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PROCESS FOR THE CHEMICAL STABILIZATION OF PAPER AND PRODUCT

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This invention relates to the stabilization of paper whereby it is rendered non-tarnishing to metals, such as silver, bronze, etc., with which it is brought into contact and inert with respect to inks and colors, etc., applied to the paper, and more durable with age.

The invention is designed principally for the treatment of paper, such as wall paper, newspaper, wrapping paper, etc., made from chemical pulp and mechanical pulp which contains acid or acid-forming bodies. Unsized paper, such as filter paper, which has been purified or refined to a high degree, is non-tarnishing to metals and relatively stable without the treatment.

The stabilizing process consists essentially in introducing an alkaline earth metal bicarbonate, such as strontium bicarbonate, calcium bicarbonate or barium bicarbonate into the paper after the paper web has been formed and preferably after it is sized. Many sizing processes, such as the well-known alum-rosin size, require acidity and/or give rise to acidity in the paper, and the stabilizing treatment should, therefore, follow such sizing treatments in order not to interfere with the sizing treatment and also to take care of any acidity resulting from the sizing treatment.

The alkaline earth metal bicarbonate may be introduced into the paper in several ways, as will be described more fully hereinafter, such as by wetting the paper with an aqueous solution thereof, or with an aqueous suspension of carbonate which has been treated with carbon dioxide to convert a suitable portion of the carbonate into the bicarbonate or by wetting the paper with a solution of the alkaline earth metal hydroxide followed by treatment with carbon dioxide.

The bicarbonate is applied to the paper in relatively small amounts and does not, and is not intended to, serve to fill the paper, although some slight filling action may incidentally occur due to reversion of the bicarbonate to the normal carbonate or to the use of a solution of bicarbonate containing the normal carbonate in suspension.

The bicarbonate is of such character and is applied in such limited amount that it does not injure the paper in any way, i. e. attack and weaken the cellulose fiber, or produce discoloration, or impair the finish, or interfere with the sizing of the paper, or interfere with the use of the paper, e. g. as a wrapping paper for foods. As a result of the treatment the paper is left

substantially unchanged excepting with respect to its durability with age and tarnishing properties.

As indicated above the treatment of the paper preferably is applied on what may be termed the second section of the paper-making machine after the sizing reactions are complete and may be applied to the finished paper or as it is passing over the drying rolls.

The instability of paper and its tarnishing properties generally are attributed to or associated with its acidity, i. e. to the presence in the paper of acid-acting substances or substances which tend to develop acidity as the paper ages. This acidity or tendency to develop acidity may be inherent in the cellulosic fibrous material used, as in the case of mechanical pulp, or it may result from the chemical treatment employed for the production of the pulp, or it may result from the sizing of the paper with materials such as alum, or a combination of these causes. However, the treatment is not to be regarded as being merely a chemical neutralization of the paper because it has been found that paper may be neutralized by treatment with, for instance, caustic alkali and filled with acid-neutralizing bodies, such as calcium carbonate, without accomplishing a stabilization thereof, such as is accomplished by the process of the present invention. Paper may moreover be rendered non-tarnishing to metals by incorporating materials such as lead acetate, copper carbonate, etc., in it without effecting a stabilization of the paper. Tests have shown that it is the alkaline earth metal bicarbonate and not the normal carbonate which exerts the desired stabilizing action, although the normal carbonate and other bases may under certain circumstances exhibit a neutralizing action accompanied by some non-tarnishing and stabilizing action.

It is essential that the alkaline earth metal bicarbonate be applied in such a way as to exert the desired effect on the constituents of the paper, i. e. in the form of a solution, to the formed sheet, and if a sizing treatment requiring the presence of acid or resulting in the presence of acid is used, the treatment must be applied after the sizing. Materials such as calcium carbonate introduced into the paper at an earlier stage in the formation of the paper are not effective, probably because they react with the acid or acid-forming constituents of the paper too slowly and incompletely.

The instability of paper may be shown and tested in various ways, for instance by testing its strength after an accelerated aging, or by testing its tarnishing action on metals under accelerated conditions. The following method has been found to be most convenient for test purposes. A specimen of paper is coated with a suspension of gilt powder in a starch gum paste and placed in a closed glass vessel containing water so as to maintain a high humidity and allowed to stand usually for about 48 hours at room temperature. The gilt or metal powder is an alloy of copper, zinc and aluminum in about the following proportions: copper, 91.2%; zinc 6.1%; and aluminum, 1.7%. The starch paste is of the type commonly used in the paper industry and is composed of starch, borax, glucose, phenol and water. If the paper specimen is unstable the gilt will show a definite tarnishing.

While this test determines only the tarnishing properties of the paper, it has been found that it is also a fairly accurate indication of the stability of the paper because ordinarily a paper which will tarnish is also unstable. However, instability, that is, tendency of the paper to deteriorate, particularly in strength, with age may not be directly proportional to the tarnishing properties of the paper and this may be determined by the so-called oven test. This test is not as delicate as the tarnishing test, but has been found to show that paper which has been stabilized in accordance with the present invention generally suffers only about one-half as much in loss of strength as untreated papers, other than those of the type of high grade filter paper, which are inherently non-tarnishing and stable.

