The present invention relates to waterproofed, "preserved", and dyed textile material, in which term I include not only woven fabrics but also all other kinds, knitted and netted, and also threads, yarns, fibres, and the various associations thereof. One object of the invention is to provide dyed textile material which is also repellant to water and highly resistant or repellant to the injurious influences of atmospheric gases and moisture, whereby the color imparted to the material by the dye or coloring medium or media, will be more permanent and less likely to fade.

Another object of the invention is to produce a dyed textile material which will be highly resistant or repellant to fungous growth and bacterial attack, and which will be more repellant to water and less subject to shrinkage than materials dyed by the commonly used processes.

Another important object of the invention is to produce or deposit within or upon the fibres of the textile material, prior to or simultaneously with the dyeing operation, insoluble compounds or substances of a basic character which shall be capable of absorbing or neutralizing acidic substances or acid radicals which may develop from the molecule of the water or fungus-repellant compounds or substances referred to above, to the end that the dyestuffs, coloring media or color lakes thus enclosed shall be more or less protected from the influence of atmospheric agencies, heat, light, and moisture, and will thereby be rendered faster to light and also more resistant to fading in washing.

The objects above mentioned are achieved in the present invention by the use, in or upon the fibres of the textile material, of suitable metallic compounds, preferably of metals of the rare earth group (among which may be mentioned thorium, cerium, neodymium, praseodymium, lanthanum, yttrium and erbium) and, in some cases, by the use of chromium, aluminum, magnesium, titanium, etc. These metals possess the important property of being precipitated as hydroxids when their compounds are acted upon by alkaline sulfids. Many of these hydroxids when formed or precipitated upon or within the fibres of textile material impart marked water-, mildew-, and bacteria-repellent properties, and, in addition, many of the hydroxids have strong and definite colors. For example, chromium hydroxid is grayish green, cerium hydroxid is yellowish white, neodymium hydroxid has a reddish tone, praseodymium hydroxid has a green and erbium hydroxid a purple-red color. The hydroxids of these elements are all strongly basic, as are also their carbonates, and are in a high degree capable of neutralizing acids. While alkaline sulfids precipitate hydroxids of the above mentioned metals, on the other hand copper, nickel, cobalt, antimony, iron, cad-
mium, and manganese are precipitated as sulfids, some of which have high tinctorial value. Thus antimony sulfid is orange in color, cadmium sulfid is yellow, and copper sulfid blackish brown. Such colors are, in general, more decided than those of the corresponding hydroxids, and when mixed in varying proportions are capable of producing varied tones and shades of a wholly mineral character. But nearly all the sulfids are capable of more or less easy oxidation to sulfates, which latter, because of their solubility, may be readily washed out, or because of their tendency to dissociate may liberate acidic ions which react upon and hydrolyze the cellulose of the fibres upon which they may have been precipitated, thereby rendering the fibres and eventually rendering the fabric useless. It is therefore of the highest importance to have present, in or upon the fibre, basic elements or compounds which will neutralize or destroy acidic ions as rapidly as the latter may be formed and set free.

The presence of the insoluble rare earth compound (usually an hydroxid) renders the textile material repellant to water and to fungous and bacterial growth, as explained in my copending application Serial No. 639,219 filed May 15, 1923.

Some of the sulfids referred to above (for example antimony, cadmium and copper sulfids) are when dry considerably resistant to oxidation, and especially so when they are enclosed or embedded in a mass of basic material, or are protected from atmospheric agencies by water repellant coatings or non-absorbent and repellant compounds such as the metallic soaps and hydroxids of the class alluded to, and I have found it practicable to precipitate cadmium, copper, antimony, nickel, cobalt, and iron, etc., as sulfids in the same chemical reaction or process that produces hydroxids of the rare earth metals and hydroxids of aluminum, titanium, magnesium and chromium. In many such cases the resulting color is a blend of wholly mineral origin, possessing the intrinsic fastness of mineral colors to light. Many of the shades thus produced are unique, and the colors may be further varied by various admixtures of tin, antimony, or cadmium sulfids, used separately or combined together.

The destructive effect of sulfuric acid ions can also be avoided, or measurably and substantially diminished, by the use of insoluble or difficultly soluble compounds of the alkali earth metals, as calcium, strontium and barium, or the related magnesium; among which compounds may be mentioned hydroxids, carbonates, tannates, and insoluble organic compounds in general. Such compounds have a very strong affinity for the sulfuric acid ion, and once united therewith are very difficult of dissociation therefrom. With the exception of magnesium, they have the advantage that the compounds formed with sulfuric acid are very insoluble, barium sulfate being one of the most insoluble compounds known.

The scope and utility of the invention are not limited to the production and application of the so-called mineral dyes, but on the contrary the invention admits of a wide extension and application to the field of substantive and adjective dyeing in which organic coloring media are also used. This is strikingly illustrated in the field of direct dyes, and especially the so-called sulfur dyes, where the coloring medium is dissolved in and applied with a strong solution of sodium or other alkaline sulfid. If the sulfur dye be applied in an alkaline sulfid bath to a fabric already impregnated with a soluble salt of one or more of the elements and substances already noted, the sodium sulfid or other alkaline sulfid will decompose the impregnating salt, forming an insoluble hydroxid, which hydroxid will, as it is formed, be thoroughly permeated by the color medium, occluding it in a colloidal or gelatinous mass which when dry strongly protects it from light or radiant energy in general and from atmospheric agencies. The action is not essentially different when used with certain mordant dyes, such as for instance those of the anthraquinone series (including alizarin), which in general are applied in strongly alkaline solution.

