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METHOD OF IMPARTING DURABLE MILDEW RESISTANCE TO FIBROUS CELLULOSE MATERIALS

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This invention relates to the imparting of durable mildew resistance to fibrous cellulose materials.

Cellulose materials such as textile fabrics, are subject to attack by fungi, particularly in certain localities, which causes serious degradation of and alteration in the cellulose, resulting in undesirable changes in appearance and physical characteristics, primarily in a very marked loss in tensile strength. This phenomenon is usually referred to as "mildewing" and is responsible for the rapid destruction of textile fabrics in many portions of the world.

We have discovered that if acid be chemically combined with cellulose in the dry state to produce an acid-cellulose complex, the fabric or other fibrous material is not only rendered mildew resistant but the finish is durable to water and will withstand weathering for long periods of time. Moreover, this result can be obtained through the use of relatively small quantities of acid so that tendering of the fabric is substantially avoided and the fabric in very large part retains its original strength. The finish also does not interfere with other finishes, such as waterproofing, which are frequently employed in the textile field. It also does not interfere with dyeing and is very effective on dyed goods.

As illustrative of the invention, we prepare an aqueous solution of an acid, such as orthophosphoric, impregnate the fabric with said solution, preferably with a 100% solution pick-up by weight of the fabric in the dry state, after which the fabric is dried and then baked or cured at elevated temperatures, i. e., from 300° F. to 400° F. for a period of time ranging from 30 minutes to 2 minutes, in an oven to bring about the chemical reaction between the acid and the cellulose. The drying and the baking may be performed as a single step, but it is preferable to first dry the material employing conventional drying temperatures. By proceeding in this fashion there is less likelihood of tendering of the fabric.

Similarly, to avoid tendering as much as possible, it is desirable to incorporate in the solution a nitrogen containing organic base soluble in acid solution and basic therein, as a buffering agent, such, for example, as urea, which competes with the cellulose for the acid but which does not prevent the chemical combination between the acid and the cellulose during the baking. The ratio of carbon to nitrogen in the base should not be higher than 2 to 1. The reason that it is desirable to incorporate such a buffering agent is that "mass" action is involved and more acid must

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be applied to the fabrc than is represented by the amount of base element of the acid (or the amount of acid in terms of base element of the acid) combined in the finished, washed fabric. The presence of such a buffering agent in the solution tends to avoid tendering during the drying operation. Some nitrogen may be carried into the complex by the acid, but the presence of nitrogen in the final complex is of no importance in obtaining the mildew resistance.

The mildew resistance is obtained by the replacement of hydroxyl groups in the cellulose by acid groups.

The concentration of the solution itself is not critical, as the needed amount of acid to secure the desired degree of mildew resistance may be applied to the fabric by several impregnations of a dilute solution. We prefer, however, to use a concentration which will result in the application of the desired amount of acid by a single application of the solution with 100% solution pick-up on the weight of the fabric in the dry state, and in all of the examples hereinafter given a 100% solution pick-up by weight of the dry fabric is employed. Parts are by weight.

As illustrative of the practice of the invention, undyed cotton cloth was impregnated with the following solution:

300 parts orthophosphoric acid (75%)
600 parts urea
4100 parts water

and squeezed to 100% solution pick-up, dried and aged or cured for 5 minutes at 340° F., after which the cloth was washed thoroughly in water at about 180° F.–190° F. and finally dried. The dried cloth and a piece of the same cloth untreated was then buried in soil for 8 weeks to test resistance to mildewing, the latter being determined by measuring the tensile strength retention of the treated fabric as compared with the tensile strength before burial and with the tensile strength of the untreated fabric after burial.

The tensile strength tests were as follows:

	Pounds
Warp strength treated fabric before burial	130
Warp strength treated fabric after burial	121
Warp strength untreated fabric after burial (too weak to measure)	0

The strength tests were conducted on a regular Scott tester, using 1 inch x 3 inch test samples.

These results show the protective action afforded by the process with this acid, with a ratio of acid groups to pyranose units of 1 to 20 in the

finished, i. e., the washed, dried fabric, or .96% phosphorus.

