United States Patent Office 3,529,925 Patented Sept. 22, 1970

3,529,925

PROCESS FOR INTERFIBER BONDING OF CELLULOSIC FIBROUS WEBS

Berwyn B. Thomas and Judson H. Holloway, Shelton, Wash., assignors to ITT Rayonier Incorporated, a corporation of Delaware

No Drawing. Filed Sept. 25, 1967, Ser. No. 670,404
Int. Cl. D06m 1/00; D04h 1/06, 1/50
U.S. Cl. 8—118 8 Claims

ABSTRACT OF THE DISCLOSURE

The interfiber bonding of the fibers of cellulosic fibrous webs, such as papers and textiles, is effected by treating the web with a solution of dimethyl sulfoxide containing from about 3 to 20% by weight nitrogen dioxide under carefully controlled and coordinated conditions of time, temperature, and nitrogen dioxide content of the solution. A wide variety of parchmentized or vulcanized products having increased wet strength and dimensional stability and if desired reduced porosity are obtained.

BACKGROUND OF THE INVENTION

The present invention relates to a new process for the interfiber bonding of such cellulosic fibrous webs as paper and textiles. The process of the invention is particularly applicable to the production of paper having increased wet strength and to the production of vegetable parchments from parchment paper stock.

In the absence of special treatment to increase its wet strength, ordinary paper has very little tensile strength when wet. To improve the wet strength of paper so that it can be used, for example, in the manufacture of tea bags or paper towels and the like, it is common practice to incorporate in the paper web, or to coat the paper web with a nitrogenous resinous material, or cellulose acetate, or cellulose regenerated from viscose solution, or vinyl acetate and vinyl chloride copolymers, and the like. Although high wet strength papers can be produced by this procedure that are suitable for most applications, the wet strength of the paper is the result of the addition of extra material to the cellulosic paper fibers.

Moreover, at the present time practically all commercial cellulosic fiber-bonding operations, such as parchmentizing and vulcanizing, are based on the use of either concentrated sulfuric acid or zinc chloride as swelling agents for the cellulose. Both of these swelling agents, however, are strong reagents that not only dissolve the cellulose but also have a tendency to react with and destroy the cellulose. The adverse effects are frequently hard to control, and residual reagents and by-products are difficult to remove from the finished parchment or the vulcanized fibers.

It has recently been discovered that cellulose will dissolve in a solvent consisting of dimethyl sulfoxide containing up to about 35% by weight nitrogen dioxide to form clear solutions of cellulose that are substantially free of cellulose fibers. The solution of cellulose in this solvent is described in U.S. Pat. 3,236,669 issued Feb. 22, 1966, to Williams. We have carried out an intensive independent investigation of the formation and properties of such cellulosic solutions with particular reference to the preparation of solutions from which cellulose can be regenerated in the form of films or filaments. In the

course of our investigations, we made the unexpected and surprising discovery that by careful control of certain reaction conditions cellulosic fibrous webs, such as paper and textiles, can be treated with a dimethyl sulfoxide and nitrogen dioxide solution to effect interfiber bonding of the cellulosic fibers of the web without the destruction thereof. Moreover, we have made the further discoveries that cellulosic fibrous webs treated in accordance with our process have greatly increased wet strength, and that a parchmentized paper product can be produced without the limitations and difficulties encountered in the aforementioned conventional wet strengthing and parchmentizing procedures.

