# United States Patent

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[54] METHOD FOR DECREASING AGING OF PAPER WITH SULFITES AND/OR BISULFITES AND PRODUCT

3 Claims, No Drawings


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**ABSTRACT:** A dried paper web is impregnated with a soluble sulfite and/or bisulfite salt, such as sodium sulfite or bisulfite which salt may be incorporated in an aqueous starch, or starch clay, surface-sizing composition to decrease the aging of the paper.

# METHOD FOR DECREASING AGING OF PAPER WITH SULFITES AND/OR BISULFITES AND PRODUCT

This invention relates to a method for maintaining the brightness of paper and to a surface sizing composition for paper which tends to prevent deterioration and discoloration of paper.

Paper tends to deteriorate by any of a number of means to provide a product of darkened color and/or reduced brightness. Many impurities or chemical additives used in paper manufacture tend to darken over a period of time probably due to oxidation effects involving the paper and the chemical additives. Common metallic ion impurities such as iron and magnesium when oxidized, form colors which reduce the brightness and change the color of paper.

These problems are particularly aggravated in papers manufactured from paper pulps containing large amounts of lignin. Such pulps are commonly referred to as mechanical (groundwood), chemi-mechanical and semichemical to distinguish them from the purely chemical pulps. Lignin deteriorates rapidly with natural aging. Heat and ultraviolet light tend to accelerate the natural aging process still further. The problems associated with oxidized metallic ion impurities is also aggravated in high-lignin papers since, in addition to the colored oxidation products, the metal impurities also react with lignin to produce colored complexes.

It is also characteristic of papers containing large amounts of unbleached sulfite or chemi-mechanical pulp prepared by the sulfite-type of cooking process to age more rapidly (with corresponding increased rate of deterioration) than paper manufactured from pure bleached chemical pulp. It is believed that this results from the oxidation of lignosulfonic acid to a form exhibiting a reddish color, to the formation of ferric iron complexes with lignosulfonic acid to produce a pink or red shade material and/or the presence of stilbene-type color compounds which, on oxidation, form a pink coloring material.

In addition to the foregoing special situations, essentially all papers have a tendency to darken and become embrittled and weak when exposed to high temperatures such as those commonly encountered in duplication machines and preburners on printing presses and in paper driers encountered in the printing processes following the presses. In essence, this type of deterioration is an accelerated aging which can be traced directly to the exposure at elevated temperatures. Similarly, aging of any paper can be accelerated by exposure to sunlight as well as to any conditions normally associated with an increase in oxidation rate.

It has now been found that impregnation of the surface of "dry" paper, i.e., paper from the dry end of the paper making process containing up to about 10 percent water, with a water-soluble sulfite or bisulfite, or a mixture of these, will greatly assist in maintaining paper brightness, and greatly retard the aging of the paper from any or all of the sources discussed above.

A convenient method for impregnating the surface of the paper with the sulfite and/or bisulfite is to incorporate the water-soluble salt in the surface-sizing compositions used to treat dry-end paper.

As is well known in the art, it is common to saturate papers with starch or clay-starch solutions or like aqueous colloidal and/or pigmented solutions used for whitening and surface sizing paper. These solutions (including suspensions) can be advantageously employed to aid in the introduction into the surface of the paper and the holding therein of the sulfite and/or bisulfite salts. The appropriate soluble sulfites and soluble bisulfites may be added to the coating composition during its preparation and thus be cooked with the coating or can be added to the coating after it is prepared. The sulfites and bisulfites can be added to the coating either as dry material or in the form of suitable aqueous solution. The term "soluble sulfites and bisulfites" is intended to refer to the sodium, potassium and ammonium salts.

The soluble sulfite or soluble bisulfite is applied to the paper at a dosage of from about 5 to 20 lbs. per ton of paper. If significantly less than this amount is employed, the reduced aging characteristics are not sufficiently obtained. On the other hand, if the amount of the mixture exceeds about 20 lbs. per ton of paper, only slight gains are observed.



The present invention does not impose a limit on the operable pH range of the treating solution. Any pH which is consistent with the other characteristics of the paper being treated, including ultimate intended use of the paper, can be employed for the practice of this invention. With the above proviso, a pH in the range of about 5 to 8, and preferably about 6 to 7 has been found quite suitable.

Fresh pulp cooking liquor of the sodium, potassium and/or ammonium sulfite/bisulfite type is suitable for use as the source of sulfite or bisulfite. Typical cooking liquors of this kind may have a pH of about 5.9 to 6 and from about 0.5 to 18 percent sulfite/bisulfite (expressed as $SO_2$). The relative amount of sulfite and bisulfite may range from predominantly sulfite to predominantly bisulfite. The cooking liquor referred to in subsequent examples was prepared by dissolving about a half-pound each of sodium sulfite and sodium bisulfite per gallon of solution.

