

UNITED STATES PATENT OFFICE

WILLIAM N. DOUSHKES, OF EASTON, PENNSYLVANIA, ASSIGNOR, BY MESNE ASSIGNMENTS, TO MILTON C. JOHNSON COMPANY, OF NEW YORK, N. Y., A CORPORATION OF NEW YORK

SAFETY PAPER

No Drawing.

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This invention relates to safety papers and more particularly those of the type which are adapted to prevent fraudulent changes on checks, drafts, etc., by the application of materials such as eradicators.

There have been many suggestions along these lines in the prior art in which various types of compounds have been utilized and which upon the application of oxidizing agents such as those employed in ink eradicators lead to color changes developed, due to the oxidation of materials incorporated in the paper. However, many of the prior art suggestions have not proved practical due to the fact that in some instances the compositions suggested are not sensitive enough to the various agents that may be used in obliterating the writing on such paper, while in other cases the materials suggested have been so sensitive as to undergo substantial color change due to the action of air and light.

One of the objects of this invention is the preparation of a safety paper containing materials which undergo color changes upon the application of ink eradicators and analogous materials.

A further object of this invention is the preparation of a safety paper containing substances adapted to produce a color change upon appropriate treatment with chemical reagents, and also containing a substance which is adapted to protect the first named materials against premature oxidation and/or changes in color due to the action of air and/or light.

Further objects and advantages will appear from the more detailed disclosure set forth below, it being understood, however, that various changes may be made therein by those skilled in the art without departing from the scope and spirit of this invention.

Among the compounds which may be used in the practice of the present invention in order to disclose color changes on paper made

in accordance with this invention, the most important are the leuco compounds of indamines, or the leuco compounds of indophenols. These substances when incorporated with or applied to the paper produce a very desirable color change when bleaching or oxidizing agents are applied to the paper, which immediately exhibits any attempt that has been made to obliterate any writing or other characters on the paper. The indamines and indophenols constitute a class of great importance for the purposes of inventions of this character. In utilizing them they may be adapted one of two ways: first, the leuco indamine or leuco indophenol may be incorporated into the paper pulp or into the paper itself. In the second place, these chemicals may be used as a coating upon the completed paper.

While the leuco indo-compounds referred to above and made from indamines or indophenols are particularly desirable in inventions of this character, leuco compounds may also be prepared from many other materials and utilized in a similar manner. For example, certain aromatic amines and related compounds have been used in the making of safety papers. They have been open to a number of objections. In accordance with the present invention instead of using such amines or related analogous materials, these may first be oxidized to form the colored compounds and the resulting oxidized colored material may then be reduced back to form a leuco compound which may then be utilized in preparing the safety paper. It is thus seen that this phase of the invention has particularly broad application in connection with safety papers.

The invention is further concerned with the reduction of the sensitivity of such safety papers or the materials used in making such safety papers to the action of light and air. As pointed out above, there has been frequent difficulty in connection with safety

papers due to the fact that there has been a tendency evidenced by such papers to show color changes upon standing due to the action of light and air or either of those agents, especially when water solutions of these chemicals are used as a coating or bath for the paper. The invention disclosed in this application is also concerned therefore with the reduction of such sensitivity. It has been found that the incorporation or additional application of metallic sulphates to the paper when a white safety paper is desired, or the inclusion of metallic sulphates in the aniline dyes if a colored safety paper is desired, will satisfactorily retard the sensitivity of the material so that while it is not effected by light and air upon standing, it is still sensitive enough to show the desired color changes when an attempt is made to obliterate writing from such papers by the use of ink eradicators and analogous materials. Of the various metallic sulphates which will serve for this purpose, manganous sulphate is particularly desirable and will be considered in more detail below in connection with examples illustrating this invention. But while the examples given below are concerned specifically with the use of such metallic sulphates in connection with compositions containing leuco indamine or leuco indophenol compounds, it should be noted that the use of such metallic sulphates is not limited to these particular types of compounds but may be utilized broadly in connection with the various compositions that have heretofore been suggested in the art for the preparation of safety papers, since such metallic sulphates and particularly manganous sulphate exercise this retarding of sensitivity in connection with the various materials that have heretofore been used in the art for making of safety papers. The use of a coating or a bath of manganous sulphate as the case may be, or of any analogous and substantially colorless metallic sulphate to prevent premature oxidation, is of course exceedingly advantageous in the art. The manganous sulphate and analogous materials partly precipitate the chemicals in the paper, particularly when an aqueous solution of such color producing compounds has been used, and this precipitation in turn tends to prevent premature oxidation. The metallic sulphates also form a non-oxidizing coating on the paper in so far as air and light effect the materials normally used in the preparation of such papers.