SUMMARY OF THE INVENTION

As a result of the aforementioned investigations and discoveries we have devised a new process for the interfiber bonding of cellulosic fiber webs which comprises treating the cellulosic fiber web with a solution of dimethyl sulfoxide (hereinafter referred to as DMSO for convenience) containing from about 3% to 30% by weight nitrogen dioxide (NO_2) in the presence of from about 0.2 to 1.0% by weight water. The treatment should be carried out at a temperature of from about 40° to 80° F. for a period of from about 10 to 300 seconds, the required time of treatment increasing within said limits as the NO_2 concentration of the solution increases and as the treatment temperature decreases. The thus treated cellulosic fibrous web is then removed from contact with the DMSO-NO_2 solution, and the web is washed to remove the solution and then is dried to obtain a product having high wet strength. If the fibers are compacted while in contact with the DMSO-NO_2 solution the finished paper can be made low in porosity. A highly porous paper, if not compacted, can be increased in wet strength without loss of its porosity. The optimum length of time for the treatment of the fibrous web depends not only upon the concentration of NO_2 in the DMSO solution and the temperature of this solution but also upon the nature of the web being treated and the type of product being produced. For example, to obtain optimum increase in wet strength and decrease in porosity a typical parchment paper stock is treated in accordance with our invention for about 120 seconds with a DMSO solution containing about 15% by weight NO_2 at a temperature of about 60° F. Any increase (or decrease) from said median concentration of 15% NO_2, or any decrease (or increase) from said median temperature of 60° F., should be accompanied by a corresponding increase (or decrease) in said median time of 120 seconds. Although the thus treated cellulosic web normally requires no further treatment other than washing and drying, it is sometimes desirable to press or compact the treated web prior to washing the web in order to obtain a more tightly bonded and less porous product.

DETAILED DESCRIPTION

The cellulosic fibrous webs that may be treated in accordance with our new process include such relatively thin and porous webs as the paper stock employed in the manufacture of tea bags and the like, and such relatively thick and compact webs as the paper stock employed in the manufacture of vegetable parchment. Woven or nonwoven cellulose (i.e. cotton or rayon) textiles may also be treated in accordance with the practice of our invention to enhance the wet strength and stiffness and to re-

duce the porosity of the finished textile product. In all cases, treatment of the cellulosic fibrous webs with a solution of NO_2 in DMSO under the conditions herein specified results in the creation of interfiber bonds between the individual fibers of cellulose. The interfiber bonding is due, we believe, to the swelling and softening of the individual fibers as a result of the treatment with the aforesaid solution, the increased contact between fibers while swollen, and the deswelling of the bonded fibers during the washing and drying steps of the process.

The finished cellulosic fibrous webs will, when treated in accordance with the practice of our invention, have increased wet strength, increased dimensional stability and stiffness and, if desired, decreased porosity as hereinafter more fully described.

Pure DMSO is a clear, colorless hygroscopic liquid having a boiling point of 189° C. and a melting point of 18.5° C. at atmospheric pressure. At ambient temperature and atmospheric pressure it will dissolve up to about 30% by weight of gaseous nitrogen dioxide to form a hydroscopic dark brown liquid of relatively low viscosity. The NO_2 and DMSO solution used in the practice of our invention is prepared by bubbling gaseous NO_2 into liquid DMSO while excluding excess atmospheric moisture until a solution containing the desired concentration of NO_2 is obtained. Once formed, the solution is preferably used as soon as possible, but if storage is required, it is preferably cooled to about 10° C. in order to avoid undesirable evolution of NO_2, and the solution should be kept in a sealed container to exclude atmospheric moisture which it readily absorbs.

The cellulosic fibrous web is treated with the DMSO-NO_2 solution for the prescribed period of time, preferably by immersing the web in the solution, and then is washed with water or alcohol or some other liquid in which the treatment solution will dissolve and which is inert with respect to cellulose, and the washed web is dried in a conventional dryer to obtain the desired finished product. The cellulosic webs can be immersed in the treatment solution either batchwise in the form of relatively small individual sheets or continuously by the use of conventional continuous treatment apparatus which unrolls, treats, washes, dries, and re-rolls extended lengths of the web. Alternatively, the cellulosic web can be treated with the DMSO-NO_2 solution by padding the solution onto the web or otherwise impregnating the web with the solution for the required length of time.

Treatment of the cellulosic web with the DMSO-NO_2 solution followed by washing and drying of the treated web causes interfiber bonding of the cellulosic fibers of the web with consequent increase in the wet strength of the finished product. We have found that the interfiber bonding of the cellulose fibers can be further improved, and the density and imporosity of the product increased, by pressing or compacting the treated web prior to the washing and drying steps of our process. In the batch treatment of individual sheets of the web, each treated sheet removed from the DMSO-NO_2 solution is advantageously placed between sheets of an inert plastic film, such as Teflon, and the sheet is then passed through a pair of wringer rollers to effect the desired compaction of the wet sheet. The thus compacted sheet is then washed and dried in the usual manner. In a continuous operation, the roll compaction of the treated web is readily accomplished with existing continuous paper treatment apparatus. We have also found that for best results the treatment of the cellulosic web with the DMSO-NO_2 solution should be carried out in the presence of about 0.2 to 1.0% by weight water. The water may be present either in the solution or in the cellulosic web or in both. In practice it is preferred to maintain this small but critical amount of water present during the treatment step by pre-conditioning the cellulosic web in a humidifier-dryer so that the web contains about 4% to 8% moisture prior to treatment with the essentially anhydrous DMSO-NO_2 solution.