Cotton cloth was impregnated with the same solution and the same procedure was followed, with the exception that the temperature employed for curing was 300° F. and the time 10 minutes.

The results obtained were substantially the same as those obtained in the first example.

Cotton fabric was impregnated with the same solution and the same procedure followed, with the exception that in this instance the temperature of curing was 400° F. and the time 2 minutes.

Substantially the same results were obtained as in the first example.

In the aforesaid examples, the base element of the acid, i. e., phosphorus, is present in the finished, i. e., washed and dried fabric, the ratio thereof in terms of acid to pyranose units being 1 to 20. This ratio gives very effective mildew resistance and is about as high a ratio as should be employed when using an acid substantially as strong as orthophosphoric acid.

If a less degree of mildew resistance is desired, the amount of acid may be reduced.

Thus, for example, a cotton fabric was impregnated with the following solution:

100 parts orthophosphoric acid (75%)
300 parts urea
41,600 parts water by weight

and the same procedure was followed as before, with a curing temperature of 350° F. and a time of 8 minutes. In the washed dried fabric the ratio of phosphorus in terms of acid to pyranose units was about 1 to 600 or .0294% phosphorus. With this ratio appreciable mildew resistance was obtained but not as good as obtained in the previously mentioned examples. With orthophosphoric acid, this is about as low a ratio as should be employed.

With such ranges, the amount of orthophosphoric acid applied to the material will range from .2% to 4.5% by weight of the material in the dry state, having in mind also the particular temperature and time within the temperature time ranges given.

As to the pH of the solution, the initial pH thereof is unimportant so long as the pH on the cured cloth comes down during the curing and before washing to from 2 pH to 7 pH as determined by indicator solutions. The reaction between the acid and the cellulose occurs only under acidic conditions. Urea is a relatively weak base, i. e., change in the amount thereof has no pronounced effect on the pH of the solution. During the curing certain reactions take place which cause the pH to fall within the range above indicated. In fact the pH of the solution may even be on the alkaline side so long as the pH comes down during the curing due to the reactions occurring during the curing. The preferred pH on the cured cloth before washing is from 3 to 6 pH as determined by indicator solutions. The urea may be used in amounts ranging from 1 mol to 10 mols of urea to 1 mol of acid, the preferred range being 1 mol to 4 mols to 1 mol of acid.

In place of the phosphoric acid, other acids may be equally well substituted, such, for example, as metaphosphoric acid, pyrophosphoric acid, ortho, meta- and pyrophosphorus acids, phosphamic acid, phosphotungstic acid, sulfuric acid, sulfamic acid, phytic, and similar relatively

strongly effective acids. Also weaker acids may be used, such as tartaric, lactic, maleic, malic, malonic, phthalic, citric, succinic, pyroantimonic, dehydroxydiphenic, molybdic, tungstic, vanadic, telluric, selenic, salicyclic, fluosilicic, benzoic and nitric. In fact any soluble acid, organic or inorganic, substantially non-volatile, which will react with the cellulose to replace hydroxyl groups under the temperature and time ranges hereinbefore stated is suitable. Since there is a variation in effectiveness, this must be taken into consideration and an amount of acid should be employed which gives an effect at least substantially equivalent to that obtained in the case of orthophosphoric acid with a ratio ranging from 1 to 20 to 1 to 600 of acid to pyranose units in the finished fabric after washing and drying.

Metal salts and organic substituted salts of the acids having free acidity for combination with the cellulose may also be employed. The excess acidity may be temporarily neutralized by means of a base volatile during curing, such, for example, as ammonium hydroxide.

In fact many substituted acids are very effective as the substituents may have anti-fungus properties which enhance the effect of the acid combined with the cellulose, being carried into the complex by the acid. When substituting these for orthophosphoric acid, the amount employed should be at least sufficient to give equivalent effects of orthophosphoric acid when employed alone.

