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PROCESS FOR STRENGTHENING SWELLABLE FIBROUS MATERIAL WITH AN AMINE OXIDE AND THE RESULTING MATERIAL

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20 Claims

ABSTRACT OF THE DISCLOSURE

Process for strengthening fibrous materials comprising imbibing an amine oxide into said fibrous material and exposing the imbibed fibrous material to a temperature at which said amine oxide will swell the fibers of said fibrous materials. In a highly preferred embodiment, said amine oxide is a cyclic mono(N-methylamine-N-oxide) compound such as, for example, N-methylmorpholine-N-oxide, N-methylpyrrolidone-N-oxide, N-methylazacycloheptane-N-oxide, nicotine-1-oxide, etc. One aspect of this invention relates to articles of manufacture made by the above process.

This invention relates to a process for improving the wet and dry strength of fibrous materials by treating them with certain amine oxides.

Fibrous materials such as papers, felts, and fabrics made from fibers are widely used, especially in such areas as packaging, clothing, and supports for photographic emulsions where strength is required, both when the materials are dry and when they are wet. It is beneficial to strengthen these materials by a quick, simple, and inexpensive process which does not unduly modify the normal desirable characteristics of these materials. This process should result in no degradation of the material, impart no color to it, and leave no potentially dangerous or unpleasant residue in the material. The strength imparted to the materials should be permanent or long-lasting and should not be affected by washing the material with water. These objectives are fulfilled when the fibrous materials are strengthened with certain amine oxides.

It is an object of this invention to provide a process for improving the wet and dry strength of fibrous materials.

Another object is to provide strengthened fibrous materials.

Still further objects will become apparent from the following specification and claims.

According to my invention, it has been found that a fibrous material may be strengthened by imbibing an amine oxide into the fibrous material and exposing the imbibed fibrous material to a temperature at which the amine oxide will swell the fibers.

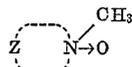
The class of amine oxides useful in accordance with the invention for strengthening fibrous materials has the general formula:



wherein each of R_1 , R_2 , and R_3 represents a member selected from the group consisting of monovalent alkyl, cycloalkyl, aralkyl and heterocyclic radicals, and heterocyclic rings comprising two of said members and the N-atom of the formula.

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A subclass of amine oxides, within the above formula, especially preferred for the invention are cyclic mono(N-methylamine-N-oxide) compound having the formula



wherein Z represents the atoms to complete a saturated heterocyclic ring. Some preferred cyclic mono-(N-methylamine-N-oxide) compounds within this last formula include N-methylmorpholine-N-oxide, N-methylpiperidine-N-oxide, N-methylpyrrolidone-N-oxide, N-methylazacycloheptane-N-oxide, nicotine-1-oxide, and the like. A typical example of a useful amine oxide within the first formula above is triethyl amine-N-oxide.

The amine oxide may be imbibed into a fibrous material directly in liquid form, or it may be imbibed in solution, that is dissolved in a liquid solvent. When solvents are used, one may use a volatile solvent which is easily removed by evaporation, or one may use a liquid solvent which will not evaporate. In the latter case, the solvent must be one that does not interfere with the strengthening action of the amine oxide.

While the amine oxide is imbibed in the fibrous material to be treated, it is necessary to attain a temperature sufficiently high to let the amine oxide act as a solvent or swelling agent on the fibers. This temperature will vary, depending on the particular amine oxide, particular fiber composition, etc. In cases where the amine oxide is imbibed pure or with a solvent that evaporates, the melting point of the amine oxide is the minimum required temperature. When a solvent not removed by evaporation is used, the minimum required temperature is simply the temperature required for the solution to cause the fibers to swell or begin to dissolve and will depend on the particular constituents of the solution and their concentrations.

Suitable volatile solvents for imbibing the amine oxides into the fibers include water, methanol, acetonitrile, and the like. Useful solvents that are not removed by evaporation include dimethylsulfoxide, N-methylpyrrolidone, sulfolane, and the like.

After the amine oxide has acted on the fibrous material to effect hardening, it may be removed and a convenient way to do this is by washing with water or other selective solvent for the amine oxide.

The term "fibrous material" is used in describing my invention in a broad sense to comprise any woven or non-woven fabric containing a substantial proportion of fibers that are soluble or swellable in the amine oxide, including natural cellulosic fibers such as wood pulp, cotton, linen and the like, animal fibers such as wool, fur and the like, and synthetic fibers such as nylon, rayon, polyester fibers, etc. and mixtures of such fibers. These fibers may be aggregate, as in papers of various kinds, felted and non-woven fabrics and the like, or may be woven fabrics. A particularly preferred embodiment of the invention is the strengthening of papers comprising cellulosic fibers, by means of amine oxides.

A possible mechanism by which the amine oxides strengthen fibrous materials can be explained by reference to cellulosic paper as an example. In strengthening paper, apparently the amine oxide partially dissolves or swells surface areas of the individual fibers of cellulose which make up the paper causing them to melt or fuse together forming a strong fiber lattice. Before treatment with the amine oxide, the paper consists of fibers which are held together mainly by interfiber friction. After treatment, the fibers are actually physically locked together. This mechanism of the strengthening process has been observed in photomicrographs of a cellulosic paper monolayer made before, during, and after treatment with the amine oxides. It also appears that during treatment, loose fines in the

paper are melted and fused into the cellulose fibers, becoming an integral part of the paper, thus reducing the dusting characteristics of the paper. By the same mechanism scaling is reduced in scaly fibers such as wool. In strengthening woven fabrics, the amine oxides function by the same mechanism to fuse the warp threads to the woof threads, as well as to strengthen the individual threads by fusing the fibers in the thread, resulting in a stronger physical connection of the fibers and threads than by mere interfiber friction.

Most methods of improving wet and dry strength of papers known in the prior art involve coating of a material onto the surface of the paper or imbibing a material into the body of the paper. This material may then chemically react with the paper to strengthen it, and may remain a part of the treated paper. Such treatments may degrade the paper or may leave harmful or undesirable chemicals in the paper. Paper has also been strengthened by coating with a material which forms a strengthening continuous phase within the body of, or on the surface of, the paper. This type of strengthening is usually costly and may give stiff or brittle paper. The amine oxides used in this invention do not react chemically with the paper, or with other fibrous materials which may be treated, nor is it necessary that they remain a part of the strengthened product.

The invention avoids many disadvantages of the known methods of strengthening paper. Since the amine oxides used do not react with the fibers of the paper and the temperatures to which the paper must be heated are not extreme, there is no chemical degradation of the fibers. The finished strengthened product need not contain any of the amine oxide, and, thus, the process does not discolor the product or require presence of any odorless or dangerous chemicals in the finished product.

Another advantage of the invention is that since the amine oxide agent does not react with the fiber and need not remain within the fabric, the amine oxide may be recovered and used again. Thus, the process of this invention is relatively low in cost, simple and efficient.

Since the improvement in wet and dry strength imparted to fibrous materials does not depend on presence of any strengthening agent in the finished material, the strengthened material may be further treated without need for precautions to protect the strengthening agent. Strengthened papers may be washed with water, aqueous acid, aqueous base, or organic solvents such as methanol or acetone and redried without losing the improved strength. If a strengthened paper is to be used as a support for coated layers, the coatings can be applied with solvents without affecting the strength of the support. Similarly, if a fabric which has been strengthened by the process of the invention is to be dyed, the dye solvents employed will not affect the improved strength of the fabric.

To illustrate the invention and to demonstrate a most preferred mode of carrying out the invention we refer to the following specific examples embodying the invention.

EXAMPLE 1

In a shallow tray thermostated at 110° C. was melted 20 grams of N-methylmorpholine-N-oxide. A strip of Whatman #4 paper was passed rapidly through the liquid and immediately washed with methanol (water may be used instead of methanol) and dried. The paper had the following wet and dry burst strengths (p.s.i.—Minden):

	Untreated	Treated
Wet.....	0	59
Dry.....	12	103

EXAMPLE 2

A solution of 10 grams of N-methylmorpholine-N-oxide in 20 ml. of dimethyl sulfoxide was heated in a shallow tray thermostated at 100° C. A strip of Whatman

#4 paper was passed through this solution at such a rate that both sides of the sheet were thoroughly wetted. The paper was then heated to 120° C., washed in methanol (water could also be used), and dried. The paper had the following wet and dry burst strengths (p.s.i.—Minden):

	Untreated	Treated
Wet.....	0	39
Dry.....	12	62

EXAMPLE 3

A 25 percent methanolic solution of N-methylmorpholine-N-oxide was imbibed into a piece of Whatman #1 filter paper. The paper was heated to 120° C. for one minute, then washed in water and dried. The paper had the following wet and dry burst strengths (p.s.i.—Minden):

	Untreated	Treated
Wet.....	0	42
Dry.....	19	76

The strength of the treated paper was unaffected by washing in water, aqueous acid, or aqueous base. Samples of the N-methylmorpholine-N-oxide paper were stored in running water for 18 months with less than 5 percent loss in either wet or dry strength.

EXAMPLE 4

Table I shows the effectiveness of a number of amine oxides as paper strengthening agents. A 50 percent methanolic solution of each amine oxide listed in Table I was prepared and each solution was placed in a shallow tray. A sheet of Whatman #1 filter paper was immersed in each solution, then removed, drained to remove excess solution, and heated to 120° C. The paper had the following wet and dry burst strengths (p.s.i.—Minden):

TABLE I

Amine oxide	Wet strength	Dry strength
None (untreated paper).....	0	19
N-methylpyrrolidine-N-oxide.....	35	61
N-methylpiperidine-N-oxide.....	61	109
N-methylazacycloheptane-N-oxide..	45	85
N-methylmorpholine-N-oxide.....	65	118
Nicotine-1-oxide.....	58	92

EXAMPLE 5

Table II shows a relationship of concentration of an amine oxide in the methanol solution used for strengthening a selected paper. The procedure described in Example 4 was employed except using varying concentrations of N-methylmorpholine-N-oxide in methanol in the respective treating solutions as indicated in the table. The treated papers had the following wet and dry burst strengths (p.s.i.—Minden):

TABLE II

Conc. of N-methylmorpholine-N-oxide, percent	Wet strength	Dry strength
None (untreated paper).....	0	19
50.....	65	118
25.....	42	76
12.5.....	31	58

EXAMPLE 6

A 20 percent solution of N-methylmorpholine-N-oxide in methanol was imbibed into a piece of a paper composed of 85 percent bleached sulfite pulp and 15 percent polyethylene terephthalate fibers. The paper was heated to 120° C. for one minute, then washed in water and dried. The paper had the following wet and dry burst strengths (p.s.i.—Minden):

	Untreated	Treated
Wet.....	0	42
Dry.....	12	78

EXAMPLE 7

A 20 percent methanolic solution of N-methylazacycloheptane-N-oxide was imbibed into a piece of a paper composed of 75 percent bleached sulfite pulp and 25 percent rayon fibers (30 denier, 1.5-inches long). The paper was heated to 120° C. for one minute, then washed with water and dried. The paper had the following burst strengths (p.s.i.—Minden):

	Untreated	Treated
Wet.....	1	37
Dry.....	9	98

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention as described hereinbefore and as defined in the appended claims.

I claim:

1. A process for strengthening swellable fibrous materials comprising imbibing an amine oxide into said fibrous material and exposing the imbibed fibrous material to a temperature at which said amine oxide will swell the fibers of said fibrous material, said amine oxide having the following formula:



wherein R_1 , R_2 , and R_3 may be substituted or unsubstituted alkyl, cycloalkyl, aralkyl, or heterocyclic groups, and any two of the groups R_1 , R_2 , and R_3 may be taken together to form a heterocyclic ring.

2. The process of claim 1 wherein said fibrous material is a paper comprising cellulosic fibers.

3. A process for strengthening swellable fibrous materials comprising imbibing a cyclic mono(N-methylamine-N-oxide) compound into said fibrous material and exposing the imbibed fibrous material to a temperature at which said amine oxide will swell said fibrous material.

4. The process of claim 3 wherein said amine oxide is N-methylmorpholine-N-oxide.

5. The process of claim 3 wherein said amine oxide is N-methylpiperidine-N-oxide.

6. The process of claim 3 wherein said amine oxide is N-methylpyrrolidone-N-oxide.

7. The process of claim 3 wherein said amine oxide is N-methylazacycloheptane-N-oxide.

8. The process of claim 3 wherein said amine oxide is nicotine-1-oxide.

9. The process of claim 3 wherein a solution of said amine oxide is made in a nonvolatile liquid solvent, and the amine oxide is imbibed in said solution into said fibrous material.

10. The process of claim 9 wherein said nonvolatile liquid solvent is chosen from the group consisting of dimethyl sulfoxide, N-methylpyrrolidone, sulfolane, and mixtures thereof.

11. The process of claim 3 wherein a solution of said amine oxide is made in a volatile liquid solvent, said solu-

tion is imbibed into said fibrous material, and said volatile liquid solvent is removed from said fibrous material prior to exposing said imbibed fibrous material to a temperature at which said amine oxide will swell the fibers of said fibrous material.

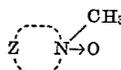
12. The process of claim 11 wherein said volatile liquid solvent is chosen from the group consisting of methanol, water, acetonitrile, methanol-dioxane, methanol-acetone, and mixtures thereof.

13. The process of claim 3 wherein said amine oxide is removed from said fibrous material subsequent to exposing said imbibed fibrous material to a temperature at which said amine oxide will swell the fibers of said fibrous material.

14. An article of manufacture comprising a fibrous material which has been strengthened by the process described in claim 3.

15. The article of manufacture of claim 14 wherein said fibrous material is a paper comprising cellulosic fibers.

16. A process according to claim 3 wherein said cyclic mono(N-methylamine-N-oxide) compound is a compound of the formula:



wherein Z represents a saturated heterocyclic ring.

17. A process according to claim 3 wherein said imbibed fibrous material is heated to at least the melting point temperature of said cyclic mono(N-methylamine-N-oxide) compound.

18. A process according to claim 3 wherein said fibrous material is a paper comprising cellulosic fibers.

19. A process for strengthening fibrous materials comprising imbibing an amine oxide into said fibrous material and exposing the imbibed fibrous material to a heat source which will melt said amine oxide; wherein said amine oxide is N-methylmorpholine-N-oxide, N-methylpiperidine-N-oxide, N-methylpyrrolidone-N-oxide, N-methylazacycloheptane-N-oxide or nicotine-1-oxide.

20. An article of manufacture comprising a fibrous material which has been strengthened by the process of claim 19.

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8—130.1; 117—21, 138.8, 141, 143

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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Inventor(s) Dee Lynn Johnson

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 12, "N-methylpyrrolidone-N-oxide" should read ---N-methylpyrrolidine-N-oxide---

Column 6, line 40, "N-methylpyrrolidone-N-oxide" should read ---N-methylpyrrolidine-N-oxide---

Signed and sealed this 2nd day of November 1971.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
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