The substance utilized in connection with the present invention for incorporation or coating of paper in order to form satisfactory safety papers, may be a product obtained by the oxidation of two amines to form an indamine or a product obtained by the oxidation of one amine and a member of the

phenol or naphthol group to form an indophenol. And the subsequent reduction of the above forms indamine or indophenol to their respective leuco compounds, which would be known in the order of the above descriptions as a leuco indamine or a leuco indophenol. These leuco compounds may then be introduced into the paper pulp utilized for manufacturing the safety paper, or the leuco compounds may be applied to a paper which has already been made, more or less as a coating or bath therefor.

Preferably the paper is first impregnated with or mixed in the pulp stage with the indamine or indophenol leuco compound, or a water solution of the chemical is used as a bath for the paper and then the paper is dried or partially dried and is again run thru a bath of manganous sulphate. These materials all being soluble can be utilized in aqueous solution which is, of course, a cheaper method of use than in connection with insoluble compounds which may be and must be applied in other ways. The paper can be passed through or into a bath containing the materials stated above for the purpose of saturating such materials with the compound contained in the solution. Or, if desired, the paper may be passed through a bath of the character just described for the purpose of impressing warning indicia thereon. The metallic sulphate and particularly manganous sulphate set forth above, when used as a subsequent or second coating or bath for the paper, serves to prevent premature oxidation of the color forming compound.

While as pointed out above, it is sometimes desirable and more economical to use materials which are soluble in water in making up the compositions which contain amines, indamines or indophenols, such materials may be utilized in the form of insoluble salts and particularly when they are to be introduced into the paper during the pulp stage of the latter, or when they are to be formed into a colorless ink such as is used for printing invisible warning indicia on paper. The particular manner in which these materials are applied to the paper is not of great importance except in particular instances where certain preconceived results are desired. But in general, the desired compounds may be applied to the paper either by introducing the desired materials whether soluble or insoluble into the pulp material from which the paper is to be made, or by applying the color forming materials to the paper after the same has been formed into the paper web, or by printing with the leuco indamine or the leuco indophenol invisible warning indicia or other design on the paper.

In using the leuco compounds, a ten per cent solution thereof has proven satisfactory. In the use of the metallic sulphate, the paper

may, for example, be run through a solution containing five pounds of metallic sulphate to twenty gallons of water.

Not only may the leuco compound be utilized as set forth above, for incorporation into the paper or as a coating therefor, but these chemicals may be used as inks for printing substantially invisible protective indicia or designs on the paper.

It is also possible within the purview of this invention to prepare the leuco compounds within the paper itself whether in sheet or pulp form. For example, the mixture of amines or of amines and phenols may be applied to or incorporated into the paper, then oxidized to the corresponding indamine or indophenol, and finally reduced back to the leuco derivative. The leuco derivative will thus be formed in situ within the paper whether in sheet or pulp form.

Having thus set forth my invention, I claim:

1. A safety paper containing a leuco indamine compound.
2. A safety paper having a leuco indamine applied thereto.
3. A safety paper containing a leuco indamine compound and a protecting metallic sulphate.
4. A safety paper carrying a leuco indamine and manganous sulphate.
5. A safety paper made from paper pulp containing a leuco indamine compound and subsequently treated with manganous sulphate.
6. A safety paper made from paper pulp containing a leuco indamine material, said paper carrying a coating of manganous sulphate.
7. A safety paper containing chemical compounds capable upon treatment with chemical agents of being converted into a compound of the indamine indophenol group.
8. A safety paper containing chemical compounds capable upon treatment with appropriate chemical agents of being converted into a compound of the indamine indophenol group, and a protecting metallic sulphate to protect said compound against the action of light and air.
9. A safety paper carrying a coating containing indamine producing substances and manganous sulphate.
10. In a process of making safety paper, the step of incorporating into the paper pulp a composition containing chemical substances capable upon treatment with appropriate chemical agents of being converted into a compound of the indamine indophenol group.
11. In a process of making safety paper, the step of adding to the paper a leuco indamine material and a protecting metallic sulphate.

12. In a process of making safety paper, the step of coating paper with a composition containing a mixture of amines capable upon treatment with appropriate chemical agents of being converted into a compound of the indamine type.

13. A substantially colorless ink containing a leuco indamine compound.

14. A safety paper having protective indicia thereon, such indicia being printed with an ink containing a leuco indamine compound.

Signed at Easton, Pennsylvania, this 21st day of February, 1928.

WILLIAM N. DOUSHKESS.

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