Many suitable organic compounds may be attached to the acids by substitution, such, for example, as phenyl, phenol, cresol, bromocresol, dihydroxyhexachlorodiphenylmethane, chlorophenyl, chlorophenol, B-naphthol, chloronaphthalene, dihydroxydichlorodiphenylmethane, alkylphenols, dichlorodiphenyltrichloromethane, naphthalene, alkylnaphthalene, thymol, chlorothymol, xylene, chloroxylene, O-phenylphenol, chloro-o-phenylphenol, toluol, chlorotoluol, anthraquinone, chloroanthraquinone, and hydroxyanthraquinone.

It will be seen that these listed compounds or groups are of a ring structure and contain one or more rings in their constitution and may, therefore, be classified as carbocyclic compounds. Chlorine, fluorine, bromine and iodine may also be introduced into said compounds, thereby increasing the mildew resistance in the substituting material.

In using the compounds just mentioned it is sometimes advantageous to attach more than one acid group to the same mildew resistant groups. For example, phenol disulfonic acid, 2-naphthol-6,8-disulfonic acid, anthraquinone-1,5-disulphonic acid, and phenyl diphosphoric acid, may be used. In the case of the di- or polysulfonic acids, polybasic properties are introduced into the compound by the use of two or more acid groups, and this, as will be further explained, is very beneficial.

The use of monobasic acids is not practical unless the substitution leaves a free reactive acid hydrogen to react with the cellulose and the required reactions, therefore, will take place. To illustrate, substitution in nitric acid, as, for example, nitrobenzene, will not produce a compound capable of reacting with the cellulose as there is no free acid group available.

Quaternary ammonium compounds, especially those containing aromatic groups, and hydroxyl chloro or bromo substituted aromatic groups, have good mildew-preventing properties. These basic

compounds, when substituted in the aforementioned acids, as, for example, in orthophosphoric acid, may be used with success, as, for example, lauryldimethylphenol ammonium acid phosphate, alphaalphagammagammatetramethylbutylphenoxyethoxyethyldimethylbenzyl ammonium acid phosphate and dimethyllauryl benzyl ammonium acid phosphate, the substituted phosphoric acid in these cases combining with the cellulose under the conditions of the process giving mildew resistance. At the same time the quaternary ammonium complex which in itself, as mentioned above, is a mildew resistance group, has increased durability to leaching and soaping by virtue of its combination with the acid-cellulose complex.

In many polybasic acids, substitution may also be made with inorganic elements, such, for example, as fluorine, mercury, copper, cadmium, zinc and zirconium. For example, fluophosphonic acid may be used as already mentioned. The greater part of the elements listed above have a basic character toward the relatively strong acid, so that a salt is formed when the metallic element, in the form of a salt, an oxide or hydroxide, is added to the impregnating solution. The salt of the inorganic element may be of a weak acid not substantially reactive with the cellulose, such as, for example, acetic or it may be of a strong acid capable of reacting with the cellulose, such as orthophosphoric. In the latter case the acid introduced by the salt into the solution should replace a corresponding quantity of acid in the solution formula. In the former case, the acid introduced with the salt does not react with cellulose and the regular quantity of reactive acid must be used. In case an insoluble precipitate is formed in solution between the basic element and the acid, the method is not practical without steps being taken to solubilize the insoluble salt. With a salt such, for example, as copper phosphate, excess ammonium may be used with advantage to obtain a clear solution for impregnation.

Mildew resistant organic groups may also be introduced into the acid through an inorganic element, for example, phenylmercuric acid phosphate, and phenyl cadmium acid phosphate may be used under the conditions described above.

The acid employed which, in addition to being active enough to combine with the cellulose under the conditions of the process, should not be excessively volatile during processing, should preferably be soluble in the solution, and should not detrimentally alter the physical characteristics of the substituted mildew resistant compounds and should preferably show good durability toward water.

The enhancing mildew resistant substance or substances may be introduced through the basic or buffering material, instead of directly through the acid. To this end, in addition to the presence in the solution of the base as such, the substituted base is added. This ordinarily is not as economical. It is to be understood that where the mildew resistant substance is introduced with the buffering material, it is nevertheless still carried to some extent into the complex by the acid.