The soluble sulfite and/or bisulfite may be incorporated in an aqueous starch, or starch-clay, surface-sizing composition. Starch solutions may be prepared by slurrying starch in water and cooking the slurry at, for example, 190° F. for about 20 minutes. These starch solutions contain about 3 to 15 percent by weight of dissolved solids. The viscosity of the solution can be varied depending on the manner in which it is to be applied. Commonly, a size press is employed, but these techniques are well known in the art. The clay-starch or pigment-starch solutions are similarly prepared. The clay or pigment may, however, be added to the starch solution at any stage of preparation, i.e., before, during or after cooking. Typical clays used in the process include the kaolin clays. In general, the surface-sizing solution is applied in an amount of about 160 gallons per ton of paper treated. This is usually increased by the amount of sulfite solution added to the usual sizing solution.

The following tests and/or methods were employed for the evaluation of properties and characteristics of treated papers:

Brightness Determined according to TAPPI testing standard T 453 ts–63

Bursting Strength (Mullen) Determined according to TAPPI testing standard T 403 m–53

Tearing Resistance (Tear) Determined according to TAPPI testing standard T 414 ts–65

Brightness reversion Determined as the difference between the initial brightness of a test specimen and the faded brightness, i.e., the brightness after subjecting the specimen to a treatment which tends to fade the specimen.

Paper $SO_2$ content Determined by extracting 5 grams of sample with 150 ml. of distilled water, measuring pH, acidifying with sulfuric acid, addition of starch-potassium iodide indicator, and titrating with 0.00125 N $KIO_3$ to the first lasting color change. The number of cc's of $KIO_3$ solution required is an indication of the amount of $SO_2$ in the sample.

The effect of aging on the several characteristics of the paper can be indicated by accelerated aging of the paper with comparison of the properties before and after aging. In the case of brightness, these effects are referred to as fading and/or brightness reversion. Oven, or heat aging is effected by the general accelerated method described in TAPPI tests T 453 ts–63 and RC–280, modified to employ an oven temperature maintained in the range 215° to 220° F. with the specimens held in the oven for 6 hours. Light aging is effected by exposing the test specimens to a bank of six G.E. sun lamps for 6 hours while maintaining the ambient temperature below 100° F.

Gas aging is effected by hanging the test specimens in a stream of cooled combustion gases from a bunsen burner

operating wide open. The gases are cooled to a temperature below 100° F.

In the examples which follow, "paper weight" refers to the weight of a ream made up of 24 inch ×36 inch sheets, unless otherwise indicated. All of the tests and aging were conducted as described above unless otherwise indicated.

## EXAMPLES 1–13

Starch solution was applied to white tablet paper of 37 pound weight and to white form paper of 46 pound weight. The papers were made up of mixtures of chemi-mechanical, bleached kraft and bleached sulfite pulp. Part of the paper was also treated with sodium sulfite-bisulfite (fresh cooking liquor) in accordance with the practices of the present invention. After treatment, some specimens were subjected to accelerated aging which, in these examples, was conducted for 24 hours at 130° C. A comparison of the physical properties of the paper before and after aging, with sulfite-bisulfite treatment and without, is provided in table I.

TABLE I

| Paper weight, lbs. | Sulfite-bisulfite treated | Original tear | Oven-aged tear | Original mullen | Oven-aged mullen |
|---|---|---|---|---|---|
| 37 | No | 42 | 23 | 20.8 | 12.6 |
| 37 | No | 40 | 22 | 21.0 | 12.0 |
| 37 | No | 40 | 22 | 22.1 | 12.7 |
| 37 | Yes | 40 | 38 | 21.5 | 19.3 |
| 37 | Yes | 42 | 38 | 21.9 | 18.9 |
| 46 | No | 48–52 | 32–36 | 24.0 | 15.1 |
| 46 | No | 56–58 | 36–38 | 23.0 | 12.3 |
| 46 | No | 56–58 | 32–34 | 26.3 | 14.6 |
| 46 | No | 52–58 | 30–36 | 29.2 | 13.9 |
| 46 | Yes | 54–56 | 54–54 | 28.1 | 25.0 |
| 46 | Yes | 56–58 | 50–56 | 29.5 | 27.1 |
| 46 | Yes | 56–56 | 52–54 | 26.0 | 23.2 |
| 46 | Yes | 50–54 | 50–52 | 24.5 | 21.7 |

