alkali to render it soluble. Albumen, e. g., egg albumen, may also be used as the binder. Binders such as the foregoing are desirable, since they are white or substantially colorless or only slightly colored and do not interfere with the detection of the development of the color of the dyestuff upon moistening the coating. It is to be understood, however, that the binder may be somewhat colored and still have the development of the color of the dyestuff apparent by way of color contrast.

Somewhat more generally it is apparent that in providing a moisture-sensitive coating for articles, there is great latitude in the composition of the coating. The only prime requisite is that the dyestuff in the amount used be adequate when in its normal colored condition to impart color to the coating and that the dyestuff be decolorized by the presence therewith of alkaline earth hydroxide when applied to an article as a coating. Other than the dyestuff and decolorizing agent, a binder should be present so that the coating will not rub off too easily, unless such rubbing off is not regarded as undesirable. The presence of filler merely acts to give bulk to the coating so that it may be applied more readily and in increased amounts and so that a better surface for writing, printing, etc., may be provded.

In addition to sodium salt of dibenzyldiethyldiamino-triphenylcarbinol disulphonic acid anhydride, other dyes may be used. Those dyes in the diamino-triphenylmethane group are suitable, especially those in the Color Index of the Society of Dyers and Colourists Nos. 657 to 675 inclusive. Examples of such dyes in addition to that above given are sodium salt of dibenzyldiethyldiamino-o'-chloro-triphenylcarbinol disulphonic acid anhydride ($C_{37}H_{34}N_2O_6S_2ClNa$) (No. 667) and sodium salt of dibenzyldimethyldiamino-triphenylcarbinol trisulphonic acid anhydride

($C_{35}H_{30}N_2O_9S_3Na_2$)

(No. 669). The former of the last mentioned dyes is commonly designated as Erioviridine B and the latter is commonly designated as Acid Green B. The acid dyes in the diamino-triphenylmethane group are particularly desirable.

Where a dyestuff such as sodium salt of dibenzyldiethyldiamino - triphenylcarbinol disulphonic acid anhydride has been decolorized by means of an alkaline earth hydroxide and applied as a coating, the color of the dyestuff can be developed merely by the application of distilled water thereto, or other aqueous medium having a pH of about 7. Aqueous media having a pH under 7 may also be used and the acidity of such media even has an accelerating effect on the development of the color upon moistening the coating. On the other hand, if a medium having decided alkalinity, namely, in the case of sodium salt of dibenzyldiethyldiamino-triphenylcarbinol disulphonic acid anhydride, for example, a pH greater than 8, the development of the color is slight and is negligible at a pH of about 8.5 or higher. However, even in such case, mildly alkaline solutions such as solutions of sodium bicarbonate or borax will cause a readily-apparent color development upon application to the moisture-sensitive coating material. The nature of the reaction whereby alkaline earth hydroxides decolorize the diamino-triphenylmethane dyes is not understood at the present time. If the decolorization were simply due to the alkalinity of such materials, then it is understandable that aqueous media having an acid reaction should restore the color because they neutralize this alkalinity. However, my discovery that pure wa-

ter, neutral solutions, and even mildly alkaline media will also restore the color indicates a much more complex effect of the alkaline earth hydroxides on these dyes. Another special property of the diaminotriphenylmethane dyes is that, after decolorization in the presence of alkaline earth hydroxide and drying a coating containing the decolorized dye, the color of the dye can be developed by application of heat to the coating.

In view of that fact, that sensitivity of the decolorized dyestuff to color restoration is increased under acidic conditions, it is usually desirable not to apply the coating material to a base such as paper, cardboard, or the like which has a pH under about 5.5. However, excessive acidity of the base material can to a large degree be counteracted by the use in the coating composition of filler or other material that tends to neutralize any such acidity of the base material to which the coating is applied. Thus, use of calcium carbonate or other alkaline earth carbonate as at least part of the filler (e. g., in an amount that is at least five times the amount of dyestuff) is preferable on application of the coating composition to paper or cardboard.

In order to provide a coating that will be sensitive to moisture of any pH, it is desirable to incorporate with the coating a substance that is adapted to develop a color change upon being raised from one pH value to a higher pH. Thus, if in the foregoing formula, given by way of example, there is added about 1.25 pounds of phenolphthalein, a coating is provided that is sensitive to moisture regardless of pH. At the pH of the coating, the phenolphthalein is colorless. If, however, the pH value of the coating is raised substantially above 8 by application of alkaline moisture, the coating turns a pronounced pink color wherever the moisture is applied. On the other hand, if moisture having a pH below 8 is applied to the coating, then, in the case of the dyestuff sodium salt of dibenzyldiethyldiaminotriphenylcarbinol disulphonic acid anhydride, the green color of the dyestuff develops to reveal the application of the moisture. Alternatively, if moisture having a pH above 8 is applied to the coating with development of pink coloration, and attempt is made to lower the pH below 8, then the pink color may disappear but in its place the developed green color of the dyestuff will remain permanently to evidence application of moisture to the paper.

