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WATER-DETECTING PAPER AND A WATER-DETECTING COATING COMPOSITION THEREFOR

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The invention described herein may be manufactured and used by or for the Government of the United States for governmental purposes without the payment to us of any royalty thereon in accordance with the provisions of the act of April 30, 1928 (Ch. 460, 45 Stat. L. 467).

This invention relates to the detection of water and it particularly relates to the exposure and detection of invisible writing which has been done with aqueous invisible inks.

Prisoners of war are generally accorded the privilege of writing letters to their homes. Advantage is often taken of this privilege to smuggle vital defense information out of the country by means of invisible writing on stationery containing permitted correspondence. To nullify this practice, it is necessary for censoring authorities to examine all such correspondence for invisible or secret writing before forwarding it to the addressee. However, under the rules of the Geneva Convention, the correspondence cannot be mutilated in the course of the examination. Many invisible inks are known which are undetectable by the ordinary non-destructive detecting means; such as angular light, ultraviolet light, and heat treatment. Many such inks depend on an aqueous diluent or carrier in order to apply the invisible ink. These inks are varied in chemical characteristics, some are acidic, some are alkaline, some are oxidizing agents, and some are reducing agents; a few simple examples are: citric acid, tartaric acid, milk, sodium carbonate, sodium bicarbonate, trisodium phosphate, sodium sesquisilicate, sodium hydroxide, sodium hypochlorite, sodium peroxide, sodium hyposulfite, sodium hydrosulfite, hydrazine sulfate and the like. Various methods of overcoming this problem, such as microfilming and photostating, are unsatisfactory because of the cost involved, the time delay, and the complexity.

Accordingly, it is an object of this invention to provide a means of quickly, easily, and cheaply detecting invisible writing done with aqueous inks. It is another object of the invention to provide a water detecting means. Other objects and advantages will be apparent or will appear hereinafter.

These objects are accomplished in accordance with this invention wherein a suitable base material has deposited thereon or impregnated therein a film of a coating composition adapted to detect the presence of water thereon comprising an organic dyestuff which is relatively colorless in thin layers but which develops strong coloration in contact with moisture, having incorporated therewith a dispersing agent, a viscosity controlling resin which forms non-brittle substantially water permeable films, and an organic mutual solvent for said dispersing agent and said resin and said solvent to be incapable of substantially developing the tinctorial characteristics of said dyestuff.

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The invention accordingly comprises the means for detecting invisible writing.

The selection of a suitable dyestuff imposes numerous problems of chemical stability and solubility. Because of the varied nature of the secret inks the dye must not be susceptible to the action of dilute acids, alkalis, oxidants, reducing agents, and the like, either in the dehydrated or hydrated state. While there are many dyes that will meet these conditions, the additional conditions imposed by other components of the formula, such as the necessity of complete insolubility of the dyestuff in the grinding medium and diluent to preclude premature development of the tinctorial characteristic, makes the selection of a dyestuff difficult. Suitable dyestuffs for purposes of this invention include chemical dyestuffs which are neutral or light tincture when anhydrous and which on dissolution or dehydration develop a high tinctorial strength. Suitable dyestuffs for purposes of the invention include the diammonium salt of dibenzyldiethyldiaminotriphenylcarbinol trisulfonic acid otherwise known as Lithasol Brilliant Blue E, Patent Carmine Blue, Erioglaucine, or Acid Brilliant Blue (Color Index No. 671); sodium salts of dimethoxy-diphenyl-disazo-bis-8-amino - 1 naphthol 5:7 disulfonic acid and sodium salts of dimethoxydiphenyl-disazo-bis-8-amino-1 naphthol 3:6 disulfonic acid otherwise known as Direct Sky Blue, Pontamine Sky Blue, or Niagara Sky Blue (Color Index Nos. 518 and 520), and Xylene Cyanol (Color Index No. 715) or the sodium salt of meta hydroxydiethyldiaminophenylditolylcarbonyl disulfonic acid anhydride. Lithasol Brilliant Blue E is presently preferred because of its solubility in water, its insolubility in many organic solvents, its good grinding properties, and its resistance to discoloration as used in this invention.

Suitable base materials for purposes of this invention include: absorbent and fibrous materials such as diatomaceous earth, wood, cloth, and various types of paper and like cellulose sheet materials, such as coated and uncoated papers including book paper; ground wood and sulfite writing and bond paper; rag and sulfite manifold, bond, ledger, and index papers having weights

from about 15 to 90 pounds per 1000 sheets of 17 by 22-inch stock. A preferred member is an uncoated writing paper having a neutral or white shade; this type is presently preferred because of its special adaptability for writing purposes.