When the mildew resistant groups are to be attached to base material, it is preferable to attach them to a strong base because the strong base usually tends to attach itself more readily to the acid. The substituent group or groups must not be such as to alter the basic properties of

the base to such an extent that its function as a base during the curing will be destroyed or excessively altered.

The amount of buffering base should be at least such as to secure adequate buffering of the acid. When used in the quantities giving the pH values hereinafter set forth, satisfactory results are obtained.

For the urea other organic buffering agents of the character described may be employed, such, for example, as biuret, acetamide, dicyandiamide, guanyl urea, amino-guanidine, biguanide, guanidine carbonate, oxalamidine, carbohydrazidine, and the like. Where strong bases are used they should be used in combination with weak bases, such, for example, as urea and guanidine, for the reason that the initial pH of the solution presents no particular difficulty where a combination of strong and weak bases is employed, whereas if only strong bases are employed then it is necessary to very carefully control the pH of the solution so as to ensure its being on the acidic side during the curing. Non-metallic salts of the base may be employed. Substituted bases may be employed.

The general requirements of the buffering base are that it should be soluble, free of metal, basic toward the acid, and non-volatile under the curing conditions.

Generally speaking, the lower the temperature of curing the longer the time and vice versa. Similarly, the lower the acid concentration in the solution the higher should be the temperature and in some cases, the longer the time. The preferred temperature is from 340° F. to 375° F. and the time from 8 to 4 minutes.

In the following examples a single application of solution with roughly a 100% solution pick-up by weight on the dry material was employed, with all parts by weight.

Example I

A scoured and dyed cotton fabric was impregnated with the following mixture:

375.0 parts phosphotungstic acid
330.0 parts urea
250.0 parts water

squeezed, dried, aged 15 minutes at 340° F., washed thoroughly in running water 180–190° F., and finally dried.

The treated fabric and a piece of untreated similar fabric were buried in the soil for 8 weeks to test the resistance to deterioration, the latter being determined by measuring the tensile strength retention of the treated fabric as compared with the fabric strength before burial and with the fabric strength of the untreated fabric after burial. The untreated sample test also serves as a guarantee that the soil contained ingredients causing cellulose deterioration.

The tensile strength tests were as follows:

	Pounds
Warp strength treated fabric before burial	135
Warp strength treated fabric after burial	127
Warp strength untreated fabric after burial (too weak to measure)	0

The strength tests were conducted on a regular Scott tester, using 1 inch x 3 inch test samples.

Phosphotungstic acid is a strong and very effective acid, in consequence of which very effective mildew resistance is obtained with a ratio of acid to pyranose units of 1 to 4000 which was ob-

tained in this example. Substantial resistance can be obtained with even a much lower ratio as will appear hereinafter.

Example II

A scoured and dyed cotton fabric was padded with the following mixture:

290.0 parts telluric acid
440.0 parts urea
1000.0 parts water

followed by drying, curing 30 minutes at 340° F., washing thoroughly in hot water and finally drying.

The treated fabric and a piece of untreated sample were buried in the soil for 8 weeks and the following tensile strength retention tests obtained.

	Pounds
Warp strength treated fabric before burial	119
Warp strength treated fabric after burial	51
Warp strength untreated fabric after burial	0

Example III

A desized, scoured, mercerized and dyed fabric was treated as in Example I, curing being done 5 minutes at 350° F. The impregnating mixture consisted of:

720.0 parts molybdic acid anhydride
1320.0 parts urea
1000.0 parts ammonium hydroxide (28%)
500.0 parts water

The treated and untreated fabrics were soil buried for 8 weeks and the following tensile strength tests obtained:

	Pounds
Warp strength treated fabric before burial	138
Warp strength treated fabric after burial	69
Warp strength untreated fabric after burial	0

Example IV

A pure cotton fabric was padded through the following mixture:

450.0 parts lactic acid
1320.0 parts urea
1000.0 parts water

dried, aged 5 minutes at 340° F., washed 15 minutes in hot running water (180–190° F.) and finally dried.

