Patented Jan. 23, 1951 2,538,784

UNITED STATES PATENT OFFICE

2,538,784

PROCESS FOR IDENTIFYING NORMALLY INVISIBLE MARKINGS AND COMPOSITION THEREFOR

Morris S. Kantrowitz and Earl J. Gosnell,
Washington, D. C.

No Drawing. Application April 12, 1946,
Serial No. 661,641

2 Claims. (Cl. 250—71)

(Granted under the act of March 3, 1883, as amended April 30, 1928; 370 O. G. 757)

1

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 identifiable paper having a normally invisible writing or design thereon, to processes for preparing such paper and to developing compositions for rendering the said writings or designs visible. Heretofore, identifiable papers have been prepared by incorporating chemicals into the papers, which can later be treated to yield a characteristic identification in the paper. Also, the so-called secret inks have previously been known, which inks could be rendered visible by chemical treatment or were visible under ultra-violet radiation without any chemical treatment. However, insofar as is known, there has never been produced an invisible writing or design on paper or other sheet material prior to this invention which was not identifiable under ultra-violet light, not developable by chemical treatment, but which could be rendered visible under ultra-violet light by chemical treatment.

Accordingly, this invention has for an object the production of identifiable paper having a normally invisible writing or design thereon not initially identifiable under ultra-violet illumination, but can, by chemical treatment, be made to yield a writing or design which becomes visible when exposed to a source of illumination comprising substantially all ultra-violet radiation. Another object is to produce an identifiable paper in which a normally invisible writing or design is imprinted thereon in such small quantities that the identifying agent cannot be detected by ordinary analysis. Another object is to provide an identifying agent for printing or writing on paper which is normally present in the paper in such large quantities that its presence is masked or obscured. Further objects are to provide a process and reagents for developing or detecting identifiable papers.

The foregoing and other objects hereinafter apparent are accomplished in accordance with this invention wherein there is provided an identifiable paper having a normally invisible writing or design thereon, said writing comprising a soluble compound of a metal selected from Group II, Periods 1–5, of Mendeleeff's Periodic Arrangement of the Elements, said soluble metal compound preferably being present in an amount insufficient for detection by ordinary chemical analysis. This invention also provides a developing composition for rendering the invisible writing or design visible under ultra-violet light, such composition comprising an alkaline solution of 8-hydroxyquinoline dissolved in a polar organic solvent. In another feature, this invention provides a process for identifying paper having such a normally invisible writing or design thereon, by treating such paper with the above developing composition and then exposing the thus-treated paper to ultra-violet light, whereby said normally invisible writing or design fluoresces and becomes visible under ultra-violet illumination but remains invisible under ordinary light.

2

Any ordinary papers can be made indentifiable in accordance with this invention; such as for example, bond paper, sulfite paper, so-called rag papers, cardboard, kraft paper, and similar papers. If desired, fibrous sheet material generally can also be employed provided the surface of such material is capable of taking ink.

Suitable compounds for writing or printing upon the paper to render it identifiable in accordance with this invention include soluble compounds of the metals selected from Group II, Periods 1–5, of Mendeleeff's Periodic Arrangement of the Elements, such as soluble compounds of beryllium, magnesium, calcium, strontium, barium, zinc, and cadmium. Generally, the soluble salts of the foregoing metals with inorganic acids are convenient for employment in accordance with this invention, such as for example, salts of the foregoing metals with such acids as sulfuric, nitric, and preferably hydrochloric acids, although a soluble salt of the foregoing metals with organic acids such as formic, acetic, propionic, glycolic, citric, tartaric and similar organic acids can as well be employed. Preferably, magnesium salts are employed, since very small quantities of the magnesium compound are required, and since extremely large amounts of magnesium compounds normally occur in paper and paper products due to the large amounts of clay filler material normally incorporated in the paper. The large amounts of normally-occurring magnesium compounds thus completely mask the presence of any slight additional amounts employed in the invisible inks of this invention, while at the same time do not interfere with the identification of the invisible inks when carried out in accordance with this invention.

Generally speaking, the invisible writing or design is printed or otherwise impressed upon the paper to be identified by application with an ordinary hand swab, aniline-type printing press or other suitable device designed to apply a very

dilute solution of the selected metal compound to the surface or outer fibers of the paper. It has been found that an ink made up of approximately 50 percent aqueous alcoholic solvent and containing from 0.01 percent to 2.4 percent by weight of the selected metal compound, calculated as the metal, provides a suitable viscosity and concentration. Preferably, the ink contains from 0.05 to 0.5 percent by weight of the selected metal, suitably magnesium, calculated as metal. It will be apparent that the foregoing very small amounts of a selected metal in the entire ink composition will yield a finished identifiable paper containing only minute traces of the selected metal at spaced portions in the outer fibers of the paper being marked for identification. Obviously, the selected metal salt should be colorless, and to this end it is preferred to employ magnesium chloride. In a typical instance, only 5 pounds of ink containing about 0.6 percent by weight of magnesium in the form of magnesium chloride, was applied as a design to a surface of 100 pounds of paper being marked. The total quantity of added magnesium was thus almost infinitesimal based on the weight of paper, and was wholly insufficient for detection by analysis, even when the paper contained no normally-occurring magnesium compounds in the filler employed. However, substantially all papers normally employed in the art contained very large quantities of magnesium compounds as above indicated, mostly occurred in the form of magnesium silicates in the clays used as filler material. It has been found that the uniform distribution of the normally-occurring magnesium compounds in the paper does not interfere in any way with the detection of the identifying design or writing of this invention.