Our investigations have shown that the length of time of the treatment of the cellulosic web with the DMSO-NO_2 solution will, in general, be within the range of from about 10 to 300 seconds. Within this general range the time of treatment is dependent upon and must be coordinated with a number of variable factors including the concentration of NO_2 in the DMSO-NO_2 solution, the temperature at which the treatment is carried out, the nature of the cellulosic web being treated, and the type of product being prepared therefrom. As previously noted, the DMSO solution can contain from about 3% to 30% by weight NO_2, the higher concentrations of NO_2 paradoxically requiring longer periods of treatment to obtain the same degree of interfiber bonding for a given cellulosic web at a given temperature. We have also found that the interfiber bonding of the cellulosic web proceeds so slowly at temperatures below about 40° F. as to render the process impractical at such low temperatures, and we have further found that the interaction between the web and the solution proceeds so rapidly at temperatures in excess of about 80° F. as to make the process difficult to control at these elevated temperatures. Accordingly, the treatment of cellulosic fibrous webs in accordance with our invention requires that the web be treated with a DMSO-NO_2 solution containing between 3% to 30% by weight NO_2 for a period of time of between 10 to 300 seconds and at a temperature of between 40° to 80° F.

Our investigations have shown that the length of time required to effect the desired or optimum degree of treatment of a given cellulosic web is minimum at a relatively low concentration of NO_2 in the DMSO solution and then tends to increase as the concentration of nitrogen dioxide in the DMSO solution is increased. We have also found that an increase in the temperature of the solution has the effect of shortening the time required to effect the desired degree of treatment of the cellulosic web. That is to say, we have found that when the DMSO solution contains a relatively low concentration of NO_2 (for example, about 5% by weight NO_2) the time of treatment should be relatively short (say, from 10 to 30 seconds), whereas when the concentration of NO_2 in the solution is relatively high (for example, 20% to 30% by weight NO_2 the time of treatment is normally relatively much longer (say, from 4 to 5 minutes). Similarly, the treatment of a certain cellulosic paper stock with a 15% NO_2-DMSO solution might require 90 seconds to obtain the optimum degree of wet strength at a temperature of 60° F., whereas it might require 120 seconds to obtain the same degree of wet strength at 40° F. and only 30 seconds at 80° F.

Although the optimum time of treatment tends to increase roughly in proportion to the increase in NO_2 content of the DMSO solution and to decrease roughly in proportion to an increase in the temperature of the treatment, there is considerable latitude in the time of treatment, especially at the higher concentrations of NO_2 and in the middle and lower temperatures within the range specified. The time of treatment of a typical cellulosic web at various NO_2 concentrations and at various temperatures is illustrated in the following table:

TABLE I

	Treatment time (in seconds) at—		
NO_2 conc., percent by wt.	40° F.	60° F.	80° F
5	30–90	10–60	10–30
10	45–180	20–120	10–60
15	60–240	30–180	20–120
20	75–300	40–300	20–180
25	90–300	50–300	30–240
30	120–300	60–300	30–300

EXAMPLE 1

Lightweight tea bag paper stock was obtained from the manufacturer (C. H. Dexter) and samples of this paper were treated in accordance with the practice of our in-

vention. This tea bag paper stock normally is bonded by impregnation with diluted viscose solution and regeneration of the cellulose from the viscose to obtain a finished paper from which tea bags can be made. However, the paper stock employed in this example did not have the aforesaid viscose impregnation applied thereto. Samples of the "unbonded" tea bag paper stock were treated with a 10% DMSO–NO_2 solution at ambient temperature for periods of 10 and 20 seconds, and additional samples were treated with a 20% DMSO–NO_2 solution for periods of 15, 30, and 45 seconds. The wet strength of the treated paper as compared with the wet strength of the control sample is reported in the following table:

