Patented June 30, 1942 2,288,147

UNITED STATES PATENT OFFICE

2,288,147

SAFETY PAPER

Burgess W. Smith, Rochester, N. Y., assignor to The Todd Company, Inc., Rochester, N. Y., a corporation of New York

No Drawing. Application March 12, 1941, Serial No. 383,030

9 Claims. (Cl. 117—1)

This invention relates to safety paper and it comprises a safety paper having incorporated therein small amounts of the leuco form of a triphenylmethane dye so that upon the application of a potassium permanganate ink eradicator, a colored triphenylmethane dye is developed; it further comprises safety paper containing such leuco triphenylmethane dyes, together with a color-forming compound which develops color upon the application of hypochlorite solutions thereto.

Safety paper for making bank checks, drafts, bonds, or other documents is composed of a paper base impregnated with chemicals which develop a conspicuous stain or color upon the application of chemical ink eradicators. In one form such chemicals are applied to the paper by printing so that the word "void," for example, flashes up in color when chemical ink eradicators are applied. For a long time the art has desired to broaden the scope of the response of such papers to ink eradicators. The most common eradicafor is a solution of hypochlorite of soda preceded or followed by a solution of an organic acid, such as tartaric or oxalic. There are various chemicals which respond to this particular ink eradicator by developing a conspicuous stain or color. But most of the color-forming substances used in a safety paper are not entirely satisfactory when ink eradicators of the permanganate type are employed. A dilute solution of potassium permanganate may cause these substances to develop color but when the permanganate solution is followed by a reducing agent, such as bisulfite of soda, the color is discharged.

Consequently, the art has sought ways of preparing safety paper which would be responsive to sodium hypochlorite solutions in the presence of acid and additionally would be responsive to potassium permanganate solutions followed by sodium bisulfite. By chemicals responsive to such solutions I mean, of course, chemicals which develop conspicuous stain or color. It is not always necessary that the chemical as applied to the paper be colorless. Chemicals which have a slight color can be used with tinted or patterned papers which obscure the color of the impregnated color. But in any event, the chemical impregnant should develop a conspicuous color upon the application of these eradicators.

It has been particularly difficult to find chemical substances which can be used as an indicator when potassium permanganate eradicators are employed for obliterating writing on the paper. The color-forming substances must develop a conspicuous stain and the stain must be resistant to the action of bisulfite solutions or other reducing agents.

I have now discovered a class of chemical substances which solve the problem of finding a suitable color-forming material reactive with potassium permanganate. This class of chemical substances can be broadly defined as the leuco form of the triphenylmethane dyes. Most of these leuco dyes are colorless and develop color upon the application of oxidizing agents, such as potassium permanganate. The color thus formed is resistant to bleaching by the application of sodium bisulfite. Moreover, these leuco derivatives of triphenylmethane dyes develop color upon the application of sodium hypochlorite solutions. Many of the colored compounds thus formed are not bleached entirely or completely by the application of additional quantities of sodium hypochlorite. Where these colored compounds are markedly bleached by sodium hypochlorite I overcome the disadvantage by also impregnating the paper with color-forming chemical substances which are suitable for use with sodium hypochlorite ink eradicators. Benzidine and many of its derivatives, for example, develop a conspicuous stain upon the application of a hypochlorite under acid conditions and this stain is resistant to any attempt to remove it by the application of more sodium hypochlorite.

Thus the present invention embraces first the preparation of a safety paper containing the leuco derivative of a triphenylmethane dye and second a safety paper containing a leuco derivative of a triphenylmethane dye, together with other color-forming chemicals which are responsive to hypochlorite solutions.

Prior art patents have disclosed many hypochlorite-responsive, color-forming compounds which can be used. Benzidine itself is entirely satisfactory and various substituted benzidines, such as the sulfate, have been described. Instead of benzidine I can use a diphenol since it is also reactive with hypochlorite solutions to form relatively permanent stains. Consequently, in the appended claims I have referred to "color-forming chemicals reactive with sodium hypochlorite solutions" for the purpose of generically describing this class of compounds. This language embraces substances ilke benzidine, benzidine sulfate, diphenols, benzothiazole, and benzidine derivatives having substituents in the 3,3' positions. The latter benzidine derivatives are more specifically described and claimed in my co-pending application, Serial No. 358,523 filed September 26, 1940.

A large number of the leuco derivatives of the triphenylmethane dyes have been used in the practice of my invention. Among them are: Leuco of Patent Blue A, of Kalle, Color Index No. 714, Shultz No. 545, m-hydroxy-dibenzylethyldiamino-triphenylmethane, condensation product of m-hydroxy-benzaldehyde and benzylethyl-ani-

