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3,674,632

PROCESS FOR MOISTURE STABILIZING CELLULOSIC SHEET MATERIAL USING A POLYOXY-ALKYLENE GLYCOL AND A POLYOXY-ETHYLENE-OXYPROPYLENE GLYCOL BLOCK POLYMER

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12,172/68

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U.S. Cl. 162—168

12 Claims

ABSTRACT OF THE DISCLOSURE

A moisture-stabilizing composition is provided for cellulosic sheet material, such as paper, comprising a polyoxyalkylene glycol as a moisture-stabilizer, and a polyoxyethylene-oxypropylene glycol block polymer, to enhance the rate of absorption of the polyoxyalkylene glycol in the sheet material. A process for moisture-stabilizing cellulosic sheet material also is provided, which comprises incorporating such a composition in the cellulosic material.

This invention relates to moisture-stabilizing composition for cellulosic sheet materials, and to a process for stabilizing cellulosic sheet materials against changes in physical dimensions with variations in air humidity, and more particularly to a moisture-stabilizing composition comprising a polyoxyalkylene-glycol moisture stabilizer, and a polyoxyethylene oxypropylene glycol block polymer, enhancing the rate of absorption of the composition, and to a process for enhancing the moisture stability of cellulosic sheet material by applying such a composition thereto.

Variations in air humidity pose a difficult problem in coating and processing cellulosic sheet material in automatic machinery. Variations in moisture content of the material result from variations in air humidity and these variations result in shrinkage and swelling of the material. Different portions of the material do not always shrink and swell to the same extent, resulting in wrinkles, blistering, and curling, as a consequence of which the material does not lie flat.

The problems presented by lack of moisture stability are particularly apparent in the case of paper which must be fed from a pile into a high speed machine, such as, for example, an offset printing machine. If such paper does not lie perfectly flat, it can jam or wrinkle in the machine, with a resulting fault in the processing, and possibly even a paper jam, and stoppage of the machinery.

An especially severe problem is presented by shelf-lining paper, which must lie absolutely flat to satisfy the user. Such papers can be applied on different surfaces with the help of elastic adhesives, and variations in the air humidity resulting in variations in the moisture content of the paper can cause the adhesive layer to loosen and become detached from the paper, as a result of wrinkling, blistering, or curling of the paper.

Variations in the moisture content of photographic paper, Ozalid paper, Xerox paper, and copy paper for the Thermofax process result in defective copies, distorted images, and possible stoppage of the equipment, due to paper jams.

In an attempt to alleviate or overcome the problem, paper and other cellulosic sheet material have been treated with moisture-stabilizing agents. It is known that low molecular weight polyalcohols, such as ethylene glycol and glycerol, can inhibit variations in moisture content of

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cellulosic sheet material. Such polyols are relatively quickly absorbed in a large amount within a short space of time, but the difficulty is that these polyols are rather volatile, and soon are lost from the paper by evaporation, after which there is, of course, no longer any moisture stability.

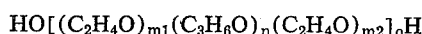
High molecular weight polyols, such as the polyoxyalkylene glycols, are less volatile. However, these materials because of their high molecular weight are only slowly absorbed in the cellulosic sheet material, and consequently they are not very satisfactory, unless they are applied to the paper long in advance of processing. There simply is not time, when the paper is being processed through high speed machinery, to apply the polyoxyalkylene glycol or other high molecular weight material and wait for it to be absorbed by the paper in a sufficient amount to impart the desired degree of moisture stability. A low molecular weight polyol, in admixture with a high molecular weight polyol, such as described in U.S. Pat. No. 3,301,680, improves the rate of absorption, but the mixture is nonetheless too slowly absorbed in the paper to be used in a glue press, where, for instance, the moisture content of the cellulosic sheet material is rather small, of the order of 5 to 15%, and the rate of treatment in the apparatus is quite high.

In accordance with the instant invention, a moisture stabilizing composition is provided that is characterized by a high rate of absorption in cellulosic fibrous material, and a low volatility. As a result, this composition can be applied to cellulosic sheet material in high speed machinery, with assurance that it will be absorbed quickly enough and in large enough amount to impart the degree of moisture stability desired for later processing of the sheet. It can also be applied to the cellulosic fibrous material before it is put in sheet form, such as to the cellulosic pulp, to the cellulosic fibers in the beater or in the furnish, or at any stage in the processing prior to or during sheet formation. In this event, the polyoxyethylene-oxypropylene glycol block polymer has the function of enhancing the moisture stabilizing effectiveness of the polyoxyalkylene glycol. Furthermore the strength of the treated paper will be greater than if the composition is added to cellulose material in sheet form.

Thus, in the process of the invention, the composition of polyoxyalkylene glycol moisture stabilizer and polyoxyethylene-oxypropylene glycol block polymer is incorporated in the cellulosic fibrous material, in the course of which the block polymer both enhances the rate of absorption of the polyoxyalkylene glycol and also may enhance its moisture stabilizing effectiveness. After this, the sheet material is found to have good moisture stability.

The moisture stabilizing compositions of the invention are based on a polyoxyalkylene glycol as the moisture-stabilizing agent, and a polyoxyethylene-oxypropylene glycol block polymer to enhance the rate of penetration of the polyoxyalkylene glycol in the cellulosic sheet material, and in some cases enhance its moisture-stabilizing effectiveness. The polyoxyalkylene glycol block polymer, although itself a polyoxyalkylene glycol, is rather different in structure, and has very different and synergizing effectiveness.

The polyoxyethylene-oxypropylene glycol block polymer has a central core of a polyoxypropylene glycol polymer, to one or both the terminal hydroxyls of which are attached polyoxyethylene block polymer units, themselves terminating in hydroxyl groups. These block polymers are known materials, and are described in U.S. Pat. No. 2,674,619, issued Apr. 6, 1954, to L. G. Lundsted. They are defined by the general formula:



m_1 and m_2 have values such that the oxyethylene groups constitute from 20 to 90% by weight of the compound, and either m_1 or m_2 can be zero. n is an integer corresponding to the number of C_2H_4O units, and the value of n is such that the molecular weight of the compound, exclusive of the oxyethylene units, is at least 900, as determined by hydroxyl number. p is an integer of one or more.

These block polymers are prepared by condensation of ethylene oxide with a polyoxypropylene glycol of at least 900 molecular weight. Other details on the preparation and characteristics of these compounds are found in U.S. Pat. No. 2,674,619.

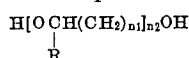
In the preferred copolymers of the invention, the sum of m_1 and m_2 is within the range from 2 to 20, n is a number within the range from 1 to 25, p is a number within the range from 1 to 5, and the average molecular weight of the block polymer is within the range from about 1000 to about 5000.

Block polymers of this type are available in commerce under the trademarks Pluronic and Berol. The Pluronic are identified by a letter L, P or F, and a number. The letter identifies the physical form, L for liquids, P for pastes, and S for solid forms hard enough to be flaked. The first digit or digits identify the typical molecular weight of the polyoxypropylene base, and the last digit indicates the approximate percent of ethylene oxide in the total molecule. Available Pluronic that can be used in the compositions of the invention and their characteristics are shown in Table I.

TABLE I

Molecular weight	Percent polyoxyethylene in the total molecule							
	10	20	30	40	50	60	70	80
950	L31				L35			F38
1,200		L42	L43	L44				
1,450								
1,750	L61	L62	L63	L64	P65			F78
2,050		L72			P75		F77	
2,250	L81			P84	P85		F87	F88
2,750		L92		P94				F98
3,250	L101		P103	P104	P105			F108
3,625								
4,000	L121	L122	P123					F127

The polyoxyalkylene glycols that are employed as moisture stabilizing agents correspond to the general formula:



In this formula, R is a hydrogen or methyl, n_1 has a value ranging from 1 to about 3, and n_2 has a value within the range from about 5 to about 350. The polyoxyalkylene glycol should be water-soluble, and can have a molecular weight within the range from about 150 to about 10,000.

Exemplary polyoxyalkylene glycols are polyoxyethylene glycol, polyoxy-1,2-propylene glycol, polyoxy-1,2-butylen glycol, polyoxy-1,3-propylene glycol, polyoxy-1,4-butylen glycol, and polyoxy-1,3-butylen glycol.

The relative proportions of the polyoxyalkylene glycol and the polyoxyalkylene glycol block polymer are in no way critical. However, there is no reason to employ more of the block polymer than is necessary to sufficiently enhance to the desired degree the rate of penetration of the cellulosic sheet material by the polyoxyalkylene glycol. In general, a considerably enhanced rate of absorption is observed when the amount of block polymer is as small as 1.0% by weight of the polyoxyalkylene glycol. The effect increases as the amount has increased, and reaches a practical maximum at approximately 2.5 to 20% by weight of the polyoxyalkylene glycol. Thereafter, although larger amounts can be used, the increase in the rate of absorption is not commensurate with the additional amount of polyoxyalkylene glycol block polymer that is added, and consequently such amounts are wasteful, although they can be used, if desired, in order to take ad-

vantage of other properties of the polyoxyalkylene glycol block polymer.

The invention is applicable to cellulosic sheet material of all kinds. It is of particular application to paper, paperboard, corrugated paperboard, Kraft paper, Kraft liner board, cardboard, and carton board. The type of cellulosic material can be widely varied also, and excellent effects will be found using papers of high rag content, as well as papers composed entirely of cellulosic pulp. Cellulosic sheet material derived from any pulp can be improved, including spruce pulp, pinewood pulp, beech pulp, birch pulp, and other wood pulp. The material can be bleached or unbleached, as desired.

The composition of the invention is easily applied to the cellulosic sheet material from an aqueous solution. The concentration of the solution is chosen so as to give the desired amount of polyoxyalkylene glycol on the paper following the treatment. The composition can be applied by dipping or immersion, by spraying or by brushing, or by other conventional techniques, as will be apparent to those skilled in this art. If dipping or immersion is used, the cellulosic sheet material can be pressed or squeezed so as to reduce the amount of solution absorbed to the desired pick-up. If desired, cellulosic material can then be dried, at room temperature, or in an oven.

The moisture-stabilizing compositions of the invention can also be applied to the cellulosic material at any stage in the processing from pulp to sheet, such as in the pulp slurry or paper furnish, to the cellulosic fibers after sheet-forming, during or after dewatering and laydown or the Fourdrinier wire, before, during and after drying of the sheet and before, during or after pressing. They can also be applied in conjunction with other treatments, such as during sizing, pigmenting, coating, moisturizing or seasoning, or wet-strength treating. Thus, the compositions are quite versatile in their application. Their unusually high rate of absorption is however observed only when applied to cellulosic fibrous material in sheet or bulk form, and not of course when applied to aqueous suspensions or furnishes thereof.

It is possible using small amounts of the polyoxyalkylene glycol block polymer to increase the absorption rate of the polyoxyalkylene glycol by the cellulosic sheet material by from 1.5 to 2 or more times. Therefore, it is possible to treat the cellulosic sheet material while it is dry or wet. Moreover, a lesser amount of polyoxyalkylene glycol can be used to obtain the desired degree of moisture stability than when using compositions that do not contain the polyoxyalkylene glycol block polymer, and of course, the treating time can be very considerably shortened.

The effect of the polyoxyalkylene glycol block polymers of the invention is apparently unique, and is not displayed by other wetting agents or detergents. Such materials in combination with polyoxyalkylene glycols cause an undesired hygroscopicity and rewetting power in the cellulosic sheet material, and moreover do not give the noted increase in the rate of absorption in the polyoxyalkylene glycol by the sheet material.

The following examples in the opinion of the inventors represent preferred embodiments of their invention.

EXAMPLES 1 TO 3

A number of polyoxyethylene glycol moisture stabilizing compositions were tested, using paper sheet of unbleached quality, Dynapac extensible Clupac paper. The paper was dipped for two seconds in a 20% by weight aqueous solution of the polyoxyethylene glycol compositions shown in Table II below, after which excess solution was removed in a roll press. The sheets were allowed to dry for twenty-four hours in an oven held at 105° C. The sheets were air-conditioned weighed before and after the treatment, and the weights compared. The difference in weight is shown in Table II as the absorbed amount of polyethylene glycol, expressed in percent by weight of the dried paper.

TABLE II

Example number	Parts by weight					Absorption, percent	
	Water	Ethylene glycol	Block polymer Berol TVM 370*	Polyethylene glycol			
				400*	1,500*		4,000*
Control:							
A	35			65		9.1	
B		35		65		11.2	
1	33		2	65		18.2	
Control:							
C	35				65	8.6	
D		35			65	11.4	
2	33		2		65	19.6	
Control:							
E	35				65	10.2	
F		35			65	13.3	
3	33		2		65	19.6	

*A polyoxyethylene-oxypropylene glycol, molecular weight , containing per- cent ethylene oxide.

*molecular weight 400.

*molecular weight 1,500.

*molecular weight 4,000;

It is apparent from the data that the addition of the polyoxyethylene-oxypropylene glycol block polymer in Example 1 doubles the rate of absorption of the polyoxyethylene glycol 400, as compared to Control A, because twice the amount was absorbed in the same time. Ethylene glycol in Control B only very slightly increased the rate of absorption of polyoxyethylene glycol, in contrast. Similar results are shown in Example 2 for polyoxyethylene glycol 1500 as compared to Controls C and D, and in Example 3 for polyoxyethylene glycol 4000, as compared to Controls E and F. Thus, the benefits of the polyoxyethylene-oxypropylene glycol block polymer are evident from the data.

EXAMPLES 4 to 6

A similar series of experiments were carried out, measuring the time required for the paper sheet to become fully saturated with the aqueous treating solution by absorption from the surface of the solution. In this test, writing paper sheet of a surface-sized writing quality was tested, and the treating solutions were 20% by weight aqueous solution of the polyoxyethylene glycol compositions shown in Table III. The paper sheet being tested was placed on top of the surface of the solution, kept in a transparent pan. A light source was applied beneath the pan, consisting of a strong fluorescent tube, mounted behind an opal glass plate. Then, the time required for the paper to become fully saturated with the treating solution was noted, by observation from the top. The untreated paper immediately after placing on the surface of the solution transmits considerably more light than the fully saturated paper sheet. Thus, the time is measured from the time the sheet is placed on the surface of the solution until the light is no longer visible to the same extent, and undergoes no further diminution in intensity. After 120 seconds, if the paper was still not saturated, the test was discontinued and the result taken as over 120 seconds.

The results are shown in Table III.

TABLE III

Example number	Parts by weight						Time for absorption (seconds)
	Water	Ethylene glycol	Block polymer Berol TVM 370	Polyethylene glycol			
				400	1,500	4,000	
Control:							
G	35			65			>120
H		35		65			>120
4	33		2	65			3
Control:							
J	35				65		>120
K		35			65		>120
5	33		2		65		5
Control:							
L	35					65	>120
M		35				65	>120
6	33		2			65	4

It is evident from the data that in the case of each Control composition, more than 120 seconds was required for the paper to become fully saturated with the test solution. In contrast, when the polyoxyethylene-oxypropylene glycol block polymer was present in the composition, the absorption time ranged only from 3 to 5 seconds.

EXAMPLES 7 TO 20

Writing paper sheets of the same type as used in Examples 4 to 6 were tested according to the test procedure of Examples 4 to 6, using a wide range of proportions of the polyoxyethylene-oxypropylene glycol block polymer. The data obtained is shown in Table IV.

TABLE IV

Example No.	Parts by weight		Time of penetration (seconds)
	Polyethylene glycol 400	Block polymer Berol TVM 370	
Control N-----	100.0	0	>1800
7-----	99.5	0.5	>1800
8-----	99.0	1.0	600
9-----	98.5	1.5	150
10-----	98.0	2.0	10.7
11-----	97.5	2.5	5.6
12-----	97.0	3.0	4.1
13-----	96.5	3.5	3.0
14-----	96.0	4.0	2.2
15-----	95.5	4.5	1.8
16-----	95.0	5.0	1.4
17-----	94.5	5.5	1.1
18-----	94.0	6.0	0.9
19-----	93.5	6.5	0.7
20-----	93.0	7.0	0.6

It is evident that at proportions in excess of 1% by weight of the polyoxyethylene glycol, the polyoxyethylene-oxypropylene glycol block polymer gives a significant reduction in the time required for penetration of the sheet. Optimum results are obtained at from 2.5 to 7% by weight of the block polymer, where the difference in time is so small as to be almost insignificant. It is evident

that as the amount is increased from 4%, the reduction in the time required for penetration is rather small, and may not justify the use of the larger amount of block polymer (nearly double, 7%, in Example 20) except in very exceptional circumstances.

The addition of a polyoxyethylene glycol moisture stabilizing composition during different stages of the manufacture of paper on the paper machine was also tested. The paper manufactured during these tests was an MG grade. In both Examples 21 and 22, the moisture stabilizing composition was an aqueous solution of polyoxyethylene glycol 400 (97%) and Berol TVM 370 block polymer (3%). For each of Examples 21 and 22, the control samples (P and Q) were prepared in an identical manner, except for the substitution of plain water for the moisture stabilizing composition.

EXAMPLE 21

In the press part of the paper machine, when the paper had a dry content of about 30% (the second press), a 20% water solution of the moisture stabilizer composition, described above, was sprayed onto the upper press roll using a sprinkler tube fed by a proportioning pump.

EXAMPLE 22

In the size press of the paper machine, when the paper had a dry content of about 95%, the paper was treated with a 5% water solution of the moisture stabilizer composition, described above. The physical properties of the paper product for each Example were determined, and are tabulated in Table V, below.

The moisture stabilization of the paper was tested according to the following method:

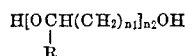
An elastic adhesive is applied on one side of samples of dry test sheets of the paper prepared according to the above examples. The paper sheets are mounted on a flat board plate. The test pieces are exposed to a 65% relative humidity during a period of 24 hours. The test sheets of Examples 21 and 22 showed no change in appearance following this exposure to the humid conditions. The controls P and Q, however, were blistered and showed surface unevenness.

TABLE V

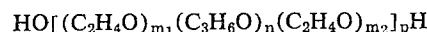
	Basis weight, g./m. ²	Thickness, mm.	Bulk, cm. ³ /g.	Burst factor	Polyalkylene glycol composition, percent
Press part trial:					
Control P.....	77.4	0.092	1.19	27.3	0
Example 21.....	76.5	0.092	1.20	29.5	1.2
Size press trial:					
Control Q.....	82.9	0.081	0.977	33.2	0
Example 22.....	80.9	0.078	0.964	24.1	1.1

Having regard to the foregoing disclosure, the following is claimed as the inventive and patentable embodiments thereof:

1. A process for increasing the rate of absorption and the moisture stabilizing effectiveness of polyoxyalkylene glycols in cellulosic fibrous material, which comprises incorporating in the cellulosic fibrous material a composition comprising a polyoxyalkylene glycol moisture stabilizer having the formula



wherein R is selected from the group consisting of hydrogen and methyl, n_1 has a value within the range from about 1 to about 3, and n_2 has a value within the range from about 5 to about 350, and a polyoxyethylene-oxypropylene glycol block polymer having the formula



wherein m_1 and m_2 have values such that the oxyethylene groups constitute from 20% to 90% by weight of the compound and either m_1 or m_2 can be zero, n is an integer corresponding to the number of $\text{C}_3\text{H}_6\text{O}$ units, and has a value such that the molecular weight of the compound exclusive of the oxyethylene units is at least 900 as determined by hydroxyl number, and p is an integer of one or more, the block polymer both enhancing the rate of absorption of the polyoxyalkylene glycol and also enhancing its moisture stabilizing effectiveness.

2. A process according to claim 1 in which the composition is applied to cellulosic sheet material.

3. A process according to claim 1 in which the composition is applied to paper by dipping in an aqueous solution of the composition.

4. A process according to claim 1 in which the composition is applied to cellulosic pulp.

5. A process according to claim 1 in which the composition is applied with other papermaking chemicals in the manufacture of paper.

6. A process according to claim 1, in which the composition is applied to paper during the sheet-forming, dewatering and couching on a paper machine.

7. A process according to claim 1, in which the composition is applied to paper in the pressing part of a paper machine.

8. A process according to claim 1 in which the composition is applied to paper in the drying part of a paper machine.

9. A process according to claim 1, in which the composition is applied to paper on the paper machine in connection with surface-sizing, pigmenting, or coating processes.

10. A process according to claim 1 in which the composition is applied to paper in connection with surface treatment in a paper machine.

11. A process according to claim 1, in which the composition is applied to paper in connection with its moistening.

12. A process according to claim 1, in which the composition is applied to paper in connection with and by means of surface-sizing pigmenting, or coating processes in separate operations outside the paper machine.

References Cited

UNITED STATES PATENTS

2,674,619 4/1954 Lundsted 252—357 X
3,301,680 1/1967 Nycander et al. 96—85

S. LEON BASHORE, Primary Examiner

F. FREI, Assistant Examiner

U.S. Cl. X.R.

162—158, 164; 117—155 VA

UNITED STATES PATENT OFFICE CERTIFICATE OF CORRECTION

Patent No. 3,674,632 Dated July 4, 1972

Inventor(s) Johan J. Wennergren et al

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

Column 2, line 71 : "HO[C₂H₄O]_m₁(C₃H₆O)_n (C₂H₄O)_m₂]_o H'"
should be --HO[C₂H₄O]_m₁(C₃H₆O)_n (C₂H₄O)_m₂]_p H--

Column 3, line 27 : "indicatees" should be --indicates--

Column 4, line 41 : "oft he" should be --of the--

Column 4, line 52 : "polyoxyalkyleneg lycol" should be
--polyoxyalkylene glycol--

Column 4, line 72 : after "conditioned" insert -- and--

Column 6, line 38, Table IV :

TABLE IV			
Parts by weight			
Example No.	Polyethyl- ene glycol	Block polymer Berol TVM	Time o penetration (seconds)
	400	375	

should be

TABLE IV			
Parts by weight			
Example No.	Polyethyl- ene glycol	Block polymer Berol TVM	Time of penetration (seconds)
	400	375	

Column 7, line 60 : "polyoxyalklene" should be --polyoxyalkylene--

Signed and Sealed this

fourth Day of May 1976

[SEAL]

Attest:

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