TABLE II.—TREATMENT OF TEA BAG PAPER WITH DMSO-NO_2 (UNBONDED LIGHTWEIGHT PAPER

	Tensile break length [1]		Stretch dry, percent
	Dry, m.	Wet, m.	
Control:			
No soak	1,715	0	0
Treated with 10% DMSO-NO_2:			
Soaked 10 sec	2,860	840	8.1
Soaked 20 sec	2,960	1,080	7.9
Treated with 20% DMSO-NO_2:			
Soaked 15 sec	2,540	750	7.9
Soaked 30 sec	2,560	700	7.6
Soaked 45 sec	2,430	1,050	7.6

[1] Tested gross direction.

EXAMPLE 2

Heavyweight tea bag paper stock was obtained from the manufacturer (C. H. Dexter) and samples of this paper were treated with 10%, 20%, and 30% DMSO–NO_2 solutions for varying periods of time as in Example 1. Some of the treated samples were washed with water and dried without any other treatment as in Example 1. Other samples were rolled with a hand roller to compact the treated fibers partially before being washed and dried. The wet strength of the treated paper stock, both rolled and not rolled, as compared with the wet strength of the untreated "unbonded" control paper is reported in the following table:

TABLE III.—TREATMENT OF TEA BAG PAPER WITH DMSO-NO_2 (UNBONDED HEAVYWEIGHT PAPER)

	Tensile break length [1]		Stretch dry, percent
	Dry, m.	Wet, m.	
Control: No soak	2,520	230	
Treated with 10% DMSO–NO_2 and rolled:			
Soaked 15 sec	5,760	825	
Treated with 20% DMSO–NO_2, not rolled:			
Soaked 30 sec	2,940	320	2.0
Soaked 60 sec	2,710	410	1.4
Soaked 120 sec	2,550	410	1.0
Treated with 20% DMSO–NO_2 and rolled:			
Soaked 30 sec	2,640	610	1.3
Soaked 60 sec	2,960	610	2.0
Soaked 90 sec	2,980	490	2.0
Soaked 120 sec	2,770	680	1.4
Treated with 30% DMSO–NO_2 and rolled:			
Soaked 30 sec	2,280	390	1.9
Soaked 60 sec	2,150	390	1.7
Soaked 120 sec	1,970	370	1.4
Soaked 180 sec	1,800	370	1.0
Soaked 300 sec	1,580	330	0.8

[1] Tested goss direction.

EXAMPLE 3

Paper stock intended to be used in a zinc chloride vulcanizing process was obtained from the manufacturer (National Vulcanized Fibre Company). The paper stock was of low strength and was unsized. Samples of the paper stock 6 x 7 inches were placed in a clamp of stainless steel and immersed for specified periods of time up to 300 seconds in DMSO–NO_2 solutions of specified concentrations. The treatment of the paper stock was carried out at ambient temperature (25° C.). The treated sheets were not compacted by rollers prior to being washed. The Mullen bursting strength, the wet and dry tensile strength, and other properties of the treated paper as compared with the corresponding properties of the control sample are reported in the following table:

TABLE IV.—TREATMENT OF VULCANIZING PAPER WITH DMSO-NO_2 DIP AT 25° C. (TREATED SHEETS NOT ROLLED)

Dip time, sec.	Mullen	Machine direction tensile		Dry stretch, percent
		Dry, m.	Wet, m.	
Control samples—No DMSO treatment				
Dry	19	2,160	180	1.5
Wetted, redried	20	2,090	210	1.7
Dipped in DMSO with 0% NO_2				
15	18	1,970	180	1.7
30	17	1,960	180	1.8
45	17	1,960	160	1.8
Dipped in DMSO with 10% NO_2				
30	27	2,620	330	1.7
60	53	4,010	910	2.2
120	46	2,800	770	1.9
180	35	2,250	620	2.2
240	Sheets too weak to handle			
Dipped in DMSO with 15% NO_2				
60	27	2,060	300	1.1
180	33	2,850	300	1.8
Dipped with DMSO with 20% NO_2				
15	33	3,020	540	2.5
30	38	3,230	740	2.4
45	42	3,680	800	2.7
60	48	3,960	980	3.0
90	52	4,530	1,170	3.1
120	57	4,780	1,190	3.7
150	54	4,640	1,320	3.0
180	68	4,780	1,620	3.9
210	60	4,880	1,390	3.0
240	55	3,550	1,110	3.1