## EXAMPLES 14–20

Following the foregoing procedures, the effect of soluble sulfite-bisulfite treatment on brightness was determined during continuous processing of white form paper. After continuous operation was established with a standard starch surface-sizing solution, fresh sodium sulfite-bisulfite cooking liquor was mixed with the starch solution in a proportion of 11 gallons of cooking liquor per 160 gallons of starch solution. This corresponded to a sulfite-bisulfite addition to the paper in the range of about 11 to 12 pounds per ton. The brightness and brightness reversion on accelerated aging were determined before and during sulfite-bisulfite treatment. The amount of sulfite-bisulfite picked up by the paper and contained in the starch was monitored regularly and reported as cc's of 0.00125 N $KIO_3$ under the heading "$SO_2$". The results of these tests are provided in table II.

TABLE II

| Starch characteristics | | | Original brightness | Loss in brightness after aging by— | | | Paper | |
|---|---|---|---|---|---|---|---|---|
| pH | Percent solids | $SO_2$ | | Light | Gas | Hear | pH | $SO_2$ |
| 6.0 | 8.2 | 0.2 | 74.8 | 4.9 | 1.3 | 3.0 | 5.7 | 8.2 |
| | | | 74.9 | 4.9 | 1.3 | 3.0 | 5.7 | 7.4 |
| | | | 75.2 | 5.1 | 1.5 | 3.0 | 5.8 | 7.5 |
| 6.1 | 9.2 | 179.6 | 76.2 | 4.3 | 1.3 | 2.8 | 6.5 | 225.4 |
| | | | 77.1 | 4.2 | 1.5 | 2.4 | 6.6 | 176.9 |
| 6.1 | 8.2 | 151.8 | 77.2 | 4.1 | 1.5 | 2.6 | 6.5 | 157.9 |
| 6.0 | 8.2 | 155.4 | 76.3 | 4.5 | 2.0 | 2.6 | 6.5 | 150.0 |

## EXAMPLES 21–23

Following the foregoing procedures, three series of tests were conducted on 28 pound white form paper. A regular starch solution was applied to the paper in a size press and brightness measurements made before and after aging treatment. In the first series, the starch solution contained no additives. In the second and third series, the starch solution contained sodium sulfite-bisulfite and was prepared by adding 11 gallons of cooking liquor, as described previously, to 160 gallons of regular starch solution. The final solids content of the treating solution was 7.6 percent. The brightness data, etc. obtained for each series were averaged. Each average represents five brightness tests per sheet for 36 evaluations, or a total of 180 brightness readings. The averaged data are set forth in table III.

TABLE III

| Sulfite-bisulfite treated | Original brightness | Brightness loss after aging by— | | | Paper characteristics | |
|---|---|---|---|---|---|---|
| | | Gas | Light | Heat | pH | $SO_2$ |
| No | 77.4 | 2.2 | 4.9 | 4.00 | 5.4 | 4.4 |
| Yes | 79.0 | 1.9 | 3.9 | 2.40 | 6.3 | 149 |
| Yes | 79.0 | 1.9 | 3.9 | 1.75 | 6.3 | 106 |

## EXAMPLE 24

Following the foregoing procedures, 37 pound offset printing paper containing fluorescent dye and other brightners was treated in the manner described above. The sulfite-bisulfite treatment of the present invention provides improved brightness, significantly improved brightness reversion characteristics and significantly reduced the loss in physical properties of the paper on aging.

## EXAMPLES 25–27

In an attempt to evaluate the amount of sulfite-bisulfite addition required to obtain the advantages of the present invention, a starch solution was prepared which contained five gallons of cooking liquor per 160 gallons of starch solution rather than the 11 gallons used in previous examples. The paper treated was 46 pound white form paper and the tests were conducted in the same manner described previously with the paper tested with just the starch solution and with the starch sulfite-bisulfite solution. The results of these tests are set forth in table IV.

TABLE IV

| Sulfite bisulfite additives | Starch characteristics | | Original brightness | Brightness loss after aging by— | | | Original | | Aged | | Porosity | Mullen | | Tear | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | pH | $SO_2$ | | Gas | Light | Heat | pH | $SO_2$ | pH | $SO_2$ | | Original | Aged | Original | Aged |
| No | 6.5 | 0.2 | 76.2 | 2.5 | 5.0 | 8.4 | 5.7 | 6.0 | 5.8 | 2.5 | 21 | 23.0 | 28.3 | 52–58 | 50–54 |
| Yes | 6.1 | 79.6 | 76.3 | 2.0 | 4.1 | 6.3 | 6.2 | 66.6 | 6.4 | 37.4 | 30 | 24.3 | 26.0 | 48–52 | 46–52 |
| Yes | 6.1 | 79.6 | 74.6 | 2.0 | 4.8 | 6.0 | 6.2 | 51.8 | 6.1 | 28.0 | 39 | 29.0 | 30.5 | 56–58 | 56–60 |