Treated and untreated fabrics were soil buried for 8 weeks and then tested for tensile strength. The following results were obtained:

	Pounds
Warp strength treated fabric before burial	135
Warp strength treated fabric after burial	98
Warp strength untreated fabric after burial	0

Example V

A pure dyed cotton fabric was treated as described in Example IV, the mixture consisting of:

74.0 parts acid phthalic anhydride
125.0 parts alcohol
132.0 parts urea

Treated and untreated cloths were buried for 8 weeks and the following tensile strength tests obtained:

	Pounds
Warp strength treated fabric before burial	128
Warp strength treated fabric after burial	90
Warp strength untreated fabric after burial	0

Example VI

A pure dyed cotton fabric was treated as described in Example IV, the impregnating mixture consisting of:

75.0 parts tartaric acid
132.0 parts urea
100.0 parts water

Treated and untreated fabrics were soil buried for 8 weeks and the following tensile strength results obtained:

	Pounds
Warp strength treated fabric before burial	129
Warp strength treated fabric after burial	61
Warp strength untreated fabric after burial	0

Example VII

A pure dyed cotton fabric was treated as described in Example IV. The mixture had the following composition:

130.0 parts citric acid
132.0 parts urea
100.0 parts water

Treated and untreated cloths were soil buried for 8 weeks and the following tensile strengths obtained:

	Pounds
Warp strength treated fabric before burial	126
Warp strength treated fabric after burial	76
Warp strength untreated fabric after burial	0

Example VIII

Cotton fabric was treated as described in Example IV, the padding solution consisting of:

125.0 parts tungstic acid
132.0 parts urea
100.0 parts ammonium hydroxide
300.0 parts water

A similar fabric was padded with the above mixture, dried but not aged. It was then washed 15 minutes in hot water (180–190° F.) and dried.

The two treated fabrics and an untreated fabric were subjected to the Chaetomium test as described in U. S. Quartermaster Corps Specification P. Q. D. 447A and the following tensile strength tests obtained:

	Pounds
Warp strength aged treated fabric before test	115
Warp strength aged treated fabric after test	114
Warp strength unaged treated fabric before test	118
Warp strength unaged treated fabric after test	18
Warp strength unaged untreated fabric after test	22

This example shows the durability obtained by the aging treatment.

Example IX

A scoured and dyed cotton was padded, using the following impregnating mixture:

33 parts dicyandiamide
50 parts orthophosphoric acid (75%)
750 parts water
56 parts formamide
7 parts guanidine carbonate

squeezed, dried, aged 7 minutes at 330° F., washed thoroughly in running water 180–190° F. and finally dried.

Treated and untreated fabrics were soil buried for 8 weeks and then tested:

	Pounds
Warp strength treated fabric before burial	137
Warp strength treated fabric after burial	120
Warp strength untreated fabric after burial	0

Example X

A scoured and dyed cotton fabric was padded, using the following impregnating mixture:

15 parts phosphotungstic acid
3000 parts water
30 parts urea

squeezed, dried, aged 15 minutes at 340° F., washed thoroughly in running water 180–190° F. and finally dried.

The cloth contained .17% phosphotungstic acid or 1 acid group to every 10,600 pyranose units (average of five tests).

Treated and untreated fabrics were subjected to the Chaetomium test as described in U. S. Quartermaster Corps Specification P. Q. D. 447A and the following tensile strength tests obtained:

	Pounds
Warp strength treated fabric before test	113
Warp strength treated fabric after test	107
Warp strength untreated fabric after test	0

Example XI

A cotton fabric was treated as described in Example IV with the following mixture:

50.0 parts sulfuric acid (con.)
132.0 parts urea
350.0 parts water

A treated fabric and an untreated fabric were soil buried for 8 weeks and then tested for tensile strength.

	Pounds
Warp strength of treated fabric before burial	120
Warp strength of treated fabric after burial	108
Warp strength of untreated fabric after burial	0

Example XII

A sample of pure hemlock wood pulp was impregnated with the following mixture:

65 parts orthophosphoric acid (75%)
132 parts urea
5200 parts water

followed by drying, curing 5 minutes at 340° F., washed well in hot water, filtered and dried.

