

[54] **USE OF SODIUM BISULFITE IN AN IMPROVED PROCESS FOR THE TREATMENT OF CELLULOSE TEXTILE MATERIALS WITH CARBAMATE FINISHING AGENTS AND SULFUROUS ACID**

[75] **Inventors:** John D. Reid; Robert M. Reinhardt, both of New Orleans; Russell M. H. Kullman; Norton A. Cashen, both of Metairie, all of La.

[73] **Assignee:** The United States of America as represented by the Secretary of Agriculture, Washington, D.C.

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[56] **References Cited**

UNITED STATES PATENTS

3,776,692 12/1973 Franklin et al. 8/187 X

Primary Examiner—Stephen J. Lechert, Jr.

[57] **ABSTRACT**

An improved relationship of the strength to wrinkle recovery properties of cellulose-containing fabrics finished with methylol carbamate agents and sulfurous acid is obtained by inclusion of about 0.3–1 percent of sodium bisulfite in the treatment bath.

6 Claims, No Drawings

**USE OF SODIUM BISULFITE IN AN IMPROVED
PROCESS FOR THE TREATMENT OF CELLULOSE
TEXTILE MATERIALS WITH CARBAMATE
FINISHING AGENTS AND SULFUROUS ACID**

A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to an improvement process for obtaining finished fabrics which have higher strength to wrinkle recovery relationship than that normally encountered in fabrics which have been treated for durable press properties with a methylol carbamate and sulfurous acid. Specifically, this invention relates to the addition of small quantities of sodium bisulfite to treatment formulations containing a methylol carbamate agent and sulfurous acid so that fabrics treated with said formulations for improved wrinkle recovery will benefit by having higher strength at a given level of wrinkle recovery than fabrics similarly treated but without sodium bisulfite.

Recently developed processes for producing durable press fabrics have utilized low temperature curing with strong acid catalysts. However, careful control of treatment conditions is necessary to avoid undue loss of strength in these finished fabrics. In the treatment of cellulose-containing fabrics, sulfurous acid has been shown to be an effective acid for catalysis to promote reaction between N-methylol type crosslinking agents and the cellulose. Materials processed with formulations containing strong acids, such as sulfurous acid, and N-methylol agents frequently have low strength when high levels of wrinkle resistance (as measured by wrinkle recovery angles) are achieved. Obviously, this strength to wrinkle recovery relationship is important to the textile manufacturer who must employ fabric with suitable strength for use in durable press materials, particularly durable press wearing apparel.

In the prior art, sodium bisulfite and other compounds capable of forming HSO_3^- ions in solution have been employed for odor control in finished textiles. In U.S. Pat. No. 2,870,041, it is suggested that a reaction occurs between the HSO_3^- ions, as supplied by NaHSO_3 , and the aldehyde of the treatment solution to overcome undesirable odors. The specification also suggests that the resultant product is stable only in the presence of mildly acidic or basic reagents. They further suggest that the HSO_3^- ions furnished may function as a catalyst for curing of the finishing agent. Contrary to this, we have found that sodium bisulfite does not provide any catalytic activity to promote reaction between cellulose and methylol carbamate-type finishing agents.

The importance of an improved strength to wrinkle recovery relationship is readily apparent not only to those skilled in the art of textile finishing but also to the ultimate user of the textile product. The literature is far too voluminous to cite the many works of researchers who have attempted to find new and improved processes to achieve fabrics with durable press properties and better strength. In the prior art, such broad areas of processing as tension mercerization, polymer additives, low cure temperatures, and even certain salt additives, have been investigated in seeking better strength to wrinkle resistance relationships in durable

press fabrics. Each process has its inherent advantage but most processes suffer from an economical disadvantage or sacrifice of wrinkle recovery in achieving greater strength in the finished fabric. A simple process to achieve a better strength to wrinkle recovery relationship in textiles has been needed, particularly in the area of N-methylol carbamate finishing agents when inexpensive, strong acids, such as sulfurous acid, are employed as catalysts in the treatment formulations.

It is the principal object of the present invention to provide such a process.