For detecting the presence of a design, writing and the like impressed upon paper employing an ink made up of the metal compounds above specified in accordance with this invention, the surface of the paper undergoing treatment is treated with an alkaline solution of 8-hydroxyquinoline dissolved in a polar organic solvent. 8-hydroxyquinoline is a very peculiar chemical compound since in dilute alkaline solution of this invention it reacts with a compound of one of the above specified metals such as magnesium, to yield a compound which is normally colorless and completely invisible on paper treated as above described, but which is capable of fluorescence upon exposure to a source of ultra-violet radiation. A suitable developing solution contains from 1 to 10 percent by weight of 8-hydroxyquinoline, and preferably from 3 to 5 percent of 8-hydroxyquinoline. A more concentrated solution is unnecessary and may stain the paper, while a more dilute solution requires a larger amount of magnesium for detection.

A polar organic solvent is preferably employed for dissolving the selected alkaline and the 8-hydroxyquinoline, since it yields a permanent identification, produces a sharp fluorescent image, readily evaporates, and partakes sufficiently of the character of water to develop quickly the identifying latent image.

Suitable polar organic solvents for employment in accordance with this invention comprise ethyl acetate, methyl acetate, methyl alcohol, ethylene glycol, the ethyl and methyl mono-ethers of ethylene glycol, methyl alcohol, nitromethane, dioxane, and similar polar organic solvents. Preferably, methyl alcohol is employed as the polar organic solvent, since it has a relatively

high volatility to yield a rapid evaporation of developer, but at the same time has a sufficiently high polarity to develop a clear latent image exhibiting sharp contrast under ultra-violet illumination. It has been found that the polarity of the selected solvent should be balanced against its volatility to give the best results, that is to say, a highly volatile solvent may be less polar and vice versa.

Any suitable alkaline agent may be employed in the developing composition, such as for example, the hydroxides of sodium, potassium, and ammonium. However, it is preferred to employ organic aminoalcohol of moderate alkalinity, and of the aminoalcohols it is preferred to employ ethylmonoethanolamine. Generally, from 1 to 15 per cent by weight of alkaline agent, and preferably from 4 to 8 percent thereof by weight, is incorporated in the developing composition. When employing ethylmonoethanolamine as the preferred alkaline agent, it has been found that the developing solution possesses great stability over a long period of time, yields an image capable of ultra-violet fluorescence for an indefinite time after being developed, is non-corrosive to the operator, and appears to cooperate to stabilize the 8-hydroxyquinoline in solution.

After the magnesium salt, or other metal compound yielding a normally invisible writing or design on paper, has been treated with the above-described developing composition, it is still invisible to the naked eye under ordinary daylight or artificial illumination. However, upon exposure to a source of principally ultra-violet radiation, preferably one having the major portion of its radiation filtered or screened to wave lengths between 3200 and 3800 angstrom units, preferably while excluding visible light, the latently developed image exhibits a brilliant greenish-yellow fluorescence. If ordinary writing has been applied to the paper employing magnesium chloride ink or other compound as above described, the writing is easily legible under such a fluorescent light source. Where it is desired to identify the paper without regard to superimposed written matter, a previously applied printed identifying design can readily be identified and thus the origin of the paper is susceptible of determination.

In the operation of this invention, ordinary paper stock, suitably in rolls, is passed through an ordinary aniline-type printing press. The aniline-type printing press is fed with an aqueous alcoholic solution of magnesium chloride or other suitable metal salt as above described in the dilute solution above mentioned, and a characteristic design is printed on the paper at spaced intervals. The paper is then rolled up and may be employed for bank checks, confidential documents, or any other use where it is desirable to identify the source of the paper. Thereupon, whenever it is desirable to determine the origin of a particular sample of paper as to whether or not it came from the treated batch, it is then swabbed with cotton or other sorbent material dipped in the developer prepared as above described, and the developer is allowed to evaporate and dry. No visible image appears at this stage of the identification, and thus anyone who should accidentally come in possession of the developer solution would not be able to detect the secret writing or design on the paper. However, the next step is to expose the thus-treated paper to a suitable source of ultra-violet illumination. (Examples of suitable ultra-violet

radiation sources which may be satisfactorily employed are the low intensity "Purple-X" lamps, manufactured by the General Electric Company, which are hot filament lamps enclosed in a bulb of heat-resistant nickel oxide glass, and the high intensity, high pressure, analytic quartz mercury arc lamp made by the Hanovia Chemical and Manufacturing Company.) Obviously, for the best results, the exposure to ultra-violet light should be carried out in a darkened room, or other precautions taken to exclude ordinary light. Upon exposure, a brilliantly fluorescent image becomes visible and the characteristic design or writing appears in great brilliance. When again restored to ordinary light, no image is visible to the eye.

