Dec. 7, 1943. J. RUSSELL 2,336,299

SENSITIVE MATERIAL

Filed April 25, 1940

FIG. 1

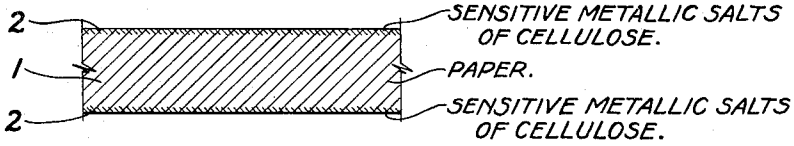
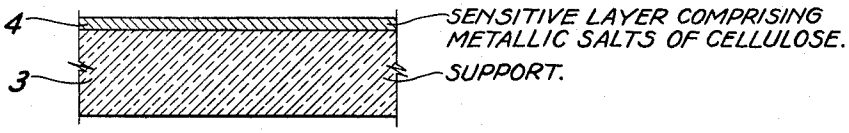


FIG. 2



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SENSITIVE MATERIAL

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4 Claims. (Cl. 95—7)

This invention relates to a new photographically sensitive material. I have found that it is possible to form, preferably in the surface of paper of the quality ordinarily used for photographic purposes, metallic salts of the cellulose of the fibers of the paper, which salts are sensitive to light, heat or electrical stimuli and capable of having photographic images formed and developed therein. In particular I have found that mercury and silver salts give the best results but that bismuth, iron, uranium, copper, lead, thallium and other metal salts give positive results. When I speak of the paper as "photographically sensitive," I use the expression in a broad sense to include responsiveness, not only to light radiations, but to chemical and electrical stimuli whereby a visible image may be made or reproduced.

The resulting sensitive paper may be used in various ways. In particular it is useful in industrial recorders of the type where a heated stylus is brought into contact with the paper, in place of an inked pen or pointer.

The preparation of the paper is ordinarily carried out in two steps: first, submitting it to an oxidizing bath or to an oxidizing atmosphere, and then to a solution of a metal salt wherein the carboxyl takes up the metallic ion and forms the sensitive salt.

Various examples of methods of forming the sensitive surfaces will first be given and then the properties and methods of treatment of these surfaces will be described.

The paper is bathed at room temperature in a solution of equal parts of concentrated sulfuric acid and of water saturated with potassium dichromate, for a period of time of the order of 30 to 60 seconds. It is then washed, until free from sulfate and dried. The paper at this stage is heat sensitive and a legible mark will be produced upon it by a stylus heated to a temperature of from 250° to 300° C. passing over it at a speed of from .1 to 1.5 millimeters per second, the image being a pale brown. Oxidation for an even shorter time, say 10 seconds, will produce a heat sensitivity that is readily detectable.

The paper may also be treated in an oxidizing atmosphere, or cellulose fibers may be oxidized in the manner described in the patent of Edwin C. Yackel and William O. Kenyon, No. 2,232,990, granted February 25, 1941, and then coated as a layer upon a sheet of paper or other material. As explained in that patent, the product resulting from oxidizing the cellulose with NO_2 is a combined uronic acid resulting from the oxidation of the hydroxyl on the primary carbon atoms of the anhydroglucose units to carboxyl, or in other words, the final product is an anhydroglucuronic acid. When this material is combined with heavy metal, as specified herein, a salt which is sensitive to heat or light is obtained. Moreover, the oxidized fibers could be treated before coating with a metallic salt solution, as hereinafter described, so that the layer is sensitive when formed on the paper support.

The paper with an oxidized surface layer is then bathed in a metallic salt solution, such as silver or mercurous acetate aqueous solution of less than 1 per cent concentration for a period of time which is not at all critical and may vary widely, for instance from a half minute to over thirty minutes. It is then washed and dried. The resulting paper is much more sensitive and will show a legible mark from a stylus at a temperature at 300° C. moving at a speed of 8 to 10 mm. per second. The second bath is given under dark-room conditions, a filter absorbing only blue and violet light being used.

Referring to the accompanying drawing, Fig. 1 shows an enlarged section of a sheet of paper 1, the surfaces 2 of which have been treated in the manner described to form in the superficial fibers sensitive metallic salts of carboxylic groups produced on the cellulose, and Fig. 2 shows a similar section of a support 3; such as paper, upon one surface of which has been formed by coating a layer 4 of metallic salts of cellulose.

Other salt solutions than those mentioned may be used, in each case the solution being one per cent, or saturated if the solubility is less than 1 per cent, some of the solutions giving useful results being mercuric nitrate, mercurous nitrate, silver nitrate, ammonium metavanadate, ammonium molybdate, ferric nitrate. The mercury and silver salts gave outstandingly good results. Other solutions giving legible marks only at a very slow speed, were bismuth acetate, bismuth nitrate, cobaltous acetate, cuprous chloride, cupric acetate, ferric acetate, lead acetate, lead nitrate, manganous acetate, thallous acetate, uranium acetate, uranium nitrate.

The papers made as above described were also tested for their printing out properties when exposed to a Cooper Hewitt quartz mercury vapor arc operaitng at a potential drop of 150 volts across its terminals and those containing mercury or silver gave strong images in less than one minute exposure at a distance of 30 cm. from such an arc while those containing bismuth, iron

or uranium yielded a faint image after a ten minute exposure.

Some of the papers also were found to have a photothermographic property, that is the property of yielding a visible image when heated following exposure to light. In those containing mercury, this was particularly noticeable, while it was less in those containing bismuth, copper, lead or thallium.

It was also found that the papers containing mercury or silver were capable of having images chemically developed therein, following exposure to light, in a 2 per cent hydroquinone solution containing 1 per cent acetic acid, or in an M. Q. developer.

The paper should be of high quality purified cellulose, but I have found that results vary widely between different papers, so that any data here given are to be taken as typical and illustrative of results found in actual experiments with certain samples of paper.

What I claim is:

1. A product sensitive to heat and/or light essentially consisting of a paper sheet surfaced with a salt of anhydroglucuronic acid and a metal selected from the group consisting of mercury, silver, vanadium, molybdenum, iron, bismuth, cobalt, copper, lead, manganese, thallium, and uranium.

2. A photographically sensitive product comprising a sheet composed of cellulose fibers, at least one surface of said sheet having thereon a photosensitive material essentially consisting of metallic salts of cellulose carboxylic groups, said groups having been produced on superficial fibers of said sheet by oxidation thereof and being capable of having a visual image formed thereon by the action of heat, light, or electrical stimulant.

3. A photographic product comprising a sheet composed of cellulose fibers, one surface of said sheet having thereon a photosensitive material essentially consisting of silver salts of cellulose carboxylic groups, said groups having been produced on the superficial fibers of said sheet by oxidation thereon.

4. A photographic product comprising a sheet composed of cellulose fibers, one surface of said sheet having thereon a photosensitive material essentially consisting of mercury salts of cellulose carboxylic groups, said groups having been produced on the superficial fibers of said sheet by oxidation thereon.

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