We have found that contrary to suggestions in the patent literature, sodium bisulfite will not act as a catalyst for the treatment of cellulose textile materials with N-methylol carbamate agents to produce improved wrinkle recovery. Surprisingly, however, we have discovered that the use of small quantities of sodium bisulfite in conjunction with sulfurous acid in the treatment of cellulose textile materials with carbamate agents provides a finished fabric with greater strength at a given level of wrinkle recovery than when sodium bisulfite is not included in the treatment formulation.

Generally stated, the process of the present invention consists of impregnating fabric with a formulation containing an N-methylol carbamate finishing agent, sulfurous acid and sodium bisulfite followed by drying and curing the impregnated fabric. The fabric may be cured under a wide range of treatment temperatures and we have found that the strength to wrinkle recovery relationship, as compared with that of treatments without sodium bisulfite, improves with higher curing temperatures.

Textile materials which can be treated by this process include cellulose-containing fabrics that are woven, knitted, or nonwoven. The cellulose may be natural, such as cotton, linen, ramie, and the like, or regenerated, such as viscose and other types of rayon. In addition to textiles consisting wholly of cellulose, blends of cellulose fibers and synthetic fibers can be treated.

N-Methylol carbamate finishing agents that can be used in the formulations and process of this invention include formaldehyde adducts of alkyl carbamates, alkoxyalkyl carbamates, hydroxyalkyl carbamates and the like. N-Acetoxyethyl and N-alkoxyethyl derivatives of these carbamates also can be used. The amount of agent used may vary from about 3 to about 20 percent, by weight, based upon the weight of the treatment bath. About from 10 to 15 percent of the N-methylol carbamate agent, or the equivalent of N-alkoxyethyl or N-acetoxyethyl carbamate agent is preferred.

Small quantities of sodium bisulfite are effective in the process of this invention. The concentration of sodium bisulfite used may vary from about 0.1 to about 1 part per 100 parts, by weight, of the treatment formulation. A preferred range is from about 0.3 to 1 part per 100 parts of treatment formulation.

Temperatures that may be used to cure the impregnated fabric are from about 80° to 160°C, correlated respectively with times from about 4 minutes to about 2 minutes, the preferred temperatures being about from 100° to 160°C. While the concentration of sulfurous acid applicable in this invention is from about 0.05 to 0.3 part per 100 parts, by weight, of the treatment formulation the preferred range is from about 0.1 to 0.2 part per 100 parts, by weight, of treatment formulation.

In summary, the use of small quantities of sodium bisulfite with a carbamate finishing agent and sulfurous acid in the treatment of cellulose-containing textile materials has advantages over the use of the carbamate agent and sulfurous acid in the absence of the said salt. By adding sodium bisulfite to the treatment formulation, a wider range of curing temperatures may be used to achieve a better strength to wrinkle recovery relationship in the treated textile material than that obtained by treatment with formulations containing a methylol carbamate finishing agent and sulfurous acid. The sodium bisulfite may be employed in finishing processes using pad-dry-cure steps and in the mild cure finishing process.

The following examples are provided for illustration and in no way are intended to limit the scope and spirit of the invention. Numerous changes and modifications to the detailed and specific examples will be readily apparent to those skilled in the art.

In the descriptions of solution formulations given in these examples, all parts are by weight unless otherwise specified.

EXAMPLE 1

A formulation (100 parts) was prepared containing 10 parts of dimethylol methyl carbamate, 4 parts of sodium bisulfite, and 86 parts of water. A cotton printcloth, Sample A, was impregnated with the formulation and passed through squeeze rolls to obtain about 90 percent wet pickup of the formulations on the fabric. The fabric was dried at 60°C for 7 minutes and cured at 120°C for 3 minutes. Residual chemicals in the fabric were removed by washing and the fabric was tumble dried.

In another treatment, an aqueous formulation (100 parts) was prepared to contain 10 parts of dimethylol methyl carbamate, 4 parts of sodium bisulfite, and 0.1 parts of sulfurous acid. A portion of cotton printcloth was treated (Sample B) as was Sample A.

The treated fabrics and an untreated control (Sample C) were tested for wrinkle recovery by the method of the American Society for Testing and Materials: Test D1424-56T and analyzed for nitrogen content by the Kjeldahl method. Results are listed in Table I.