## EXAMPLES 28–38

Three surface-sizing solutions were prepared. The first consisted of a 7.6 percent starch solution. The second consisted of the same starch solution but contained, in addition, sufficient clay (kaolin) to provide 1½ pounds of clay per 37 pound ream of 24 inch ×36 inch paper. The third solution was the same as the second solution but contained, in addition, 10 gallons of sodium sulfite-bisulfite cooking liquor for each ton of paper to be treated (i.e., 10 gallons of liquor per 160 gallons of starch solution). 37 pound offset printing paper was treated in a sizing press with the three sizing solutions. The results are set forth in table V. For the heat aging in the tests the oven was maintained at 215° F.

## EXAMPLES 39–44

Paper prepared from 100 percent full bleached chemical pulp (bleached kraft and bleached sulfite), which had already been surface sized with starch, was divided into two batches. The first was treated solely with water. The second was treated with an aqueous solution of sodium bisulfite. Brightness tests were then conducted on the specimens before and after aging and the change in brightness determined. In a significant

TABLE V

| Coating | Original brightness | Brightness loss after aging by— Gas | Light | Heat | Original pH | Original $SO_2$ | Heat aged pH | Heat aged $SO_2$ | Original Mullen | Original Tear | Heat aged Mullen | Heat aged Tear |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Starch | 73.5 | 4.8 | 4.0 | 4.7 | 6.2 | 460 | 6.3 | 160 | 20.5 | 28-36 | 22.4 | 22-28 |
| Starch-clay | 74.2 | 4.1 | 4.0 | 4.8 | | | | | 20.3 | 32-44 | 22.9 | 26-36 |
| Do | 73.3 | 3.9 | 3.9 | 4.5 | | | | | 21.7 | 28-38 | 22.6 | 26-32 |
| Do | 73.1 | 4.3 | 3.6 | 3.7 | | | | | 21.5 | 26-36 | 19.8 | 26-32 |
| Do | 72.5 | 4.4 | 4.1 | 4.6 | | | | | 22.5 | 32-36 | 22.7 | 26-32 |
| Do | 72.2 | 4.0 | 3.5 | 4.5 | 6.4 | 328 | 4.6 | 92 | 20.7 | 30-36 | 20.2 | 26-30 |
| Starch-clay-sulfite | 73.3 | 3.3 | 2.9 | 4.0 | 6.6 | 6,400 | 6.5 | 4,504 | 20.5 | 28-34 | 21.2 | 22-26 |
| Do | 73.2 | 3.5 | 3.3 | 3.8 | 6.6 | 7,060 | 6.2 | 5,060 | 22.5 | 24-34 | 22.0 | 26-28 |
| Do | 73.2 | 3.1 | 2.8 | 3.7 | 6.6 | 6,320 | 6.3 | 7,480 | 20.5 | 32-34 | 21.0 | 22-30 |
| Do | 73.4 | 2.4 | 2.8 | 3.6 | 6.5 | 8,000 | 6.6 | 5,380 | 22.0 | 28-32 | 23.2 | 28-30 |
| Do | 73.4 | 2.4 | 2.9 | 4.5 | 6.5 | 6,880 | 6.4 | 4,932 | 21.5 | 32-34 | 21.0 | 24-30 |

number of cases the brightness actually increased on aging. The data are summarized in table VI with a plus sign indicating an increase in brightness and a negative sign indicating a loss in brightness.

## EXAMPLES 45-50

Following the foregoing procedure, tests were conducted with 37 pound tablet paper. The starch solution employed contained 7.2 percent solids. To 160 gallons of the starch solution were added 10 gallons of sodium sulfite-bisulfite cooking liquor to provide a treating solution containing 3728 p.p.m. of $SO_2$. The results of the test are set forth in table VII.