Samples of treated and untreated pulp were given the Chaetomium test. The untreated pulp showed heavy fungus growth while the treated pulp remained unaffected.

Example XIII

A piece of pure dyed viscose rayon fabric was impregnated with the following mixture:

66 parts orthophosphoric acid (75%)
132 parts urea
1100 parts water

dried, aged 5 minutes at 340° F., washed 15 minutes in hot running water (180–190° F.) and finally dried.

Treated and untreated fabrics were soil buried for 8 weeks and then tested:

	Pounds
Warp strength treated fabric before burial	90
Warp strength treated fabric after burial	86
Warp strength untreated fabric after burial	0

Example XIV

A scoured, mercerized and bleached cotton fabric was impregnated with the following mixture:

280.0 parts naphtha thiophosphonic acid
330.0 parts urea
1000.0 parts water

squeezed, dried, aged 12 minutes at 320° F., washed thoroughly in running water 180–190° F., and finally dried.

The treated fabric and a piece of untreated similar fabric were buried in the soil for 8 weeks to test the resistance to deterioration, the latter being determined by measuring the tensile strength retention of the treated fabric as compared with the fabric strength before burial and with the fabric strength of the untreated fabric after burial. The untreated sample test also serves as a guarantee that the soil contained ingredients causing cellulose deterioration.

The tensile strength tests were as follows:

	Pounds
Warp strength treated fabric before burial	136
Warp strength treated fabric after burial	96
Warp strength untreated fabric after burial	0

Example XV

A dyed cotton fabric was impregnated with the following padding mixture:

16 parts copper oxide
52 parts orthophosphoric acid (75%)
42 parts ammonium hydroxide
100 parts urea
1030 parts water

dried, aged 5 minutes at 340° F., washed 15 minutes in hot running water (180–190° F.) and finally dried.

Treated and untreated fabrics were subjected to the Chaetomium test as described in U. S. Quartermaster Corps Specification P. Q. D. 447A and the following tensile strength tests obtained:

	Pounds
Warp strength treated fabric before test	104
Warp strength treated fabric after test	103
Warp strength untreated fabric after test	0

Example XVI

A cotton fabric was impregnated with the following sizing mixture:

49 parts phenol-disulfonic acid
810 parts water
200 parts urea
82 parts guanidine carbonate

dried, aged 5 minutes at 340° F., washed 15 minutes in hot running water (180–190° F.) and finally dried.

Treated and untreated fabrics were tested as described in Example XV. The following results were obtained:

	Pounds
Warp strength treated fabric before test	107
Warp strength treated fabric after test	106
Warp strength untreated fabric after test	0

Example XVII

A cotton fabric was padded with the following mixture:

40.0 parts phenyl phosphonic acid
66.0 parts urea
200.0 parts water

dried, aged 10 minutes at 340° F., washed 15 minutes in hot running water (180–190° F.) and dried.

Treated and untreated fabrics were soil buried for 8 weeks and then tested:

	Pounds
Warp strength treated fabric before burial	135
Warp strength treated fabric after burial	121
Warp strength untreated fabric after burial	0

Example XVIII

A cotton fabric was impregnated with the following mixture:

100.0 parts orthophosphoric acid (75%)
65.0 parts dicyandiamide
150.0 parts urea
28.0 parts phenylbiguanide
1869.0 parts water

dried, aged 5 minutes at 340° F., washed 15 minutes in hot running water (180–190° F.) and finally dried.

Treated and untreated fabrics were buried for 8 weeks and then tested:

	Pounds
Warp strength treated fabric before burial	140
Warp strength treated fabric after burial	110
Warp strength untreated fabric after burial	0

Example XIX

A cotton fabric was impregnated with the following mixture:

53.0 parts orthophosphoric acid (75%)
81.0 parts urea
65.0 parts phenyl-guanidine carbonate
800.0 parts water

dried, aged 5 minutes at 340° F., washed 15 minutes in hot running water (180–190° F.) and finally dried.