The following illustrative examples show how the invention may be carried out, but it is not restricted thereto:

Example I

A sheet of sulfite paper was written upon with a solution made by dissolving 17 grams of magnesium chloride hexahydrate in 100 cubic centimeters of 30 percent aqueous ethanol. The sheet was dried and the writing thereupon became invisible both under daylight and ultra-violet light.

A developing solution was next made up of the following ingredients:

(*a*) 2.5 grams of 8-hydroxyquinoline dissolved in 50 cubic centimeters of 95 percent ethanol.

(*b*) 2.0 grams of KOH dissolved in 50 cubic centimeters of water to which 5 cubic centimeters U. S. P. glycerine was added.

Solution (*a*) was then mixed with solution (*b*).

The invisible writing on the paper sample was swabbed with the developer solution. No perceptible change in color was noticed under daylight or tungsten illumination. However, on illumination by a General Electric "Purple-X" ultra-violet light in a dark room, the writing was clearly legible as a greenish-yellow fluorescence.

Example II

Sheets of (1) rag bond, (2) sulfite bond, and (3) kraft papers were printed and written upon with inks made by dissolving in separate portions of 30 percent aqueous ethanol, sufficient $ZnCl_2$, $CdCl_2$, $Zn(NH_3)_4(OH)_2$ and

$$Cd(NH_3)_4(OH)_2$$

to make 2 percent solutions, based on metal content.

The colorless writing and printing was dried, then treated with a developing solution made by dissolving 4.0 grams of 8-hydroxyquinoline and 7.0 grams of ethylmonoethanolamine in 100 cubic centimeters of methanol. No visible change took place in the writing when viewed by daylight or tungsten-filament Mazda light, but upon exposure to ultra-violet light from a Hanovia analytic mercury arc lamp in a darkened room, brilliantly-fluorescent images as written or printed, were made visible.

It will be apparent from the foregoing that there has been provided an extremely useful means for identifying paper or other fibrous material capable of being printed or written upon. There has also been provided a secret ink of very simple composition, preferably dilute magnesium chloride solution, which can be made visible only by a combination of developing techniques. The composition for developing the paper is extremely stable, simple, and easy to prepare. The paper marked in accordance with this invention can readily be developed by unskilled operators without delay, and when once developed, the resulting paper can be identified for an indefinite length of time under ultra-violet light. The ink employed for producing the normally invisible writing or design is employed in such small amounts that it completely defies detection by ordinary chemical analysis and is further masked by impurities occurring in the paper.

Various changes can be made in the invention as illustrated and described without departing from the spirit and scope thereof since many apparently different embodiments will occur to one skilled in the art.

What is claimed is:

1. A process for identifying paper having a normally invisible writing or design thereon, said writing or design comprising a soluble magnesium salt in an amount sufficient to yield a substantial local surface concentration of magnesium salt but insufficient to influence substantially the total magnesium content of said paper, which comprises treating such paper with a developing solution containing from 1 to 10 percent by weight of 8-hydroxyquinoline, from 1 to 15 percent by weight of ethylmonoethanolamine, the balance of the solution being substantially all methanol, whereby the writing or design remains invisible but becomes capable of fluorescence upon exposure to ultraviolet radiation, and then exposing the thus-treated paper to ultraviolet radiation having a wave length between 3200 and 3800 angstrom units, whereby said writing or design is rendered visible during exposure.

2. A reagent composition for developing an ultraviolet light-fluorescent image on paper having a normally invisible writing or design thereon, said writing or design comprising a soluble magnesium salt in an amount sufficient to yield a substantial local surface concentration of magnesium salt but insufficient to influence substantially the total magnesium content of said paper, which comprises a methanol solution containing by weight from 3 to 5 percent of 8-hydroxyquinoline, and from 4 to 8 percent of ethylmonoethanolamine.

MORRIS S. KANTROWITZ.
EARL J. GOSNELL.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
283,322	Brown	Aug. 14, 1883
1,778,397	Maier et al.	Oct. 14, 1930
1,990,994	Lum	Feb. 12, 1935
2,073,381	Sell	Mar. 9, 1937
2,255,696	Clifford	Sept. 9, 1941
2,315,111	Ehrlich	Mar. 30, 1943
2,377,382	Slack	June 5, 1945
2,407,381	Pecher	Sept. 10, 1946