TABLE VI

| Original brightness | Brightness change on aging by — Light: Water treated | Light: Bisulfite treated | Gas: Water treated | Gas: Bisulfite treated | Heat: Water treated | Heat: Bisulfite treated |
|---|---|---|---|---|---|---|
| 95.5 | −1.2 | −.1 | −2.2 | +.6 | −3.2 | −1.8 |
| 88.0 | −1.2 | +.5 | −1.0 | +.9 | −2.0 | −.5 |
| 85.2 | −.6 | +.2 | −.5 | +.7 | −1.8 | −.9 |

TABLE VII

| Sulfite-bisulfite | Original brightness | Brightness loss after aging by— Light | Gas | Heat | Original pH | Original $SO_2$ |
|---|---|---|---|---|---|---|
| No | 72.9 | 4.7 | 1.8 | 4.6 | 5.9 | 328 |
| Yes | 73.0 | 3.2 | 1.4 | 3.8 | 6.4 | 4,440 |
| Yes | 74.0 | 3.5 | 1.9 | 4.0 | 6.4 | 5,560 |
| Yes | 73.9 | 3.8 | 2.1 | 4.2 | 6.2 | 5,440 |
| No | 72.6 | 4.9 | 2.1 | 4.8 | 5.8 | 820 |
| No | 72.3 | 4.7 | 1.8 | 4.5 | 5.6 | 548 |

## EXAMPLES 51-68

Following the foregoing procedures, mill average control tests were conducted during the production of 46 pound white paper produced from 30 percent bleached kraft and 70 percent chemi-mechanical bisulfite pulp, and of 28 pound form paper produced from 45 percent bleached kraft and 55 percent chemi-mechanical bisulfite pulp. In the tests, the starch was normalized at 8 percent solids. When clay was included, it was at a concentration of about a fifth of a pound per gallon of size press solution, such that it was applied in an amount of about 50 pounds per ton of paper. The sulfite/bisulfite liquid was incorporated in an amount of about a tenth of a pound (as sodium sulfite) per gallon of size press solution or approximately 11 pounds per ton of paper treated. The results of the tests are set forth in table VIII.

TABLE VIII

| Paper weight, lbs. | Coating | Original brightness | Loss in brightness after aging by— Gas | Light | Heat |
|---|---|---|---|---|---|
| 46 | Starch | 72.5 | 1.2 | 3.2 | 6.3 |
| 46 | do | 71.6 | 1.0 | 3.5 | 5.5 |
| 46 | Starch-clay | 72.3 | 2.0 | 2.6 | 4.1 |
| 46 | do | 74.0 | 2.7 | 3.3 | 4.2 |
| 46 | do | 74.3 | 2.6 | 3.3 | 4.0 |
| 46 | do | 73.7 | 2.7 | 3.5 | 3.9 |
| 46 | do | 73.9 | 3.5 | 3.5 | 3.8 |
| 46 | Starch-clay-bisulfite | 75.0 | 3.1 | 2.7 | 3.0 |
| 46 | do | 74.5 | 1.9 | 3.0 | 4.1 |
| 28 | Starch-bisulfite | 77.7 | 2.3 | 3.1 | 3.7 |
| 28 | Starch | 76.5 | 1.2 | 2.9 | 7.4 |
| 28 | do | 77.0 | 1.8 | 3.3 | 9.5 |
| 28 | do | 78.5 | 3.1 | 4.2 | 6.4 |
| 28 | Starch-clay | 76.6 | 2.2 | 3.8 | 3.8 |
| 28 | Starch | 75.1 | 2.3 | 3.1 | 6.5 |
| 28 | Starch-bisulfite (pH 5.1). | 76.1 | 2.0 | 3.1 | 2.0 |
| 28 | Starch-bisulfite (pH 4.6). | 74.5 | 1.8 | 3.3 | 2.8 |
| 28 | Starch-bisulfite (pH 4.2). | 76.5 | 2.1 | 3.4 | 2.8 |

Thus, the process of the present invention involves the surface treatment of paper at a stage subsequent to the pulp dewatering and web formation stages; and subsequent to the initial pressing and partial drying of the paper. It may, however, precede final drying, e.g., drying to final water content and/or calendering, and may be conducted in connection with, or subsequent to surface sizing (e.g., tub sizing as distinguished from engine sizing). The product is a paper having a surface impregnated with one or more of the specified sulfites and bisulfites and will be characterized by significantly retarded aging.

We claim:

1. In a process for the manufacture of paper in which a pulp is dewatered to form a web and the web pressed and dried to a water content of not more than about 10 percent, the improvement comprising impregnating the surface of said dried paper with an aqueous solution containing starch and a dissolved sulfite salt selected from the group consisting of sodium, potassium, and ammonium sulfites and bisulfites, and mixtures thereof to provide from about 5 to about 20 pounds of sulfite per ton of paper.

2. The process of claim 1 wherein the sulfite salt is a sodium salt.

3. As an article of manufacture, a dry paper web having a surface impregnated with starch and a sulfite salt selected from the group consisting of sodium, potassium, and ammonium sulfites and bisulfites, and mixtures thereof, in an amount of from about 5 to about 20 pounds of sulfite per ton of paper.

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