To prepare a paper which will immediately expose attempts to write thereon with aqueous invisible inks, the selected dyestuff is compounded with a grinding medium or vehicle in which the dyestuff is insoluble. The dye is then ground in the vehicle to such a degree of fineness that it will remain substantially dispersed in the selected diluent. The exact nature of this procedure will be evident from the ensuing description. Suitable grinding media or vehicles include drying oils such as: linseed oil, boiled linseed oil, China-wood oil, perilla oil, and treated linseed oils, such as the "Lithographic Varnishes" (which are described in Protective and Decorative Coatings, by Joseph J. Mattiello, volume III, pages 620–625, 1943 edition). The preferred vehicle is "No. 3 Lithographic Varnish" and since it has been found to possess optimum qualities as a grinding medium for the type of dyestuff we are using, it is an economical drying oil and minimizes plasticizing of other components of the formula on evaporation. Satisfactory compounding was accomplished using approximately equal quantities of dye and vehicle and passing the blend through a roll type paint or ink mill until a major portion of the dye was ground to sizes finer than 0.5 micron; and in order to minimize settling of the dispersion it is desirable that all dye particles be of colloidal dimensions. Using Lithasol Brilliant Blue E and No. 3 Lithographic Varnish in proportions of about 40 to 60 parts of the dye to about 60 to 40 parts of the dispersing agent, a sufficient degree of fineness was attained after about 8 passes through a 3-roll ink mill.

Thereafter, the vehicle was dissolved and the dye thereby suspended in a non-aqueous diluent that will not develop the color of the dye. Numerous volatile organic fluids can be used for this purpose; for example, alkylketones, ethers, alkyl esters of acetic and formic acids, nitroparaffines, and the like, either with or without a viscosity controlling agent which, after evaporation of the diluent, will act as a bonding agent for the dye and which will form a non-brittle substantially water permeable film. Suitable viscosity controlling agents for this purpose include soluble cellulose plastics or compounds of the class consisting of cellulose lower alkyl ethers and cellulose lower alkanoates such as cellulose acetate, ethyl cellulose, and the like, or soluble resins such as polyvinyl acetate. The preferred diluent is a solution of ethyl cellulose in ethyl acetate in ratios of about one part by weight of about 100 to 300 centipoise viscosity ethyl cellulose to about 45 parts by weight of ethyl acetate. This mixture is preferred for numerous reasons; the most important of which is the fact that in using this formula it is found that the ethyl cellulose protects a treated paper from reaction to humidity and handling, and when applied in very thin films it is sufficiently permeable to the water of aqueous invisible inks to permit hydration of the dyestuff before the water evaporates. Other factors of importance in the selection of the diluent include consideration of its effects on equipment being used to apply the composition to the paper; because of the negligible effect of ethyl acetate on the rubber or synthetic rubber rolls of presses its use is preferred.

The composition so prepared is then applied to both sides of the paper by suitable means; a convenient way is to pass the paper on which the compound is to be deposited through an aniline or rotogravure press and thereby apply the composition as one would apply thin film of printing ink to cover the entire surface. Printing, if desired, can be accomplished by the press at the same time.

The following example shows how the invention may be carried out, but it is not limited thereto. Parts are by weight unless specifically noted to the contrary.

Example

Substance:	Parts
Lithasol Brilliant Blue E	9
No. 3 lithographic varnish	9
Ethyl cellulose (200 centipoise viscosity)	225
Ethyl acetate	9,595

The dye and varnish vehicle were mixed and passed through a 3-roll ink mill eight times in the same manner as one would prepare a printing ink; and the ethyl cellulose was dissolved in the ethyl acetate. Thereafter, the compounded dye and vehicle were mixed with the ethyl cellulose-ethyl acetate solution using sufficient agitation to uniformly disperse the compounded dye in the diluent. The dispersion was then applied in thin films to the surfaces of stationery stock by an aniline press. This formula, while thin enough to be ideal as an aniline press ink, has sufficient viscosity to keep the finely ground dye particles in suspension for a long period of time.

A neutral shade of coated or uncoated paper stock when treated with this composition gives an essentially white sheet with high sensitivity to liquids containing water, and attempts to mark thereon with any aqueous invisible or secret ink will immediately appear as a bright blue reproduction of what is being inscribed. Writing with a visible ink will not feather or be distorted and will be as legible as that on untreated paper. The sensitized paper is relatively stable to humidity, and handling, and is unaffected by light.