In connection with the foregoing, it may be pointed out that the coating of the present invention is unlike a coating colored merely with an indicator substance or a plurality of such substances. Any indicator substance requires application either of an acid or an alkali as the case may be (change of pH) to develop a color reaction and is unaffected by pure water. Thus, in the coating above described, if pure water is applied to the coating, the phenolphthalein is unaffected. However, the coating of the present invention is unique in that the dyestuff becomes colored even though only pure water is applied thereto. The use of the decolorized dyestuff together with the indicator substance, by providing color development on application of acidic or alkaline solutions and also when pure water or other neutral solution is applied, affords a combination whereby color development occurs regardless of the acidity or alkalinity of the solution applied to the coating.

When phenolphthalein is incorporated in the coating composition, it may be added dry or may first be dissolved in a small quantity of alcohol to assist in the dispersion of the phenolphthalein on the coating composition. Ordinarily, the amount of phenolphthalein used is sufficient to strongly color the paper when caused to develop a pink color upon being rendered sufficiently alkaline; but, if the paper is to be nearly white in color, the amount used preferably is less than 75% by weight of the dyestuff in the coating. When the phenolphthalein is added to the coating composition prior to application as a coating, the composition may develop a deep reddish color, but during the drying of the coating this reddish color disappears. This initial occurrence of the deep reddish color which disappears during the drying of the coating composition is believed to be due to the fact that the freshly made up slurry containing alkaline earth hydroxide is sufficiently high in pH to throw the phenolphthalein, which has a turning point at a pH of about 8, to the colored side. However, during drying of the coating, possible conversion of alkaline earth hydroxide to alkaline earth carbonate due to reaction with carbon dioxide in the air is believed to lower the pH of the coating composition to such an extent that the phenolphthalein goes back to the colorless, or substantially colorless, condition. When, however, it is said herein and in the claims that the dyestuff is decolorized by alkaline earth hydroxide, this does not exclude the possibility that the dyestuff thus decolorized may be present in the coating with more or less of the alkaline earth hydroxide that has been converted by contact with the air to alkaline earth carbonate.

Somewhat more generally when a coating according to this invention is applied, the resulting coating is such that, upon application of moisture (pure water) the normal color of the dyestuff will be restored, the pH of the coating when moistened with pure water not being greater than the pH at or below which the decolorized dyestuff in the coating develops color upon moistening the coating with pure water. While reference is made to the aforesaid pH value, it may be mentioned that the transition point at which the color of the dyestuff fails to develop, either due to excessive alkalinity in the coating or due to application of relatively strong alkaline solution to the coating, is not sharp but as aforesaid may, in the case of sodium salt of dibenzyldiethyldiaminotriphenylcarbinol disulphonic acid anhydride, vary from about 8 to 8.5. Moreover, this value may vary depending upon the proportion of dyestuff to alkaline earth hydroxide in the coating and upon the employment of a relatively large amount of the dyestuff, both of which tend to increase the upper limit of pH value at which visible restoration of color of the dyestuff is effected.

In order to provide a coating that develops color change regardless of the pH of the aqueous material applied thereto, the indicator substance that is also incorporated in the coating should at the pH of the coating be of a color that contrasts with the developed color of the dyestuff, that is, should be of a color that is different from the color of the dyestuff after the color of the dyestuff has been redeveloped by application of moisture to the coating containing it. The indicator substance should also be adapted to develop pronounced color upon raising the pH of its environment and the pH value of the turning point at which this color change takes place (while being greater than the pH of the coating, when moistened with pure water) preferably should not be

substantially above the maximum pH at which the dyestuff in said coating will redevelop color when said coating is moistened with a solution having a pH that is higher than the pH of said coating upon said coating being moistened with pure water. While it is satisfactory in many cases that such an indicator substance should have a turning point anywhere in the pH range above the pH of the coating when the coating is moistened with pure water, the most complete protection is afforded when the turning point of the indicator substance is not at a higher pH (not above about 8 where the dyestuff is sodium salt of dibenzyldiethyldiamino-triphenylcarbinol disulphonic acid anhydride, for example) where the decolorized dyestuff fails to develop color upon application of a liquid having a higher pH than the pH of the coating when the coating is moistened with pure water so that all aqueous reagents having a pH below this point will develop the color of the dyestuff and all aqueous reagents having a pH above this point will cause the indicator substance to develop a pronounced color change in the coating.