line, Leuco of Chrome Violet paste of Bayer, Color Index No. 718, Shultz No. 549, tetramethylamino-p-hydroxytriphenylmethane-m'-carboxylic acid, condensation of tetramethyldiaminobenzhydrol and salicylic acid, Leuco of Aco Green paste of Bayer, Color Index 675, Shultz No. 510, formed by coupling salicylic acid with diazotized tetramethyldiamino-m'-aminotriphenylmethane, and the leuco of tetraethyl-4,4'-Diamino-1'' Sulfotriphenylmethane. One of the most satisfactory dyes is the leuco of that made by condensing paradiethyl amino-benzaldehyde with ethyl benzyl metatoluidine sulfonic acid. Many of these triphenylmethane dyes are condensation products between an aromatic aldehyde and an aromatic amine. They all contain the "triphenylmethane" nucleus. The leuco forms of these dyes are generally colorless materials. A few of the leuco derivatives of the triphenylmethane dyes are not highly resistant to oxidation and may develop slight color in the presence of air or light. This tendency to slight coloration is not objectionable if the paper is tinted to match the color which might develop due to this mild form of oxidation. Upon the application of strong oxidation agents, such as a solution of permanganate then, of course, the full coloration of the colored form of the dye appears. This tendency to mild oxidation can be overcome by special ways of coating and impregnating the paper base as I shall presently describe.

It would serve no useful purpose for me to describe the leuco derivatives of all the triphenylmethane dyes which can be used in the practice of my invention. I have indicated a representative number of them and it will be obvious to those skilled in the art that many others can be used in substitution for those specifically described. Although I find that the leuco derivative of the triphenylmethane dye made from the ethyl benzyl metatoluidine sulfonic acid and the amino benzaldehyde is particularly efficient, I do not wish to be limited thereto. However, I have discovered that the presence of sulfonic acid groups in the triphenylmethane dye tends to stabilize the leuco form of the dye against any minor oxidation phenomena which might occur in paper impregnated therewith.

The amount of the leuco dye and the color-forming substance responsive to hypochlorites incorporated in the paper can be varied over wide limits. A relatively small amount of these color-forming substances will develop conspicuous stains upon the application of ink eradicators. As little as one-tenth of one percent based on the weight of the paper is enough.

The leuco dye can be introduced in the beater as the mill, or in a subsequent operation as the pulp is formed into paper, or by any suitable method of impregnating or coating. For example, a 1% solution or suspension of the leuco dye in the size applied to the paper can be used for impregnating the paper in the usual way. When the paper is dried the application of permanganate ink eradicators thereto develops a permanent, conspicuous stain which is not discharged by sodium bisulfite. To paper which has been sized or impregnated with a solution or suspension of the leuco dye stuff I can then apply a surface coating of benzidine sulfate dispersed in a 3% solution of cellulose acetate in dimethyl phthalate or other suitable vehicle. I lay no claim to any particular vehicle for the application of the benzidine sulfate. Instead of impregnating or coating the paper in the manner stated the paper can be printed with warning indicia using inks containing the leuco dye and inks containing the benzidine compound. Thus, for example, I can print the paper with the word "void" using an ink vehicle containing any one of the leuco forms of the triphenylmethane dyes and then print the paper with inks containing benzidine sulfate or other color-forming chemicals responsive to hypochlorites.

Wetting agents can be added to the impregnating solution containing the leuco dye stuff so that the leuco dye is caused to penetrate throughout the safety paper. 1% of any of the well known wetting agents added to aqueous suspensions of the leuco derivative will materially aid in securing thorough impregnation of the paper base with this chemical. This expedient prevents any mild oxidation of the leuco dye to a faintly tinted color since the dye is deposited within the fiber structure of the paper and not as a simple surface layer.

Although I have more specifically described incorporating both the leuco dyes and the hypochlorite-responsive agents in the paper I do not wish to be limited to using both of these constituents. The benzidine or other chemical used for ensuring hypochlorite response can be omitted. These leuco dyes in many cases give a satisfactory response to hypochlorites, and I am the first to have discovered their utility as indicators when permanganate-bisulfite eradicators are used.

In general, however, the application of the color-forming compounds herein disclosed to the paper base is no different from that hitherto used in this art. The application of amines or phenols responsive to hypochlorite ink eradicators is well known. The leuco dyes herein described are applied in the same way.

Having thus described my invention, what I claim is:

1. A safety paper containing a leuco derivative of a triphenylmethane dye.

2. A safety paper containing a leuco derivative of a triphenylmethane dye containing sulfonic acid groups.

3. A safety paper containing the leuco derivative of the condensation product of ethyl benzyl-metatoluidine sulfonic acid and para diethyl amino benzaldehyde.

4. Safety paper containing a leuco derivative of a triphenylmethane dye and a color-forming chemical responsive to the action of hypochlorite solutions to form a color.

5. A safety paper containing a leuco derivative of a triphenylmethane dye containing sulfonic acid groups and a color-forming chemical responsive to hypochlorite solutions to form a color.

6. Safety paper containing a leuco derivative of the condensation product of ethyl benzylmetatoluidine sulfonic acid and paradiethylamino benzaldehyde and a color-forming chemical reactive with hypochlorites to form a color.

7. A safety paper as in claim 4 wherein the hypochlorite-responsive, color-forming compound contains a diphenyl linkage.

8. The safety paper as in claim 5 wherein the hypochlorite-responsive, color-forming compound contains a diphenyl linkage.

9. The safety paper as in claim 6 wherein the hypochlorite-responsive, color-forming compound contains a diphenyl linkage.

BURGESS W. SMITH.