Treated and untreated fabrics were soil buried for 8 weeks and the following results obtained:

	Pounds
Warp strength treated fabric before burial	139
Warp strength treated fabric after burial	88
Warp strength untreated fabric after burial	0

Example XX

A cotton fabric was padded with the following mixture:

65.0 parts orthophosphoric acid (75%)
132.0 parts urea
27.0 parts chromium fluoride
5200.0 parts water

dried, aged 5 minutes at 340° F., washed 15 minutes in hot running water (180–190° F.) and finally dried.

Treated and untreated fabrics were subjected to the Chaetomium test as described in U. S. Quartermaster Corps Specification P. Q. D. 447A and the following tensile strength tests obtained:

	Pounds
Warp strength treated fabric before test	110
Warp strength treated fabric after test	112
Warp strength untreated fabric after test	22

Example XXI

Tetra-chloro-phenyl phosphoric acid was prepared by first reacting together tetra-chlorophenol, phosphorous oxychloride and magnesium chloride and then vacuum distilling.

A cotton fabric was padded through the following mixture:

50.0 parts of the above distillate
50.0 parts urea
150.0 parts acetic acid

dried, aged 10 minutes at 330° F., washed 15 minutes in running hot water (180–190° F.) and dried.

Treated and untreated fabrics were tested as described in Example XX and the following results obtained:

	Pounds
Warp strength treated fabric before test	115
Warp strength treated fabric after test	115
Warp strength untreated fabric after test	22

Example XXII

A scoured and dyed cotton fabric was impregnated with the following mixture:

20 parts phenyl phosphoric ac'd
25 parts phenol disulfonic acid
200 parts urea
50 parts guanidine carbonate
800 parts water

dried, aged 24 minutes at 300° F., washed 15 minutes in hot running water (180–190° F.) and finally dried.

Treated and untreated fabrics were soil buried for 8 weeks and then tested:

	Pounds
Warp strength treated fabric before burial	102
Warp strength treated fabric after burial	90
Warp strength untreated fabric after burial	0

Example XXIII

A piece of viscose rayon fabric was impregnated with the following mixture:

50 parts anhydrous monofluorophosphoric acid
132 parts urea
3100 parts water

dried, aged 5 minutes at 340° F., washed 15 minutes in hot running water (180–190° F.) and finally dried.

Treated and untreated fabrics were soil buried for 8 weeks and then tested:

	Pounds
Warp strength treated fabric before burial	90
Warp strength treated fabric after burial	85
Warp strength untreated fabric after burial	0

Example XXIV

A sample of pure washed wood pulp was impregnated with the following mixture:

65.0 parts orthophosphoric acid (75%)
132.0 parts urea
27.0 parts chromium fluoride
5200.0 parts water

followed by drying, curing 10 minutes at 330° F., washed well in hot water, filtered and dried.

Samples of treated and untreated pulp were given the Chaetomium test. The untreated pulp showed heavy fungus growth while the treated pulp remained unaffected.

Example XXV

A cotton fabric was treated as described in Example XVIII, the sizing mixture consisting of:

200 parts salicylic acid
400 parts urea
50 parts cyanoacetamide
2000 parts water

Treated and untreated fabrics were tested as described in Example XXII. The following results were obtained:

	Pounds
Warp strength treated fabric before test	98
Warp strength treated fabric after test	97
Warp strength untreated fabric after test	0

The treated cloth gave a test for salicylic acid grouping. When the same mixture was applied and the cloth was dried and washed but not cured, the resulting fabric failed to give a test for salicylic acid, showing that no combination with the fabric is obtained in the latter case.

Example XXVI

A cotton fabric was treated as described in Example XVIII, the sizing mixture consisting of:

500 parts monofluorophosphoric acid
640 parts guanidine carbonate
1500 parts water

The cloth contained 2.5% monofluorophosphoric acid, or 1 acid group to every 25 pyranose units.

Treated and untreated fabrics were soil buried for 8 weeks and then tested:

	Pounds
Warp strength treated fabric before burial	116
Warp strength treated fabric after burial	110
Warp strength untreated fabric after burial	0

Example XXVII

A cotton fabric was treated as described in Example XVIII, the sizing mixture consisting of:

500 parts tetrachlorophthalic anhydride
1000 parts urea
1000 parts ammonium hydroxide solution

Treated and untreated fabrics were buried for 8 weeks and then tested.