Any substance which is adapted to change color upon changing the pH of its environment is referred to herein, for the sake of brevity, as an acid-alkali indicator substance, and many such substances are familiar. Examples of indicator substances other than phenolphthalein are P-cresol phthalein and M-nitro-phenol. The last-named indicator substance, unlike phenolphthalein, is not colorless in the coating, but imparts a slight yellowish color to the coating. However, this color is not inconsistent with the detection of developed color of the dyestuff, and this last-named indicator substance therefore is illustrative of the use of an indicator substance that is normally colored in the coating.

More generally, when reference is made to the indicator substance, or filler, or binder, or the coating as a whole being of contrasting color as compared with the developed color of the dyestuff, it is meant that, upon development of the color of the dyestuff, the developed color will be readily ascertainable by inspection of the coating. However, coatings that are white or nearly white or are of light color are normally preferable, a light color being regarded as one of less color depth than the developed color of the dyestuff.

Any dyestuff that has been decolorized by alkaline earth hydroxide and applied in a coating, the color of the dyestuff being restorable by application of moisture, may, of course, be employed according to this invention.

When reference is made herein and in the claims to the application of the decolorized dyestuff and other components of a coating composition as a coating, the coating may be in the form of a superficial layer that is essentially continuous. However, if the coating composition is applied to a porous, absorptive cardboard, for example, the coating composition will act more as a coating for the individual fibers than as a coating for the sheet as a whole; but in this case also the applied material is to be regarded as a coating, and it is apparent that it will behave in the same way, as far as color development is concerned, that it will behave when applied as a superficial layer. However, use of any such porous absorptive material is ordinarily undesirable, and for application to paper and cardboard it is usually preferable to utilize paper or cardboard of the nature of ordinary good grade book paper which has a relatively smooth surface and relatively low absorbency. Where protection against use of "invisible" ink is desired, it is ordinarily desirable to apply to both sides of sheet material the special moisture-sensitive coating composition. When reference is made herein and in the claims to paper, it is to be understood that the word "paper" is used in a broad sense and includes cardboard and other fibrous sheets of paper or paperlike nature.

In the manufacture of articles, e. g., paper, carrying the moisture-sensitive coating composition, considerable care has to be exercised to prevent contact of moisture with the coating composition after it has been applied and dried, and use of rubber gloves by workmen may be desirable. Moreover, the product should be well wrapped so as to exclude it from conditions of excessive humidity or other accidental moistening. The product of this invention may, however, be stored and used much as ordinary paper, for example, is used; but, due to its unique properties of moisture-sensitivity, has many special uses and advantages including those specifically mentioned hereinabove.

While this invention has been described in connection with certain specific examples of the practice thereof, it is to be understood that this has been done merely for purposes of illustration and of affording a better understanding of this invention, and that the scope of this invention is to be determined by the language of the following claims.

I claim:

1. An article comprising a base having thereon a moisture-sensitive coating, said coating comprising a diamino-triphenylmethane dyestuff decolorized by alkaline-earth hydroxide, the color of said dyestuff being restorable upon application of pure water to said coating.

2. An article comprising a base having thereon a moisture-sensitive coating according to claim 1 wherein said dyestuff is sodium salt of dibenzyldiethyldiamino - triphenylcarbinol disulphonic acid anhydride.

3. An article comprising a base having thereon a moisture-sensitive coating according to claim 1 wherein said dyestuff is sodium salt of dibenzyldiethyldiamino-o'-chloro - triphenylcarbinol disulphonic acid anhydride.

4. An article comprising a base having thereon a moisture-sensitive coating according to claim 1 wherein said dyestuff is sodium salt of dibenzyldimethyldiamino - triphenylcarbinol trisulphonic acid anhydride.

5. An article comprising a base having thereon a moisture-sensitive coating, said coating comprising a diamino-triphenyimethane dyestuff decolorized by alkaline-earth hydroxide, finely-divided solid water-insoluble filler material, and a binder that bonds said filler material to said article as a coating, the color of said dyestuff being restorable upon moistening said coating with pure water to produce a color contrasting with the color of said coating.

6. Paper sensitive to moisture, said paper carrying diamino-triphenylmethane dyestuff decolorized by alkaline-earth hydroxide, the color of said dyestuff being restorable upon application of pure water to said paper.