As shown in the foregoing description and example, a water detecting composition can readily be prepared from certain dyestuffs, such as Lithasol Brilliant Blue E, and which, when applied to paper stock, will render said paper highly sensitive to aqueous inks and will immediately deter any attempts to communicate thereon with aqueous secret inks by rendering such attempts visible.

While the invention particularly described is a composition suitable by application by means of an aniline press, it is not limited thereto, and variations can be made in the diluent to permit application by other means.

While the invention as particularly described is a composition suitable for application to paper stock, it is not limited thereto, modifications of the vehicle and diluent can easily be made to permit its application on other absorbent or non-absorbent surfaces, or its absorption by or impregnation in other materials.

While the invention as particularly described uses dyestuffs having neutral or light tinctures when anhydrous, it is not limited thereto if it is to be applied to colored base materials; in such instances the dyestuff can be the color of the base material when anhydrous.

Since many widely differing embodiments of the invention will occur to one skilled in the art,

the invention is not limited to the specific details illustrated and described, and various changes can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. A coating composition adapted to detect the presence of water thereon consisting of an organic dyestuff which is relatively colorless in thin layers but which develops strong coloration in contact with moisture, having incorporated therewith a drying oil, a cellulose plastic of the class consisting of cellulose lower alkyl ethers and cellulose lower alkanoates, and an organic mutual solvent for said drying oil and said plastic, said solvent being incapable of substantially developing the tinctorial characteristics of said dyestuff.

2. A water-detecting composition of matter consisting of essentially from about 40 to 60 parts by weight of Lithasol Brilliant Blue E uniformly blended with about 60 to 40 parts by weight of a drying oil and said blended dye dispersed in an organic solvent for said drying oil, said solvent being incapable of substantially developing the tinctorial characteristics of said dyestuff.

3. A water-detecting composition of matter consisting of from about 40 to 60 parts by weight of Lithasol Brilliant Blue E uniformly blended with about 60 to 40 parts by weight of a drying oil and said blended dye dispersed in a volatile organic solvent for said drying oil, said solvent being incapable of substantially developing the tinctorial characteristics of said dyestuff, and said solvent containing a cellulose plastic of the class consisting of cellulose lower alkyl ethers and cellulose lower alkanoates.

4. A water-detecting composition of matter consisting of finely divided Lithasol Brilliant Blue E uniformly blended with an approximately equal amount of No. 3 Lithographic Varnish and said blend dispersed in a solution of ethyl cellulose and ethyl acetate.

5. A water-detecting composition of matter consisting of about 9 parts of finely divided Lithasol Brilliant Blue E intimately admixed with about 9 parts of No. 3 Lithographic Varnish and said admixture suspended in a solution of about 225 parts of 200 centipoise viscosity ethyl cellulose in about 9,595 parts of ethyl acetate.

6. As a new article of manufacture; a base material having deposited thereon a thin film of an organic dyestuff which is relatively colorless in thin layers but which develops strong coloration in contact with moisture having incorporated therewith a drying oil, a cellulose plastic of the class consisting of cellulose lower alkyl ethers and cellulose lower alkanoates, said films having been deposited from an organic mutual solvent for said drying oil and said cellulose plastic, and wherein said dye was suspended.

7. A substantially colorless coating composition which consists essentially of a finely divided dyestuff which develops strong coloration when in solution; a drying oil in which said dye is insoluble; and a volatile diluent in which said dyestuff is dispersed and insoluble and said drying oil is soluble, said diluent having sufficient viscosity to keep the dye substantially in suspension and being incapable of substantially developing the tinctorial characteristic of said dyestuff.

8. A substantially colorless coating composition which consists of a finely divided dyestuff which develops a strong coloration when in solution; a drying oil in which said dyestuff is insoluble; a volatile diluent in which said dyestuff is dispersed and insoluble and said drying oil is soluble; and a film forming viscosity controlling agent selected from the group of cellulose plastics consisting of cellulose lower alkyl ethers and cellulose lower alkanoates which are soluble in said diluent.

9. An article of manufacture: stationery which will expose attempts to write thereon with invisible inks and which will be substantially unaffected by humidity, which comprises sheet paper stock coated with a composition which is substantially colorless in thin layers, and which consists of a finely divided dyestuff which develops a strong coloration when in solution; a drying oil in which said dyestuff is insoluble; a volatile diluent in which said dyestuff is dispersed and insoluble and said drying oil is soluble; and a film forming viscosity controlling agent selected from the group of cellulose plastics consisting of lower cellulose alkyl ethers and cellulose lower alkanoates which are soluble in said diluent.

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