Patented June 21, 1932

1,864,116

UNITED STATES PATENT OFFICE

VIKTOR BAUSCH, OF BERLIN, AND ADOLF SCHROTH, OF MECKLENBURG-SCHWERIN, GERMANY, ASSIGNORS TO THE CORPORATION FELIX SCHOELLER & BAUSCH, OF NEU-KALISS/MECKLENBURG, GERMANY

PRODUCTION OF PAPERS FOR SECURITY PURPOSES

No Drawing. Application filed October 3, 1931, Serial No. 566,806, and in Germany October 7, 1930.

The present invention relates to chemically treated paper for use in security documents which are required to resist or to indicate attempt at forgery of the documents by chemical or other action.

It is the principal object of the invention to provide a security paper giving the maximum of security against forgery. Further objects will appear from the following specification of the invention.

It is known to provide security papers with reagents sensitive to oxidizing agents. Such reagents, whose object is to indicate attempts to eradicate or bleach out written characters with the aid of oxidizing agents, may be either of an organic or inorganic character. Among inorganic reagents may be mentioned colorless or but slightly colored manganous compounds which are changed to colored manganic compounds or other dioxide compounds by oxidation.

The colored compounds so formed in security papers due to the action of oxidizing agents are however easily restored to their colorless condition by reducing agents such as hydrosulfite or bisulfite. This is particularly the case if the oxidizing agent used is not one of the strongly acting hypochlorites but, for example, the less powerful potassium permanganate such as is now frequently used in various ink-eradicating preparations.

If however benzol- or naphthalene-carboxylic acids, particularly polyvalent oxybenzoic and oxynaphthoic acids, are introduced into the security papers, either alone or in addition to the inorganic reagents which are responsive to oxidizing agents, the color stain produced in the paper by oxidizing agents is either not removable at all or only with great difficulty by means of reducing agents.

The dioxy- and trioxy-benzoic acids and their derivatives and compounds in particular give color reactions even with weak oxidizing agents, which it is scarcely possible to reverse or bleach out even by the use of the most powerful reducing agents. It is probably the case that the attempt to reduce an oxidized polyoxybenzoic acid or one of its derivatives whose oxidized product is colored, results only in a condensation giving also a colored product, perhaps of the type of a phenol-formaldehyde condensate.

Proposals have been made to use upon security papers either pyrogallic acid or gallic acid, but the object in that case was to make an invisible imprint upon the paper which, upon treatment of this paper with an oxidizing bleaching agent, would become visible in a brown coloring. The protection effected by such a printing with invisible inks on the paper is however of very questionable value because the imprint or deposit is in a thin surface film which can easily be washed off or removed. In fact the forger generally effects this washing out of the security imprinting without realizing or intending it, during the preliminary treatment of the document with dilute organic acids or potassium binoxalate solution, which normally precedes any chemical treatment for bleaching out the visible writing, and is provided for in the usual ink-eradicating preparations sold commercially.

In order to insure that gallic acid or a polyoxybenzoic acid or a derivative of such acid shall exert an effective protecting action as first described above, it is essential that the reacting substance should be applied not as a thin layer on the surface of the paper as by an imprinting operation, but that it should be thoroughly incorporated into the paper substance, that is to say the paper mass must be completely intermingled with the protective reagent. If this were not done the forger, who usually experiments first with small sections of the document to be falsified in order to detect any protecting medium, could always take steps to remove the imprinted reagent by erasure for example with a rubber eraser.

Although a security paper containing polyoxybenzonic acid or the like does not react with acids, it provides an almost complete protection against partial chemical falsification or erasure. Such a security paper is much better as a security medium than the so called security papers on the market. The protection is not quite complete however against chemical falsification. Besides a re-

action giving a color stain with oxidizing agents as used for erasure or bleaching purposes a protection against the use of even weak organic acids is desirable. This is the case because prolonged treatment of the ink writing with dilute oxalic acid or acid salts of oxalic acid for example will remove ink writing. The reaction of a good security paper to acids should be so sensitive that even weak organic acids such as citric acid if applied to the paper will produce a readily detectable color stain. The sensitizing of the paper to such acids may be effected in a known manner by treatment of the paper material with oxy-salts of iron and ferrocyanides insoluble in water but soluble in acids, such for example as lead ferrocyanide.