7. Paper sensitive to moisture, said paper being coated with a coating comprising finely-divided solid water-insoluble filler and a binder that bonds said filler to said paper as a coating suitable for the inscription of a legend thereon, said coating

containing diamino-triphenylmethane dyestuff decolorized by alkaline-earth hydroxide, the color of said dyestuff being restorable upon application of pure water to said coating, and the ratio of binder to solids on said coating being about 1.25 to 4 parts of binder for each 10 parts of solids by weight and said coating being applied at the rate of at least about two pounds per hundred square feet.

8. An article comprising a base having thereon a moisture-sensitive coating, said coating comprising diamino-triphenylmethane dyestuff decolorized by alkaline earth hydroxide, the pH of the coating, when moistened with pure water, being a pH at which said dyestuff redevelops color upon said coating being moistened with pure water, and said coating also comprising an acid-alkali indicator substance which at the pH of the coating when the coating is moistened with pure water is of a color contrasting with the developed color of the dyestuff and which has a turning point whereat upon changing the pH of its environment said indicator substance develops color change, said turning point being at a pH which is greater than the pH of said coating when said coating is moistened with pure water.

9. An article comprising a base having thereon a moisture-sensitive coating according to claim 8, said coating having as a base a finely-divided solid water-insoluble filler material and a binder, the ratio of binder to solids in said coating being about 1.25 to 4 parts by weight of binder for each 10 parts by weight of solids.

10. Paper sensitive to moisture, said paper carrying a coating comprising a diamino-triphenylmethane dyestuff decolorized by alkaline earth hydroxide, the color of said dyestuff being restorable upon application of pure water to said coating, and said coating also comprising phenolphthalein.

11. Paper sensitive to moisture according to claim 10 wherein said dyestuff is sodium salt of dibenzyldiethyldiamino-triphenylcarbinol disulphonic acid anhydride.

12. Paper sensitive to moisture according to claim 10 wherein said dyestuff is sodium salt of dibenzyldiethyldiamino - o' - chloro - triphenylcarbinol disulphonic acid anhydride.

13. Paper sensitive to moisture according to claim 10 wherein said dyestuff is sodium salt of dibenzyldimethyldiamino-triphenylcarbinol trisulphonic acid anhydride.

14. Paper carryying a moisture-sensitive coating, said coating comprising diamino-triphenylmethane dyestuff decolorized by alkaline-earth hydroxide, the color of said dyestuff being restorable upon application of pure water to said coating, said coating containing as a base a finely-divided solid water-insoluble filler material and a binder, the ratio of binder to solids in said coating being about 1.25 to 4 parts by weight of binder for each 10 parts by weight of solids, and said coating comprising an acid-alkali indicator substance which at the pH of the coating when the coating is moistened with pure water is of a color contrasting with the developed color of the dyestuff and which has a turning point whereat upon changing the pH of its environment said indicator substance develops color change, said turning point being at a pH which is greater than the pH of said coating when said coating is moistened with pure water and which is not above the maximum pH at which the dyestuff contained in said coating will redevelop color when said coating is moistened with a solution having a pH that is higher than the pH of said coating upon moistening said coating with pure water.

15. Paper carrying a coating sensitive to moisture, said coating comprising an acidic diamino-triphenylmethane dyestuff decolorized by alkaline-earth hydroxide, the color of said dye being restorable by application to said coating of aqueous material having any pH which is at or below about 8, and said coating containing a finely-divided water-insoluble solid filler and a binder, and also containing an acid-alkali indicator substance which at the pH of said coating when said coating is moistened with pure water is of a color contrasting with the color of said dyestuff and which is adapted to develop color change upon application of aqueous material to said coating having a pH at or above about 8, thereby providing a paper wherein the coating develops color change regardless of the pH of aqueous material applied thereto.

16. A method of making a moisture sensitive coating which comprises forming an aqueous mixture containing a diamino-triphenylmethane dyestuff and an alkaline-earth hydroxide, the amount by weight of alkaline-earth hydroxide being about 1 to about 5 times the amount by weight of dyestuff, thereby decolorizing the dyestuff, applying the aqueous mixture to the surface to be coated and drying the coating thereby producing a coating wherein the color of said dyestuff is decolorized and wherein the color of said dyestuff is restorable upon application of pure water to said coating.

17. A method according to claim 16 wherein said coating contains as a base finely-divided solid water-insoluble filler and a binder, the binder constituting about 1.25 to 5 parts by weight for each 10 parts by weight of solids in said coating.

FRANCIS L. SIMONS.

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2,250,980	Workman et al.	July 29, 1941