Patented Nov. 4, 1924.

1,514,222

UNITED STATES PATENT OFFICE.

WALLACE J. MURRAY, OF BOSTON, MASSACHUSETTS, ASSIGNOR, BY MESNE ASSIGNMENTS, TO TODD PROTECTOGRAPH COMPANY, INC., OF ROCHESTER, NEW YORK, A CORPORATION OF NEW YORK.

METHOD OF PRINTING DOCUMENTS.

No Drawing. Application filed April 7, 1922. Serial No. 550,477.

To all whom it may concern:

Be it known that I, WALLACE J. MURRAY, a citizen of the United States, residing at Boston, in the county of Suffolk and State of Massachusetts, have invented certain new and useful Improvements in Methods of Printing Documents; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

The present invention relates to a method of printing permanent records in such a manner as to prevent mechanical or chemical erasure.

As described in certain of my pending applications, Serial Nos. 476,310 and 550,476, the alteration of written or printed documents may be avoided by initially treating the paper before printing with a substance which will react with the ink and form an insoluble compound in and on the paper, or by impregnating the paper with a normally invisible substance which will react with the materials employed for eradicating the ink to form a colored compound in the paper. Both of these methods of protecting written or printed documents against alteration are practical and represent marked improvements over methods heretofore in vogue. The present invention contemplates a method of forming an insoluble colored compound in and on the body of the paper when the latter is written upon or printed. According to the broadest conception of the invention, two different inks are employed for printing or writing which are capable of chemically reacting to produce permanent colors. The document may be printed with the two different inks simultaneously, or the inks may be applied successively. Furthermore, both inks may be printed upon the same side of the paper or one ink may be applied to each side of the paper. The best results are probably obtained by printing the opposite sides of the paper simultaneously with two different inks, which react chemically to form an insoluble colored compound within the body of the paper. It will be evident to those skilled in the art that this method of forming the desired insoluble substance in the body of the paper permits the use of the ordinary sized paper employed for checks and other documents, avoiding the necessity of employing a specially prepared and pre-treated paper for this purpose. Furthermore, the different inks or reagents which combine chemically to form the colored compounds are applied to the paper in the form of printed characters, making it unnecessary to completely impregnate the paper with either of the reagents.

The printing of the paper with the proper inks may be accomplished by any desired form of printing mechanism, such as the mechanism now in commercial use for printing simultaneously the opposite sides of a check.

One method of producing the desired insoluble colored substances in the paper is through the medium of the diazo reaction. According to this method a primary aromatic amine such as dianisidine, a soluble inorganic nitrite such as potassium nitrite, an organic acid such as lactic acid, and a developer which may be an aromatic amine or phenol are brought together. The division of these reagents between the two inks employed for printing the paper should be such that the nitrite and acid are contained in different inks. When the paper is printed with two separate inks containing these reagents, a permanent stable colored compound is produced in the following manner. The acid first reacts with the nitrite to give free nitrous acid. This nitrous acid then reacts with the amine to give a diazonium compound and finally the diazonium compound reacts with the developer to produce the insoluble azo color. The following will serve as a specific and typical example of a method of printing paper according to my new method: The paper to be printed, which may be of any usual character, is fed between two inked rolls, one or both of which are equipped with type on their faces. The ink used in connection with one roll consists of a solution of beta-naphthol and potassium nitrite in glycerine. The ink employed in connection with the other roll consists of a solution of dianisidine and beta-naphthol in lactic acid. These two inks when applied to opposite sides of the paper by the rolls penetrate and mix

in the body of the paper itself, producing fast azo colors. An excess of beta-naphthol produces a blue color and an excess of dianisidine produces a red color. It has been found that the blue color produced by an excess of beta-naphthol is faster and more permanent than the red color produced by an excess of dianisidine. For this reason it is preferred to employ an excess of beta-naphthol. The color produced by this method of printing is located within the body of the paper itself and is therefore proof against mechanical erasure without entirely destroying the paper. In addition the color is not acted upon by chemical reagents and is insoluble so that it cannot be eradicated or obliterated by treatment of the paper with chemicals.

An insoluble compound may also be produced in the body of the paper according to my new method by the employment of the oxidation process of producing colors. According to this method, one ink consists of a solution of a small amount of paraphenylenediamine in aniline. The second ink consists of an oxidizing solution such as ammonium persulphate in water. If these inks are applied to opposite sides of the paper the first ink will penetrate the sized paper readily and react with the oxidizing solution applied to the opposite side of the paper. Although the water solution will not penetrate the sized paper, the deposit of aniline black produced by the reaction of these inks is formed entirely through the body of the paper. The employment of inks which react to produce oxidation colors will form the desired type of colored compound in the paper but the reaction which takes place proceeds much more slowly than in the case of the azo colors.

I claim:

1. A method of producing permanent records which consists in printing paper with different inks containing respectively a nitrite and a developer in a solvent capable of penetrating the paper, and an amine and an acid, the inks chemically reacting within the paper to form an azo color.

2. A method of producing permanent records which consists in printing paper with different inks containing an amine, a nitrite, an acid and a developer, the acid and nitrite being contained in different inks, and the two inks reacting chemically within the paper to produce a colored compound.

3. A method of producing permanent records which consists in printing paper with different inks containing reagents which combine to form an insoluble azo color within the body of the paper.

4. A method of producing permanent records which consists in printing paper with inks containing an amine, a nitrite, an acid and an excess of developer to produce an insoluble color within the body of the paper when the inks react.

5. A method of producing permanent records which consists in printing paper with an ink consisting of a solution of beta-naphthol and potassium nitrite in glycerine, and an ink consisting of a soltuion of dianisidine and beta-naphthol in lactic acid, the two inks reacting chemically within the body of the paper to produce a fast azo color.

WALLACE J. MURRAY.