At first it seems quite impossible to render a paper, which is made sensitive to acids as above described, also sensitive to oxides by introducing at the same time for example a polyoxybenzoic acid because this starts the acid reaction of the paper, although only slowly, due to the weakly acid character of the organic acids used. If for example a paper is taken which has been prepared with oxy-salts of iron and lead ferrocyanide or other ferrocyanide which is only soluble in acids, this paper will normally turn blue in the presence of weak acids owing to the formation of Berlin blue therein, but unfortunately gallic acid also causes the paper which was at first white to turn blue after a time, so that it then fails to show a change of color when treated with weak acids.

The use of neutral derivatives of the polyoxybenzoic acids, such for example as pentagalloyl glucoses, would avoid the production of the acid reaction in the paper, but in a nearly neutral medium and especially in the slightly alkaline medium when exposed to air, the well known brown coloration due to these compounds would appear. This follows because in preparing security papers which are very sensitive to acids, it is preferable to work with neutral or generally weakly alkaline consistency of the paper mass.

The successful application of the present invention is based upon the fortunate discovery that the brown colorattion of the polyoxybenzoic acid or its derivatives does not arise if the hydrogen ion concentration of the surrounding medium (the paper mass in this case) does not exceed a pH value of at the most 4.5 to 5. On the other hand, the acid reaction of the polyoxybenzoic acid may be lowered by the addition of alkali down to a pH value of about 3.0 without the brown coloration due to the alkali reaction taking place.

The acid reaction of the paper takes place only if the pH value is reduced below 3 or thereabouts.

The following example will illustrate the manner of applying the invention:

A paper is prepared treated with ferric oxide salts such as acetate of iron, and then with a suitable ferrocyanide soluble in acids, such as lead ferrocyanide, with the use of a paper material having a pH value kept down to 4. A solution of equal parts of pyrogallolcarboxylic acid and pentagalloyl glucose, reduced to a pH value of 3 to 3.5 by addition of alkali, is introduced and the paper is further treated and finished in the usual manner. The resultant paper will be sensitive also to oxidizing reagents, with the production of a color stain in each case, which cannot be removed by reducing reagents as for instance bisulfite.

We claim:

1. A security paper containing in the paper mass a carboxylic hydrocarbon and a reagent sensitive to acids as regards its color.

2. A security paper containing in the paper mass an oxyacid derivative of a base of the benzene ring type.

3. A security paper containing in the paper mass an oxyacid derivative of a base of the napthalene ring type.

4. A security paper containing in the paper mass a carboxylic hydrocarbon, the mass having a pH value between 3 and 5 before incorporation of the carboxylic hydrocarbon.

5. A security paper the body of which has a pH value between 3 and 5, with which is incorporated a carboxylic hydrocarbon and a reagent color-sensitive to weak acids.

6. A security paper and mass of which has a pH value between 3 and 5, and incorporating a polyoxybenzoic acid compound.

7. Process of making a security paper wherein a paper mass is at first brought to a pH value between 3 and 5 and with which thereafter is incorporated a carboxylic hydrocarbon compound.

8. Process of making a security paper wherein a paper mass is at first brought to a pH value between 3 and 5 and with which thereafter is incorporated an oxyacid derivative of a base of the benzene ring type.

9. Process of making a security paper wherein a paper mass is at first brought to a pH value between 3 and 5 and with which thereafter is incorporated an oxyacid derivative of a base of the napthalene ring type.

10. Process of making a security paper wherein a paper mass is at first brought to a pH value between 3 and 5 with which thereafter is incorporated a solution of a carboxylic hydrocarbon having a pH value approximating 3.

11. Process of making a security paper wherein a paper mass is at first brought to a pH value between 3 and 5 with which thereafter is incorporated a solution of an oxyacid derivative of a base of the benzene ring type.

12. Process of making a security paper

wherein a paper mass is at first brought to a pH value between 3 and 5 with which thereafter is incorporated a solution of an oxyacid derivative of a base of the napthalene ring type.

13. Process of making a security paper wherein a paper mass is at first brought to a pH value between 3 and 5 with which thereafter is incorporated a solution containing pyrogallol-carboxylic acid and pentagalloyl glucose whose pH value is kept in the neighbourhood of 3 by addition of alkali.

In testimony whereof we have affixed our signatures.

VIKTOR BAUSCH.
AD. SCHROTH.