TABLE I

SAMPLE IDENTIFICATION	NITROGEN CONTENT, %	WRINKLE RECOVERY ANGLE (Warp + Filling), deg.
Sample A	0.02	200
Sample B	0.03	201
Sample C	0.02	201

This conclusively illustrates that sodium bisulfite does not act as a catalyst for the reaction of a methylol carbamate finishing agent with cotton. Furthermore, if a relatively large quantity of sodium bisulfite is used in conjunction with sulfurous acid (Sample B) the catalytic activity produced by the latter is depressed so that the desired reaction between the finishing agent and cellulose does not occur and there is no improvement in wrinkle recovery.

EXAMPLE 2

An aqueous formulation (100 parts) was prepared to contain 10 parts of dimethylol methyl carbamate, 0.1

part of sulfurous acid, and 1 part of sodium bisulfite. Swatches of cotton printcloth were impregnated with the formulation, passed through squeeze rolls, dried at 60°C for 7 minutes, cured for 3 minutes at various temperatures from 80°C to 160°C, then washed and tumble dried.

Another aqueous formulation (100 parts) was prepared to contain 10 parts of dimethylol methyl carbamate, and 0.1 part of sulfurous acid but with no sodium bisulfite present. Swatches of cotton printcloth were then treated as above with this formulation.

All of the treated fabrics were tested for wrinkle recovery angles and for breaking strength (according to the procedure of the American Society for Testing and Materials: Method D1682-64).

The values of strength were plotted graphically as a function of wrinkle recovery for each treatment. From these plotted prints, a curve was drawn for the series of treatments with sodium bisulfite and another curve was drawn for those without sodium bisulfite. A comparison was made of breaking strengths for each type of treatment (treatment formulations with sodium bisulfite and treatment formulations without sodium bisulfite) at various levels of wrinkle recovery. These results are tabulated in Table II.

TABLE II

Wrinkle Recovery Angle (Warp + Filling), deg.	Breaking Strength, lbs.		% Increase in Strength with NaHSO ₃ in treatment formulation
	Treatments with NaHSO ₃	Treatments without NaHSO ₃	
240	37.5	35.5	5.5
250	34.8	32.5	7.0
260	32.2	29.7	8.5
275	26.6	22.0	21.0

It is obvious that addition of sodium bisulfite to a treatment formulation containing dimethylol methyl carbamate and sulfurous acid resulted in improvement in breaking strength of the finished fabrics at all levels of wrinkle recovery from 240° up. It was surprising to learn that the strength improvement was greatest at the higher levels of wrinkle resistance.

EXAMPLE 3

Three aqueous formulations (100 parts each) were prepared, each containing 10 parts of dimethylol methyl carbamate, 0.1 part of sulfurous acid, and 0.0, 0.3, and 0.5 part of sodium bisulfite, respectively. Cotton printcloth was treated with these formulations as in Example 1. Durable press appearance after tumble drying, as determined by the procedure of the American Association of Textile Chemists and Colorists, AATCC Test Method 124-1967 (AATCC Technical Manual, Volume 46, pages 177-8, 1970) and breaking strength of fabrics are shown in Table III.

TABLE III

% NaHSO ₃ in Treatment Formulation	Durable Press Appearance After Tumble Drying	Breaking Strength, lbs.
0.0	4.4	22.2
0.3	4.0	27.6
0.5	4.0	31.0

From these results it is seen that 0.3–0.5 part of sodium bisulfite are effective in giving strength improvement with high durable press ratings.

EXAMPLE 4

Four aqueous formulations (100 parts each) were prepared containing 15 parts of dimethylol methyl carbamate, 0.2 part of sulfurous acid, and 0.0, 0.3, 0.5, and 1 part of sodium bisulfite, respectively. Swatches of cotton printcloth were impregnated with the formulations, squeezed to about 100 percent wet pickup, then cured for 2.5 minutes at 100°C without predrying. This treatment technique is commonly referred to as mild cure finishing (cf. Textile Chemist and Colorist, Volume 2, pages 337–340, September 23, 1970). After washing and drying the treated fabrics, samples were analyzed for nitrogen and tested for breaking strength and wrinkle recovery angles. Results are given in Table IV.

TABLE IV

% NaHSO ₃ in Treatment Formulation	Nitrogen Content %	Breaking Strength lbs.	Wrinkle Recovery Angle (Warp + Filling), deg.
0.0	1.34	21.6	283
0.3	1.34	22.4	287
0.5	1.34	22.4	282
1.0	1.31	22.7	278

At the relatively low curing temperature of 100°C, sodium bisulfite is obviously beneficial to the strength of the fabric finished with dimethylol methyl carbamate. It is also evident that with 0.2 part of sulfurous acid and 15 parts of dimethylol methyl carbamate there is no reduction in reaction efficiency, as exemplified by nitrogen content, in the presence of sodium bisulfite.

EXAMPLE 5

Four aqueous formulations (100 parts each) were prepared containing 10 parts of dimethylol methyl carbamate, 0.15 part of sulfurous acid and 0.0, 0.3, 0.5, and 1 part of sodium bisulfite, respectively. Swatches of cotton printcloth were impregnated with these formulations and squeezed by rolls to obtain about 90 percent wet pickup of the formulation on the fabric. The fabrics were dried at 60°C for 7 minutes and cured at 140°C for 3 minutes. Residual chemicals were removed by washing and the fabrics were tumbled dried. Fabric properties are shown in Table V.

TABLE V

% NaHSO ₃ in Treatment Formulation	Breaking Strength lbs.	% Increase in Strength with NaHSO ₃ in Treatment Formulation	Wrinkle Recovery Angle (Warp + Filling), deg.
0.0	19.9	—	285
0.3	20.7	4	283
0.5	22.9	15	282
1.0	27.3	37	284

The significant improvement in breaking strength with increased amounts of sodium bisulfite in these formulations is surprisingly large at this curing tempera-

ture of 140°C. It is also surprising to find that there is no loss in wrinkle recovery angle along with the increase in strength.

We claim:

1. An improved process in the treatment of cellulose-containing fabrics with a methylolated carbamate-sulfurous acid formulation which process comprises adding a minor amount of sodium bisulfite to said formulation, impregnating the cellulose-containing textile with said formulation and curing the impregnated fabric to impart durable press properties with improved strength-to-wrinkle recovery relationship to the treated fabric.

2. The process of claim 1 wherein every 100 parts by weight of the methylolated carbamate-sulfurous acid formulation contains about from 0.3 to 1.0 part by weight of sodium bisulfite.

3. The process of claim 1 wherein the methylolated carbamate of the methylolated carbamate-sulfurous acid formulation is dimethylol methyl carbamate.

4. A process for treating cellulose-containing textiles to impart durable press properties with an improved strength-to-wrinkle recovery relationship, the process comprising:

a. adding a sufficient quantity of sodium bisulfite to a methylolated carbamate-sulfurous acid formulation so that in every 100 parts by weight of the formulation there is about from 10 to 15 parts by weight of a methylolated carbamate, about from 0.1 to 0.2 part by weight of sulfurous acid, and about from 0.3 to 1 part by weight of sodium bisulfite;

b. impregnating a cellulose-containing textile with a formulation from (a); and

c. curing the wet impregnated textile for about from 2 to 4 minutes at about 100° C. and washing and drying the cured textile.

5. A process for treating cellulose-containing textiles to impart durable press properties with an improved strength-to-wrinkle recovery relationship, the process comprising:

a. adding a sufficient quantity of sodium bisulfite to a methylolated carbamate-sulfurous acid formulation so that in every 100 parts by weight of the formulation there is about from 10 to 15 parts by weight of a methylolated carbamate, about from 0.1 to 0.2 parts by weight of sulfurous acid, and about from 0.3 to 1 part by weight of sodium bisulfite;

b. impregnating a cellulose-containing textile with a formulation from step (a);

c. drying the wet impregnated textile for about seven minutes at about from 60° C. and

d. curing the dry impregnated textile for about 3 minutes at about from 80° to 160° C. and washing and drying the cured textile.

6. A cellulosic fabric prepared by the process of claim 5, characterized by an improved strength-to-wrinkle recovery relationship with respect to a control fabric treated with an identical formulation to that used in claim 5 except for the omission of sodium bisulfite.

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