EXAMPLE 4

Samples of the same vulcanizing paper stock empolyed in Example 3 were treated with DMSO-NO_2 solutions at various concentrations and for various periods of time as before. The treated sheets were rolled after being

immersed in the solution in order to compact the treated fibers. The results of this treatment are reported in the following table:

TABLE V.—TREATMENT OF VULCANIZING PAPER WITH MDSO-NO_2 DIP AT 25° C. (TREATED SHEETS ROLLED AFTER DIP)

Dip time, sec.	Mullen	Machine direction tensile		Dry stretch, percent
		Dry, m.	Wet, m.	
Dipped in DMSO with 0% NO_2				
30	17	1,880	160	1.8
45	17	1,730	160	1.7
Dipped in DMSO with 5% NO_2				
30	19	1,930	180	1.5
60	17	1,830	160	1.6
120	16	1,810	160	1.6
180	17	1,850	160	1.4
300	14	1,720	140	1.4
Dipped in DMSO with 10% NO_2				
30	32	2,870	460	2.0
60	46	4,000	840	2.9
90	52	4,340	860	3.0
120	15	1,430	550	1.6
Dipped in DMSO with 15% NO_2				
30	22	2,330	340	1.8
60	31	2,570	430	1.7
120	51	3,720	970	1.9
180	64	4,280	1,070	2.2
240	75	4,790	2,050	2.3
300	Sheets too weak to handle			
Dipped in DMSO with 20% NO_2				
30	42	3,980	840	3.5
60	59	5,160	1,650	3.2
120	81	5,320	1,850	3.8
180	95	6,850	2,930	5.6
300	108	6,760	2,780	5.5

EXAMPLE 5

A quantity of waterleaf paper stock intended to be used in the manufacture of vegetable parchment by the sulfuric acid process was obtained from the manufacturer (Paterson Parchment Company). The samples were placed in wire holders and were dipped for measured periods of time in a solution of DMSO containing the desired quantity of nitrogen dioxide. Each sheet of treated paper was then removed from the solution, placed between two thin sheets of Teflon, and passed through wringer rolls. The rolled sheet was then washed with water for 10 to 20 minutes before drying at room temperature. The temperature of the DMSO-NO_2 solution was about 70° F., except for one sample treated at 80° F. and one sample treated at 86° F. The sample treated at 86° F. was too soft to handle. The results of this treatment are reported in Table VI which follows.

The process of this invention may be used also to make the product known as vulcanized fiber, in which a plurality of paper layers are pressed together while in the swollen condition and form an adherent mass after the swelling agent has been washed out. To make this product, paper sheets are impregnated either continuously or separately with the DMSO-NO_2 solution, then brought together by squeezing rolls. The swollen fibers of adjoining sheets are thus brought into contact and form bonds similar to those between fibers in the same sheet. When the combined board is immersed in water and washed these bonds unite the layers of paper into a dense, hard, stiff board usable for many industrial products.

Application of the swelling action of these DMSO-NO_2 solutions to textile fabrics is illustrated as follows: A piece of thin padding consisting of combed cotton fibers between scrim facings was treated in the manner described above for paper products. After washing and drying it was found to be stiffened and compacted to a form suitable for linings in the construction of heavy clothing. This bonding and stiffening are resistant to laundering and other handling operations.

TABLE VI.—TREATMENT OF PARCHMENT PAPER STOCK WITH DMSO-NO_2 ROLLED AFTER DIP (TEMPERATURE 70° F.)

