

UNITED STATES PATENT OFFICE.

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TEXTILE MATERIAL AND METHOD OF TREATING THE SAME.

No Drawing.

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The invention which forms the subject of the present application, a continuation, in part, of my earlier application Serial No. 544,944, filed March 18, 1922, relates to water-proofed and preserved textile material and to methods of preparing the same. The invention has for its chief object the treatment of textile material, under which term is included not only woven fabrics but also all other kinds of fabrics including knitted fabrics, netted fabrics, and also threads, yarns, fibers and various associations thereof. Another object of the invention is to produce a water repellent textile material which will retain its water repellency after repeated washings with either soap and water or hydrocarbon solvents such as gasoline, naphtha or equivalent materials such as carbon tetrachloride, acetone, alcohol, ether and the like or various combinations of such materials or treatments.

A further object of the invention is to produce a textile material which is less absorbent than ordinary textile materials and which will therefore take up less atmospheric moisture and will accordingly be more highly resistant to the injurious influences of atmospheric gases and moisture. A still further object is to produce a textile material which will be less subject to shrinking. It is also another important object of the invention to produce a textile material which will be repellent, that is, resistant, to mildew and other fungus growths. It also frequently is an object of the invention, to produce a textile material which will combine the feature of water repellency with the feature of possessing a completely fast color, especially in the case of fabrics which are dyed with a mineral color or a pigment, as for example the familiar khaki.

The objects above enumerated are accomplished in the present case by the use of compounds of the rare earth group of metals and the expression "rare earth" as used herein is intended to include the elements zirconium, titanium and thorium, which latter element seems to possess some points of superiority over the others of the group. These metals

possess the property of precipitating in a particular physical condition, if the operation is properly conducted. When dilute or cold solutions are treated, one of such solutions including a salt of an element of the rare earths, if the operation is conducted in the cold or with relatively dilute solutions, the tendency to form colloidal precipitates exists to a high degree. In the case of thorium compounds, particularly from cold and dilute solutions, the tendency is to produce jelly-like rather than slimy precipitates, these jelly-like precipitates being, under certain conditions, capable of forming within the pores of the textile material, or closely adherent thereto. These colloidal precipitates show a strong tendency to chemically combine with cellulose fibers, as well as with silk or other animal fibers, and under the influence of heat these colloids become water repellent and mildew resistant and give these properties to the textile material with which they are intimately associated. On being subjected to heat, especially with simultaneous subjection to pressure, while intimately associated with the fiber, the more or less colloidal precipitates are converted into a form in which they are not readily attackable by acids or alkalis. This phenomenon is very noticeable, whether weak or very dilute acids, organic or inorganic are employed, or whether relatively strong and usually active, acids are used. As equivalents of thorium and other rare earth elements referred to hereinbefore, at least as regards making textile material repellent to mildew and other fungus growths, I desire to include uranium, actinium, and degradation products, such as radium, mesothorium, radiothorium, and polonium. Textile material impregnated with salts or other compounds of these substances or in combination with other elements or compounds as carriers, are notably resistant to the growth of mildew spores and other bacterial forms of life, and by reason of the radioactivity of the substances mentioned material so impregnated is surrounded by an ionized field inimical to bacterial life and in a measure capable of inhibiting its growth.

Some of these substances, notably radium, mesothorium and radiothorium, are of course costly, but they are intensely radioactive and hence can be used in quantities small enough to make their employment practicable with suitable carriers, among which may be mentioned salts of the rare earths, zirconium, aluminum, etc. In addition to their radioactive properties, many of the salts and other compounds of thorium and uranium, employed as herein described, for example, impart marked water repellency, and by their use one may create a fabric which is water repellent without material loss of porosity, and which at the same time, by reason of the ultra-violet radiations incident to the phenomena of radioactivity, possesses sterilizing properties.

For the purpose of more fully explaining the nature of the present invention, the following examples are given, but it is to be understood that the invention is not restricted to these particular examples.

The operation, as I prefer to carry it out, involves a series of five consecutive steps, namely, first, the impregnation of the textile material with metallic salts of the kind referred to, namely, solutions of salts of the rare earth metals, as above described. The second step of the process may consist in drying the impregnated textile material. This is in many cases important since if the material is not dry, there may not be as good a union of the metal bases with the fiber of the textile material, and hence the precipitate when formed may separate from the textile material. The third step of the process consists in converting the metal salts or other compounds of the rare earth metals, into a water-insoluble and apparently colloidal state, by means of appropriate precipitants. The fourth step of the process consists preferably in washing the textile material in water or other liquid to remove the soluble salts, especially salts constituting the by-products of the precipitation reaction. The fifth step of the process consists in drying the washed fabric, and subjecting the same to a sufficient amount of heat or pressure, or both, to produce the insolubilization of the rare earth metal compound. While the preferred mode of carrying out this invention involves these five steps, it may not require any long period of time for the accomplishment of the results stated, it being well known that webs of fabric may be passed through several dipping or impregnating baths, precipitating baths, washing baths, and calendering machines as a continuous process.

For the production of colored effects, the textile material can also be impregnated with compounds of various metals, capable of producing colored precipitates, such as iron salts, chromium salts, nickel salts, cobalt salts, copper salts, lead salts. Also if it is de-

sired to render the product more resistant or repellent to mildew, fungous decay and disintegration, or the like, this can be accomplished by impregnation with a lead or copper compound. The salts of these metals can be mixed with the salt of the rare earth compound used in the first step or the treatment with the salts of these metals may be effected separately, either after or before the other treatment.

For most purposes the salts of thorium are found to give especially satisfactory results. Normal thorium nitrate is an extremely soluble, hygroscopic, deliquescent, crystalline salt. The same description applies to the normal chlorid. Both have a tendency to attack textile fibers, especially when the temperature is comparatively high. Moreover, on account of their strongly deliquescent character it is almost impossible to dry them unless the temperature be high or a vacuum chamber be used. Both of these conditions introduce technical complications.

If a small quantity of an ammonium salt—the nitrate or chlorid, as the case may be—be added, the solubility is greatly decreased, the salt becomes highly crystalline, and can be easily dried at normal temperatures. No great amount of ammonia is necessary, as little as 2 per cent producing a satisfactory effect. This deportment is characteristic not only of thorium, but also of cerium and most others of the rare earths, and is a marked feature of lanthanum and of the didymium complex. In a way the addition of ammonium, which addition apparently gives rise to the formation of a double salt of the rare earth and ammonium, does away to a large extent with the tendering action of the salt on fabrics, and also largely eliminates the difficulty in drying.

There is, however, a still better series of compounds, viz the sub-acid or basic salts and their derivatives. For example, nitrate of thorium dissolves large quantities of the hydroxid of thorium forming a basic nitrate, or at least a solution of the hydroxid in the nitrate. The former is probably the true explanation because of the marked change in characteristics. The solution no longer crystallizes, nor does the dried, more or less gum-like product absorb moisture, and moreover is easily dried at low temperatures. Its reactions to precipitants differ from what one finds in the case of the normal salt. Thorium nitrate solution also dissolves the carbonate of thorium, the acetate of thorium, the formate of thorium, the chlorid, or mixtures of any or all of these, making highly complex double salts, all of which have a gelatinous rather than a crystalline tendency. Also it will dissolve salts of other metals, making even more complex double salts. On account of their low acidity, or more properly on account of their lack of acidity, they

make admirable impregnating solutions for textile fabrics. What has been said in this connection of the nitrate is also true of the chlorid, although in less measure. Others of

the rare earths exhibit the same general tendency. The preferred impregnating bath for the first step is a solution of thorium sub-nitrate, say of about 20 per cent strength, or if desired, a solution containing about 16 per cent of sub-nitrate and 4 per cent of chlorid. The textile material may remain in contact with the solution for any desired length of time, it being of course preferred that the liquid should thoroughly permeate the interstices and pores of the material. With goods which are not very heavy, say like ordinary heavy sheeting, one minute or so in the impregnating bath is ample time to allow complete permeation of the liquid, into the pores of the material. The impregnation may also be effected, in some cases, by an operation similar to that used in printing fabrics; as for example by passing the material between rollers which are coated or wet with the impregnating solution. The material is then dried, for example by being subjected to the action of a series of steam heated calender rolls, these rolls furnishing both the necessary heat and pressure. The drying temperature need not be higher than 100° C. It may be stated that complete dryness is scarcely ever, if at all, necessary. In many cases the material may contain sufficient moisture to make it appreciably damp to the touch, as would be the case if subjected to firm squeezing between unheated rolls. The textile material then passes to a bath of precipitating agent.

As a precipitant any compound may be used which is capable of precipitating the rare earth metal in a closely adherent and preferably colloidal condition on the textile material. Among these the ones preferred are, in the order named, ammonia, ammonium hydroxid and salts, and alkali metal hydrates. Others that may be named are cyanids and other salts of the alkali metals, such as sulfids, fluorids, phosphates, oxalates (and oxalic acid), fluo-silicates, tungstates, stannates, titanates, molybdates, silicates, salicylates, benzoates, phenolates, and borates. Anilin and pyrocin may be used, also salicylic, benzoic, hydrofluoric, phosphoric, fluosilicic, phenolic, and boric acid. For water repellency as well as mildew repellency I prefer ammonium, sodium or potassium hydroxid, or sodium or potassium cyanid. Among reagents which give more or less soluble precipitates (which are, however, repellent to mildew) are phosphates of the alkali metals. It is seen that the choice of the precipitating agent is much wider than in processes in which aluminum, titanium or zirconium compounds are employed. I have observed that when alkali metal sulfids are used as the pre-

cipitating agents, they do not, in general, form sulfids of the rare earth metal, but hydroxids.

The precipitating bath may be maintained at ordinary atmospheric temperature, or at a lower or higher temperature. Even a boiling temperature, 100° C., does not (materially, if at all) diminish the mildew repellency; and a high temperature, especially with zirconium and thorium compounds, is distinctly favorable in the direction of imparting resistance to acids. Some compounds of these metals (for example zirconium and thorium hydroxids) precipitated hot are almost insoluble in acids, even strong hydrochloric, but are readily soluble therein if precipitated cold. Other compounds, for example thorium and other rare earth phosphates, hypophosphates, fluorids and oxalates, are practically insoluble in dilute acids even when precipitated cold. In general, rare earth metal, zirconium, and uranium, compounds, such as phosphates, fluorids, oxalates, hypophosphates, and fluosilicates, precipitated by the corresponding precipitants, impart measurable protection against weak acids, as do other compounds when strongly dried. Moreover, the presence of insoluble tungstate, stannate, molybdate or phosphate of the metals referred to, in or upon the textile material, confers a certain resistance to flame, making the material less inflammable.

The concentration of the precipitating bath is also a matter of some importance, dilute solutions being preferable. When using, say, caustic soda as the precipitating material, I preferably employ a solution of about 5-10 per cent strength, which keeps the precipitate in a highly colloidal and strongly adherent condition in which it is held tenaciously by the textile material under treatment. The length of time that the goods remain in the precipitating bath will vary, depending upon the thickness of the goods. Ordinarily the goods may remain in the precipitating bath about the same length of time which they remained in the first impregnating bath. Preferably, however, I employ gaseous ammonia (NH₃) as the precipitating bath, better results being obtained in many cases by the use of the gas than by the use of liquid ammonia. The precipitate is denser, and more repellent to water. The gas may be used at ordinary temperature and pressure, and may or may not be diluted with air, as most convenient under the circumstances.

The goods may, if desired, then pass between calendering rollers, which may be heated. The textile material then passes into a washing bath containing water or other suitable washing fluid in which the by-products of the reaction are removed. This washing fluid may contain soap, as I have observed in some cases a marked tendency for the precipitated compound to be converted thereby

into a strongly repellent fatty acid compound.

The textile material then passes again through wringing rolls and hot calendering rolls, for the complete insolubilization of the precipitate carried thereby.

From the hot calendering rolls the goods may then pass to an ordinary winding or reeling device.

I call attention to the fact that compounds of thorium or compounds of the other rare earth metals (cerium, lanthanum, and didymium) can be employed alone or in mixtures, or compounds of thorium together with compounds of one or more of the other rare earth metals, can be used, these being employed alone or with other metal compounds, such as those above referred to for producing mineral dyeings, increased resistance to mildew or fungous growths and the like. These compounds can also be employed with compounds of titanium, aluminum, zirconium and the like which themselves have some water-proofing effects. As examples of other impregnating baths the following may be noted, the figures given being per cents:

Thorium, cerium, lanthanum or didymium salt or salts (preferably nitrate or chlorid, or both) of one or more of these metals	20
Iron salt or salts	40
Chromium salt or salts	40
Water, sufficient to make a 50 per cent solution.	
Cerium, didymium (neodymium) or lanthanum acetate, or a mixture of two or more	15
Water	85
Thorium nitrate or acetate	15
Water	85
Cerium and thorium acetates, with or without aluminum acetate	15
Water	85
Cerium, lanthanum and didymium acetates	20
Iron acetate	30
Water	50
Cerium, lanthanum and didymium acetates	10
Chromium acetate	10
Iron acetate	30
Water	50
Thorium and aluminum acetates	15
Copper acetate	0.5
Water	84.5
Thorium or other rare earth metal compound, preferably subnitrate or acetate	10
Zirconium compound, preferably acetate	5
Water	85

The following baths are well adapted to impart radio-active properties to the textile material:

Aluminum and uranium compounds (each 5 per cent)	10	70
Rare earth compound	5	
Water	85	
Thorium compound	5	
Other rare earth compound	10	75
Water	85	
Uranium compound	5	
Rare earth compound	10	
Water	85	80

Actinium, radium or mesothorium, 1 part in 250,000 of the carrier used.

In the drying operation after the first step of the process, and also in the later drying operation, following the washing step, it is important that temperatures should not be used which are capable of materially injuring the fiber of the textile material, by seriously weakening the same. In the preferred form of the process these drying operations are conducted at temperatures about 100° C., or but slightly above, so as not to reduce the strength of the textile material. In the use of temperatures of about 100° C., in the final drying operation, it appears that the hydroxids of the rare earth elements are in part at least dehydrated with the formation of oxids. It is probably on this account that the precipitates will not re-dissolve if the impregnated textile material is brought into contact with dilute acids.

Salts of aluminum deposited upon textile fabrics have been used heretofore as a mordant for forming insoluble lakes with dye-stuffs, and, as before stated, for the purpose of imparting water repellency, but they have always suffered from the disadvantage of being easily removed by alkalis, for example, alkali soap solutions, the reason being apparently that owing to the acidic character of its oxid, aluminum reacts with the alkali to form soluble compounds with the alkali metals, as for example sodium or potassium aluminate. The difficulty just mentioned can be overcome in large measure by using the aluminum compound in connection or in combination with compounds of the rare earth metals, in which case the rare earth or other compound appears to occlude or cover up the aluminum salt or salts in such manner that, while not destroying the distinctive character thereof, nevertheless renders it difficult to leach out because of the difficulty of establishing actual contact of the alkaline solution with the aluminum compound so occluded or covered in the rare earth matrix.

Because of its open and absorbent character it has always been a matter of extreme difficulty to render bleached fabric effectively water repellent, and it has therefore re-

quired such a large quantity of repellent material to accomplish the desired end that the quality and character of the fabric itself have frequently been impaired by the treatment applied. By a preliminary treatment by which the internal pores of the bleached fabric are filled with insoluble and difficultly removable rare earth and other compounds as described herein, with or without admixture of aluminum compounds, the fabric can be brought to such a condition that it can be easily and effectively made water repellent by the deposition of a fatty acid compound or a repellent hydroxid, as for example thorium or aluminum hydroxid.

So far I have described herein only chemical methods of effecting the impregnation or precipitation, but the desired result can also be obtained electrolytically, as by passing an electric current through the textile material when wet with the proper solution. For this purpose the textile material may be passed continuously or step-by-step between (and preferably in contact with) a pair or several pairs of electrodes while immersed in or wet with the impregnating bath, the electrodes being connected to the appropriate poles or terminals of a suitable source of current. A voltage of from 6 to 8 volts (preferably) may be employed. The amperage used is determined chiefly by economical factors, and in general should not be so high as to waste current in the form of heat produced by resistance losses in the bath. The effect of the current is to decompose the salt, the metallic radical moving toward the cathode but being converted into the hydroxid. There also appears to be a tendency for the current to force the finely divided hydroxid into the pores of the fabric by a process of cataphoresis or electrical osmosis. In some cases the electrolytic method may be used in conjunction with the chemical method, either before or after the same. In either case the second treatment may impart or increase the "external" water repellency of the fabric, by which is meant the difficulty of being wetted.

I am aware that incandescent gas mantles have been made by impregnating textile fabric with rare earth metal oxides, and I do not claim such articles, which have no utility until burned or incinerated, but what I claim is:

1. Textile material inherently capable of supporting mildew and like fungous growth, rendered resistant thereto and also repellent to water and resistant to attack by acids, by impregnation with a rare earth metal compound which is insoluble in alkaline solutions.

2. Textile material as described in the preceding claim, which is also impregnated with

an insoluble metallic compound imparting increased resistance to mildew and like fungous growth.

3. Process of rendering textile material, inherently capable of supporting mildew and like fungous growth, repellent to such growth and also repellent to water and resistant to attack by acids, which comprises impregnating the material with a solution containing sub-nitrate of thorium, converting the sub-nitrate into a compound insoluble in alkaline solutions, washing the material to remove any soluble compounds present, and thereafter drying the material.

4. Textile material impregnated with an insoluble rare earth metal compound and with a mildew-proofing metallic compound, said material being unincinerated.

5. Process of rendering textile material, inherently capable of supporting mildew and like fungous growth, repellent to such action and also repellent to water and resistant to attack by acids, which comprises impregnating the material with a solution of a sub-nitrate of a rare earth metal, removing excess liquid from the material, treating the partially dried material with a reagent capable of converting the said salt into a compound insoluble in alkaline solutions, washing the material to remove any soluble compounds present, and thereafter drying the material.

6. Process of rendering textile material repellent to fungous growth and to water, and resistant to attack by acids, which comprises impregnating the material with a dilute solution of a rare earth metal compound, treating the impregnated material with a reagent adapted to precipitate the rare earth metal compound in a colloidal form which is insoluble in hydrocarbons and alkaline solutions, and thereafter drying the material.

7. Process of rendering textile material repellent to fungous growth and to water, and resistant to attack by acids, which comprises impregnating the material with a dilute relatively cold solution of a rare earth metal salt, treating the impregnated material with a precipitant adapted to convert the rare earth metal salt into a colloidal form and thereafter drying the textile material under pressure whereby the colloidal precipitate is rendered substantially insoluble in hydrocarbons and alkali solutions and resistant to attack by acids.

8. Textile material repellent to fungous growth, resistant to attack by acids, and repellent to water, by impregnation with a hydroxid of a rare earth metal.

In testimony whereof I hereto affix my signature.

CLARENCE B. WHITE.