	Pounds
Warp strength treated fabric before burial	120
Warp strength treated fabric after burial	108
Warp strength untreated fabric after burial	0

The fabric contained 3.1% combined tetrachlorophthalic anhydride or 1 anhydride group to 55 pyranose units.

Example XXVIII

A pure undyed cotton fabric was treated as described in Example XVIII, using:

15 parts monocopper phosphotungstic acid
30 parts urea
3300 parts water

The cloth contained 0.1% monocopperphosphotungstic acid, equivalent to 0.002% phosphorus or 1 acid group to every 18,520 pyranose units.

Treated and untreated fabrics were soil buried for 8 weeks and then tested.

	Pounds
Warp strength treated fabric before burial	145
Warp strength treated fabric after burial	118
Warp strength untreated fabric after burial	0

Example XXIX

130 parts dicyandiamide
200 parts orthophosphoric acid (75%)
200 parts water, heat to 108° C.
300 parts urea
28 parts guanidine carbonate
40,000 parts water

Padded on pure cotton herringbone twill. Dried, cured 5 minutes at 340° F., washed and dried.

Analysis showed 0.33% H_3PO_4 equals 0.104% P equals 185 pyranose units to 1 H_3PO_4.

Mildew tests used: Metarrhizium glutinosum
Duration of test: 6 days and 16 days
Results: Decrease in tensile strength by metarrhizium glutinosum

	Original tensile strength	Tensile strength decrease	
		6 days	16 days
		Per cent	*Per cent*
untreated	119	12	67
treated	108	0	26

Example XXX

130 parts dicyandiamide
200 parts orthophosphoric acid (75%)
200 parts water, heat to 108° C.
300 parts urea
28 parts guanidine carbonate
81,000 parts water

Padded on pure cotton herringbone twill, dried, cured 5 minutes at 340° F., washed and dried.

Analysis showed 0.09% H_3PO_4 equals .0284% P equals 600 pyranose units to 1 H_3PO_4.

Mildew test used: Metarrhizium glutinosum
Duration of test: 6 days and 16 days
Results: Decrease in tensile strength by metarrhizium glutinosum

	Original Tensile Strength	Tensile Strength Decrease	
		6 days	16 days
		Per cent	*Per cent*
Untreated	119	12	67
Treated	113	5	48

Example XXXI

A cotton fabric was impregnated with the following sizing mixture:

100 parts orthophosphoric acid (75%)
100 parts urea
100 parts acetamide
1500 parts water

followed by drying, curing 5 minutes at 330° F., washed 15 minutes in hot running water (180–190° F.) and finally dried.

The treated fabric and a piece of untreated similar fabric were buried in the soil for 8 weeks and then tested.

	Pounds
Warp strength treated fabric before burial	92
Warp strength treated fabric after burial	84
Warp strength untreated fabric after burial	0

This application is a continuation in part of application Serial No. 596,592, filed May 29, 1945, now Patent Number 2,482,755.

We claim:

1. The process of imparting mildew resistance to fibrous cellulose material which consists in impregnating the material with an aqueous solution of phosphoric acid and urea, the amount of solids applied to the material being equal to that applied by a single application of solution with 100% solution pick-up in the weight of the material in the dry state when the solution contains from 0.2% to 4.5% acid by weight of the solution with the urea present in the ratio of from 1 mol to 4 mols to 1 mol of acid, drying the material, baking the dried material at temperatures of from 400° F. to 300° F. for from 2 to 30 minutes, and washing and drying the material, the pH of the solution being such that the pH of the cured fabric before washing is from 2 pH to 7 pH as determined by indicator solutions, and the temperature and time selected being such as to introduce into the complex a ratio of acid to pyranose units of 1 to 20 to 1 to 600 in the washed dried material.

2. The process of claim 1 in which the temperature is from 340° F. to 375° F.

3. The process of claim 1 in which the pH is from 3 to 6.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,482,755	Ford et al.	Sept. 27, 1949