Dip time, sec.	Mullen	Cross direction tensile strength		Dry stretch, percent	Air resistance
		Dry, m.	Wet, m.		
Paper as received					
0	80	4,440	220	3.3	35
Wash with water only					
0	86	4,450	300	4.0	40
Treated with DMSO (no NO_2)					
60	90	5,080	340	3.3	34
180	92	4,870	310	2.8	34
Treated with 3% DMSO-NO_2					
20	97	4,890	310	3.6	46
40	101	5,070	350	3.9	46
60	109	5,150	325	3.4	45
90	117	6,080	380	4.0	100
120	Sheets too soft to handle				
Treated with 6% DMSO-NO_2					
10	114	5,150	500	4.5	400
20	134	5,660	625	4.6	4,270
30	152	6,780	1,055	4.7	10,000
40	Sheets too soft to handle				
Treated with 10% DMSO-NO_2					
10	103	5,160	545	4.0	87
20	137	5,650	755	3.2	5,580
40	125	6,260	1,060	4.8	6,800
60	166	7,480	2,480	2.4	20,000+
90	Sheets too soft to handle				
40 [1]	165	7,350	2,020 00005.6		20,000+
Treated with 15% DMSO-NO_2					
10	104	4,880	450	3.8	67
20	109	5,660	670	4.3	200
40	146	7,230	1,980	5.5	5,890
60	151	6,680	2,420	3.6	20,000+
120	159	7,080	2,670	5.7	20,000+
180	98	5,780	1,540	2.7	500
300	Sheets too soft to handle				

[1] Temperature, 80° F.

We claim:

1. Process for the interfiber bonding of cellulosic fiber webs which comprises:
   - contacting the cellulosic fiber web with a solution of dimethyl sulfoxide containing from about 3% to 30% by weight nitrogen dioxide at a temperature of from about 40° to 80° F. for a period of time of from about 10 to 300 seconds,
   - removing the thus treated cellulosic fiber web from contact with the dimethyl sulfoxide and nitrogen dioxide solution,
   - washing the web to remove said solution, and
   - drying said cellulosic fibrous web to obtain a product having high wet strength.

2. The process according to claim 1 in which the cellulosic fibrous web is contacted with the dimethyl sulfoxide and nitrogen dioxide solution in the presence of from about 0.2 to 1.0% of water, based on the weight of said solution.

3. The process according to claim 1 wherein the median time of treatment is about 60 to 90 seconds, the median nitrogen dioxide content of the solution is about 10–15% by weight and the median temperature is about 60° to 70° F. and wherein the time of treatment varies directly with the NO_2 concentration of the solution and inversly with the temperature of treatment.

4. The process according to claim 1 in which the treated cellulosic fiber web is mechanically compacted prior to washing the web to remove the treatment solution therefrom.

5. The process according to claim 4 in which the cellulosic fiber web is parchment paper stock and in which the treated, washed, and dried product is a high wet strength and low porosity vegetable parchment paper.

6. The process according to claim 1 in which the cellulosic fiber web is an unbonded tea bag stock and in which the treated, washed and dried product is a high wet strength and high porosity tea bag paper.

7. The process according to claim 1 in which the cellulosic fiber web is vulcanizing paper stock and in which a plurality of layers of said paper are mechanically compacted together prior to washing the combined web to remove the treatment solution therefrom.

8. The process according to claim 1 in which the cellulosic web consists at least partially of a woven textile fabric.

References Cited

UNITED STATES PATENTS

3,236,669	2/1966	Williams	8—120 X
3,357,878	12/1967	Newman	161—150

GEORGE F. LESMES, Primary Examiner

J. CANNON, Assistant Examiner

U.S. Cl. X.R.

8—119, 120; 11—77.1; 156—306; 161—150, 170

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,529,925 Dated September 22, 1970

Inventor(s) BERWYN B. THOMAS and JUDSON H. HOLLOWAY

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 15, "(UNBONDED LIGHTWEIGHT PAPER" should read -- (UNBONDED LIGHTWEIGHT PAPER) --

Column 5, line 28, Table II, Note 1, "Tested gross direction" should read -- Tested cross direction"

Column 5, line 64, Table III, Note 1, "Tested goss direction" should read -- Tested cross direction --

Column 6, line 44, Table IV, last line of Table, next to last column, "1,110" should read -- 1,100 --

Column 7, line 5, "MDSO-NO_2" should be -- DMSO-NO_2 --

Column 8, line 31, 5th column, "00005.6" should be -- 5.6 --, and should be in column alignment.

SIGNED AND
SEALED
DEC 15 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents