Patented June 25, 1946 2,402,542

# UNITED STATES PATENT OFFICE

2,402,542

## COATED PAPER AND METHOD OF MAKING SAME

Chauncey P. Foote, Jr., Yonkers, and Clifford D. Guertin, St. George, Staten Island, N. Y., assignors to American Bank Note Company, New York, N. Y., a corporation of New York

No Drawing. Application April 22, 1943, Serial No. 484,126

15 Claims. (Cl. 117—1)

1

This invention relates generally to the manufacture of paper for use in preparing codes, military orders and other documents which are to be preserved in secrecy and which should, in an emergency, be destroyed to prevent their falling into the hands of enemies or others who are not entitled to information which may be written or printed on the pages.

Codes and secret documents of various kinds used in the foreign and military services are now printed or written on various kinds of paper, and in case of an emergency about the only way of destroying them now known is to burn them. However, it is difficult to completely destroy such papers by burning, and burning is, at best, a slow operation. In addition, escaping smoke from the burning has, in the past, been taken as disclosing the fact that records were being destroyed when it was highly desirable to keep the information secret.

One object of the invention is to produce a paper for the purpose indicated which is so constructed that the coating and any matter printed or written thereon may be destroyed in a very short time by simply submerging or dipping the paper in water. The paper and the coating are so constituted that water permeates almost instantly and causes a chemical reaction by which gas is developed in large volume and in the form of bubbles to loosen the coating from the paper while at the same time the development of bubbles in the material of the coating destroys the coating. Matter printed or written on the coating is obliterated and destroyed to such an extent that nothing remains which will give any information about what appeared on the coating before it was destroyed.

Another object is to provide a paper of the kind indicated which will preserve matter written or printed on it until an emergency arises, that is, a paper which will not deteriorate or lose its effectiveness while in storage or after it has been used.

Still another object is to provide a method of making the coated paper indicated which can readily be applied to paper by the use of apparatus such as are now in common use.

Still another object is to provide a coating material which will accomplish the results desired in an effective manner and which can be applied at a comparatively low cost.

With the foregoing and other objects in view which will become apparent later on, the invention consists in a novel coating and method of applying it to produce a paper having the novel

2

advantages and characteristics herein set forth.

In carrying out the invention it is preferred to use sheets or webs of a paper which is absorbent or which may be readily penetrated by liquids such as, for example, paper of the kind which is known in the trade as waterleaf. A starch surface filler layer may or may not be used.

The materials used in preparing the reactive paper consist of two chemicals which react with each other when in presence of water. These materials may be incorporated in different binders and applied on opposite sides of paper. We have prepared a coating for the printing side of the paper as follows:

| | Per cent by weight |
|---|---|
| Methyl cellulose | About 6.5 |
| Calcium carbonate | About 78 |
| Water | About 15.5 |

The calcium carbonate used above is an example of water-insoluble alkaline-earth carbonates, which may be decomposed by the presence in a water solution of a sufficiently high hydrogen ion concentration to effect such result, producing the gas, carbon dioxide.

Small amounts of a plasticizer such as glycerin or diethylene glycol mono-ethyl ether, up to 5% may be added to advantage but are not essential to good results. Instead of methyl cellulose, gum arabic, dextrine or glue may be used in sufficient quantities to serve as a binder. The purpose of the binder is to make the mixture a viscous solution in which the other components will be maintained in uniform disposition. After the above coating has been applied to the paper and dried we would coat the reverse of the sheet with the following coating:

| | Per cent by weight |
|---|---|
| Methyl cellulose | About 2 |
| Tartaric, citric, toxilic or lactic acid | About 34 |
| Water | About 64 |

The "Toxilic acid" mentioned above is a commercial name for maleic acid

(HOOC·CH:CH·COOH)

Here again the methyl cellulose used above may be replaced by glue, gum arabic, dextrine or other similar water-soluble binders in range of 4–8%. Plasticizers may be used in this coating but are not essential to result.

A workable product can be made by superimposing the two previously mentioned coatings. The acid-containing coat is applied to the paper

first and dried, and the carbonate containing coating then applied.

Another workable product can be produced by giving the waterleaf web a sizing operation with a binder dissolved in water containing one of the reactive chemicals. This paper after drying is coated with one of the previously noted carbonate contained coatings. A suitable sizing bath can be made as follows:

| | Per cent by weight |
|---|---|
| Glue, methyl, cellulose, gum arabic or dextrine | About 8 |
| Tartaric, citric, toxilic or lactic acid | About 33 |
| Water | About 57 |

The above sizing solution is applied to the base paper by the process known in paper trade as tub sizing, then dried. The previously noted carbonate coatings can be applied and dried without setting up destructive reaction.

Another workable product can be produced by applying the carbonate coatings listed above to one sheet of paper, then laminating this paper to another sheet which has been either coated or sized with one of the acid containing solutions herein above noted, the laminating of the second sheet being done on the back of the carbonate coated sheet.

In another method of carrying out the invention, the calcium carbonate containing coating is applied to the web or sheet of paper and then dried. The coating may be of any reasonable thickness, although we prefer to use coatings which are about as thick as the usual paper coating films.

The coated and dried paper is then given a treatment to apply tartaric, citric, lactic or Toxilic acid in intimate relation with the calcium carbonate. We have done this by passing the web of paper through a solution of the selected acid dissolved in an anhydrous solvent. The solution will carry the acid quickly into the paper and into contact with the calcium carbonate. The anhydrous solvent is then volatilized by heat, leaving the coating dry and with the acid and carbonate in intimate contact.

Any of the above noted carbonate coatings may be first applied to the web of paper. The dip solution will vary considerably in composition depending upon the solvent and acid selected for use, but to cite an example we have obtained satisfactory results using tartaric acid, 15% by weight, dissolved in anhydrous alcohol, 85% by weight.

When papers of the kind indicated, prepared as above described, are put in water, the chemicals will react to evolve gas in the form of bubbles which will act to loosen the water-soluble coating on the paper while bubbles are developed in great number in the coating, thereby quickly destroying the coating and any significant matter which has been printed or written thereon. The gas evolved in all examples listed in this application is $CO_2$ and the volume of gas is great enough to be efficient in loosening the coating from the paper and destroying the texture of the coating to such an extent that there is no support left for printed or written matter on the surface of the coating.

While calcium carbonate and tartaric, lactic, citric, and Toxilic acids have been specifically mentioned as suitable materials for preparing the coating, it will be apparent that other chemicals which will quickly react in the presence of water may be employed, the principal limitation being,



that water alone should be sufficient to create the destructive reaction. Many organic acids have been tried with varying success, but the ones specifically mentioned have shown best results. The material used as a binder should, of course, also be water-soluble and binders other than the ones above specifically mentioned may obviously be substituted.

It will be readily seen that the coated paper herein disclosed has a wide field of usefulness in the preparation of codes and secret reports or orders in the foreign and military services, and that the paper may also be used in the printing of documentary stamps, internal revenue stamps and similar evidences of the payment of required fees or charges where it is desirable to make it impossible to wash off cancellation marks preparatory to attempting an unlawful re-use. In such uses, the destructive action of the paper would have to be controlled so that the paper could serve satisfactorily in practice.

While illustrative embodiments of the invention have been described in rather specific terms, it will be obvious to those skilled in the art that changes and substitutions of materials may be made, and the proportions and manner of application varied, and it is desired not to be limited by anything hereinabove contained, except to the extent indicated in the claims which follow.

What is claimed is:

1. As an article of manufacture, a sheet of water absorbent paper coated with a coating consisting of a water soluble binder and calcium carbonate and tartaric acid held by the binder in reactive relationship whereby the coating may be destroyed by dipping the coated sheet in water.

2. The method of preparing paper so that indicia thereon may be completely illegible and undiscoverable upon immersion in an aqueous liquid, comprising the steps of coating at least one side of the paper with a coating compound comprising a water soluble binder and an organic acid selected from the group which consists of tartaric, citric, toxilic and lactic acids, drying this coating, and then applying to at least one side of the paper a second coating comprising a water soluble binder and an alkaline-earth carbonate, the indicia to be rendered illegible upon immersion being solely on the carbonate-containing coating.

3. The method in accordance with claim 2, wherein said second coating is applied over the first named coating, and wherein said second coating is applied by the use of an anhydrous liquid vehicle.

4. The method in accordance with claim 2, wherein both said coatings are applied one over the other on at least a portion of one side only of the paper, the acid-containing coating being applied first.

5. The method of preparing paper so that indicia thereon may be completely illegible and undiscoverable upon immersion in an aqueous liquid, comprising the steps of successively applying two coatings to said paper, one of said coatings including an organic acid selected from the group which consists of tartaric, citric, toxilic and lactic acids and being applied to one side of said paper and the other of said coatings including an alkaline-earth carbonate and being applied to the other side of said paper, the indicia to be rendered illegible upon immersion being solely on the carbonate coated side of said paper.

6. As an article of manufacture, a sheet of coated paper for receiving indicia which will be completely illegible and undiscoverable upon im-

mersion in an aqueous liquid, two coatings, each upon at least one side of said paper, one of said coatings including an organic acid selected from the group which consists of tartaric, citric, toxilic and lactic acids, and the other of said coatings including an alkaline-earth carbonate, and adapted to receive indicia to be rendered illegible upon immersion only on the carbonate-containing coating.

7. An article of manufacture in accordance with claim 6, wherein said alkaline-earth carbonate is calcium carbonate.

8. As an article of manufacture, a sheet of coated paper for receiving indicia which will be completely illegible and undiscoverable upon immersion in an aqueous liquid, two coatings, each upon at least one side of said paper, one of said coatings including tartaric acid, and the other of said coatings including an alkaline-earth carbonate, and adapted to receive indicia to be rendered illegible upon immersion only on the carbonate-containing coating.

9. As an article of manufacture, a sheet of coated paper for receiving indicia which will be completely illegible and undiscoverable upon immersion in an aqueous liquid, two coatings, each upon at least one side of said paper, one of said coatings including citric acid and the other of said coatings including an alkaline-earth carbonate, and adapted to receive indicia to be rendered illegible upon immersion only on the carbonate-containing coating.

10. As an article of manufacture, a sheet of coated paper for receiving indicia which will be completely illegible and undiscoverable upon immersion in an aqueous liquid, two coatings, each upon at least one side of said paper, one of said coatings including toxilic acid, and the other of said coatings including an alkaline-earth carbonate, and adapted to receive indicia to be rendered illegible upon immersion only on the carbonate-containing coating.

11. As an article of manufacture, a sheet of paper for receiving indicia which will be completely illegible and undiscoverable upon immersion in an aqueous liquid, comprising two superimposed coatings on at least a portion of one side of said paper, one of said coatings including an organic acid selected from the group which consists of tartaric, citric, toxilic and lactic acids, and the other of said coatings including an alkaline-earth carbonate, the indicia to be rendered illegible upon immersion being only on the coated surface portion of said paper.

12. As an article of manufacture, a sheet of



paper for receiving indicia which will be completely illegible and undiscoverable upon immersion in an aqueous liquid, comprising a first coating on at least a portion of one side of said paper including an organic acid selected from the group which consists of tartaric, citric, toxilic and lactic acids, and a second coating superimposed on said first coating after the latter is dry and applied by the use of an anhydrous liquid vehicle, said second coating including an alkaline-earth carbonate, the indicia to be rendered illegible upon immersion being only on the coated portion of said paper.

13. As an article of manufacture, a sheet of paper for receiving indicia which will be completely illegible and undiscoverable upon immersion in an aqueous liquid, two coatings thereon, one of which is applied to each side of said paper, one of said coatings containing an organic acid selected from the group which consists of tartaric, citric, toxilic and lactic acids, and the other of said coatings containing an alkaline-earth carbonate, and the indicia to be rendered illegible upon immersion being applied only on the carbonate coated surface of said paper.

14. The method of preparing paper so that indicia thereon may be completely illegible and undiscoverable upon immersion in an aqueous liquid, comprising the steps of applying to one surface of a sheet of an absorbent paper a starch surface filling layer, applying a coating over said starch surface filling layer containing an alkaline-earth carbonate, and applying to the other surface of said paper a liquid material containing an organic acid selected from the group consisting of tartaric, citric, toxilic and lactic acids, the indicia to be rendered illegible upon immersion being applied only on the carbonate coated surface of said paper.

15. The method of preparing paper so that indicia thereon may be completely illegible and undiscoverable upon immersion in an aqueous liquid, comprising the steps of applying to at least a portion of one surface of an absorbent paper a liquid containing an organic acid selected from the group which consists of tartaric, citric, toxilic and lactic acids, drying the paper, and thereafter applying onto the same portion of the surface of said paper a coating consisting of a water permeable binder and a finely divided alkaline-earth carbonate, the indicia to be rendered illegible upon immersion being applied only onto said portion of the paper.

CHAUNCEY P. FOOTE, JR.
CLIFFORD D. GUERTIN.