The following example illustrates the invention.

An aqueous solution of barium bicarbonate is prepared by bubbling carbon dioxide through an aqueous suspension of finely divided barium carbonate until a suitable quantity of the barium carbonate has been converted to the bicarbonate and dissolved, i. e. to a concentration of about 0.15 to 0.20 percent of barium bicarbonate, if the carbonation is carried out in the cold and without pressure. A higher concentration may be obtained by carbonation under pressure. The suspension of barium carbonate may contain any desired excess thereof over that necessary to give the desired concentration of barium bicarbonate. The resulting solution of barium bicarbonate containing barium carbonate in suspension may be applied to the paper directly, or it may be first filtered to remove the undissolved barium carbonate. The paper to be stabilized is immersed in the solution for a length of time determined by tests, which time may vary from about 5 seconds, i. e. just sufficient to wet the paper up to about 2 minutes. The time required depends upon the concentration of the barium bicarbonate solution and the character of the paper, and since the cause of tarnishing and instability are not exactly known, the time required cannot be accurately determined by chemical analysis of the paper. However, some indication as to the time of immersion required may be obtained by observing the tarnishing properties of the paper in the above described tarnishing test. As a result of numerous experiments I have found that a relatively unstable paper, such as one made from ground or mechanical pulp, requires an impregnation

with about 40 pounds of barium bicarbonate per ton of paper. Other less unstable papers require correspondingly smaller amounts. After the impregnation of the paper with the barium bicarbonate solution, it is dried, preferably without the application of high temperature.

As an alternative to the above described procedure involving immersion of the paper in the barium bicarbonate solution, the paper may be sprayed on or between the drying rolls of the paper-making machine with the barium bicarbonate solution, or the paper may be impregnated with a solution of barium hydroxid either by immersion or spraying, and then treated with carbon dioxide either in gaseous form or in solution to convert the barium hydroxid to the carbonate and bicarbonate.

Although tarnishing and instability in paper appear to be associated with acidity, and my treatment has been found to result in bringing the pH value of the paper to approximately 6.5 or higher, nevertheless my treatment is not merely a chemical neutralization of the acidity of the paper, because, as has been stated above, a sample of paper may be neutralized to the same extent with sodium hydroxid without rendering it chemically stable as determined by the gilt tarnishing test described above.

The described treatment with barium bicarbonate confers upon cheap paper, such as ground wood paper, some of the properties of a highly purified paper such as filter paper. The treatment does not introduce anything into the paper which is objectionable in connection with ordinary commercial uses of paper. The treatment is inexpensive and renders many cheap papers, which otherwise would be unstable, entirely satisfactory for use as gilt or decorated wall paper, gilt printing paper and the like; and aside from the tarnishing properties the paper is rendered resistant to aging. The treatment of the paper does not interfere with the normal sizing process.

The treatment of paper with the other alkaline earth metal bicarbonates, strontium bicarbonate and calcium bicarbonate, may be identical with the procedure described above in connection with the use of barium bicarbonate, excepting that the solubility of these bicarbonates must be taken into consideration in determining the quantity of solution to be applied. Mixtures of the bicarbonates of two or more of the alkaline earth metals may of course be used and the presence of small amounts of other materials in the impregnating solution, such as sodium carbonate or bicarbonate, is not excluded, although, as is apparent, the impregnating solution should be free of any substance having a detrimental action on the paper.

I claim:—

1. Process of stabilizing paper and rendering it non-tarnishing which comprises impregnating the paper with an alkaline earth metal bicarbonate in aqueous solution.
2. Process as defined in claim 1 in which the solution of the alkaline earth metal bicarbonate contains the normal carbonate of said metal in suspension.
3. Process as defined in claim 1 in which the impregnation is accomplished by treating the paper with a solution of an alkaline earth metal hydroxid and then with carbon dioxide.
4. Process as defined in claim 1 in which the impregnation with alkaline earth metal bicar-

bonate solution is applied to the paper after it has been sized.

5 5. Process as defined in claim 1 in which the impregnation with alkaline earth metal bicarbonate solution is applied to the paper while it is being dried.

10 6. Process as defined in claim 1 in which the paper is immersed in the alkaline earth metal bicarbonate solution for from about 5 seconds to about 2 minutes.

7. Process as defined in claim 1 in which the alkaline earth metal bicarbonate solution contains about 0.15 to 0.20% of barium bicarbonate.

8. Process as defined in claim 1 in which the alkaline earth metal bicarbonate solution contains calcium bicarbonate.

9. Process as defined in claim 1 in which the alkaline earth metal bicarbonate solution contains strontium bicarbonate. 5

10. Process as defined in claim 1 in which the paper is impregnated with about 40 pounds of barium bicarbonate per ton of paper.

11. Paper which has been stabilized and rendered non-tarnishing by impregnation with an alkaline earth metal bicarbonate. 10

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