From the foregoing it will be seen that simultaneously with the actual dyeing, and as an integral part of that operation, I am able to produce or deposit upon or within the fibres, compounds which render the textile material strongly repellant to water and mildew and to bacterial attack, thereby making unnecessary, in most cases, any drastic after-treatment to effect such purposes. Such after-treatments almost invariably have an appreciable, and in some cases a very great, damaging effect upon the colors and shades of the dyed material.

Except where there is danger of the production of acid radicals or ions through oxidation or breaking down of the color molecule (as in sulfid-dyed material, for example) it is not always necessary, in my invention, that the fibres of the textile material also contain or carry compounds of a strongly basic character. In other cases the requirements of fast color, non-tendering of the fibres, etc., are met by the presence of an insoluble compound which occludes or envelopes the color lake. Many of the rare earth elements which inhibit or restrain the development of mildew or bacteria form insoluble fluorids, carbonates, phosphates, borates, benzozates, aluminates, stannates, and other insoluble compounds, which not

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only give the textile material advantageous
water-, bacteria- and fungus-repellant prop-
erties but also furnish the necessary mord-
ant for mordant dyes. These insoluble
compounds are formed and precipitated by
the action of alkaline fluorids, phosphates,
borates, etc., and in many cases the precipi-
tating solutions can be added directly to the
dye bath, so that when textile material pre-
viously impregnated with soluble rare earth
metal compounds is passed through the bath
the latter compounds will be converted in-
to insoluble compounds simultaneously
with, and as a part of, the actual dyeing
operation.

As is well known, some of the important
dyestuffs are best applied in an alkaline
bath, some in an acid bath, and others in
a neutral bath. My present invention is ap-
plicable in all three cases.

For the purpose of more fully explain-
ing my invention, its results, and mode of
application, I give below, in detail, various
examples; with the understanding, however,
that the invention is not limited thereto but
can be carried out in other ways.

Preferably, in carrying out my process as
concerned with so-called mineral dyes, I
first impregnate the textile material with a
soluble salt of a metal or element capable of
being insolubilized as hydroxid by re-
action with alkaline hydrate, carbonate or
sulfid. For the purpose of coloring the tex-
tile material the impregnating solution also
contains a salt of a metal capable of being
precipitated as a metallic sulfid of suitable
color or tint by reaction with an alkaline
sulfid. Among the salts capable of being
converted into insoluble hydroxids I may
mention chlorids, acetates and nitrates of
the rare earth elements; and as examples of
salts capable of being converted into insol-
uble sulfids which also are capable of dyes
the textile material, I may mention any salt
(preferably sulfur-free) of iron, copper,
nickel, cobalt, cadmium, antimony, and bis-
muth. The following are excellent formu-
las for impregnating baths:

(a)

<table>
<thead>
<tr>
<th>Water</th>
<th>Copper acetate</th>
<th>Rare earth metal acetate or acetates</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>50</td>
<td>25</td>
</tr>
</tbody>
</table>

(b)

<table>
<thead>
<tr>
<th>Water</th>
<th>Copper acetate</th>
<th>Rare earth acetate or acetates</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>16</td>
<td>16</td>
</tr>
</tbody>
</table>

Both the above solutions when treated with
sodium sulfid or other alkaline sulfid as a
precipitant yield a mineral dye of an olive
drab color, the shade being darker with a
greater amount of copper and lighter with a
greater amount of chromium or rare earth,
and hence a large variety of shades can be
obtained by proper proportion of the two
ingredients. The alkaline sulfid treat-
ment also precipitates upon or in the fibres
of the textile material the rare earth metal
in the form of insoluble hydroxid, which,
being strongly basic, serves to neutralize any
acid ions that may be set free by subsequent
dissociation of the copper or chromium sulf-
id in the manner previously alluded to,
thereby protecting the fibres from injury by
the tendering effect which such ions or radic-als would otherwise have. The im-
pregnation can be effected at ordinary tem-
peratures, by immersing the textile mate-
rial in the selected solution, long enough
(usually momentarily) for thorough impre-
gination. The material can then be dried,
with or without the use of heat, and treated
with the selected precipitating bath, which
may be a solution of sodium sulfid of, say,
from 3 to 20 per cent strength, at practic-
ally any temperature up to 100°, ac-
cording to the nature of the fibre; cotton,
for example, permitting a high temperature,
while silk requires a relatively low tem-
perature.

Many dyestuffs are, or can be, applied in
a strongly alkaline bath. Notable among
these are the direct dyes known as "sulfur
dyes", which are soluble only in a strong
solution of an alkaline sulfid; and dyes of
the mordant type, and their prototypes, the
madder dyes. In using a dye of these classes,
I first impregnate the textile material with
any soluble salt (preferably an acetate) of
a metal which can be precipitated in in-
soluble form by alkaline sulfids, hydrates or
carbonates. For this purpose I prefer salts
of the rare earths though I can use salts of
other metals, as aluminium, magnesium,
chromium and titanium. After impregna-
tion the textile material is dried, and is then
ready for the alkaline dye-bath. In the case
of sulfur dyes, as the material passes into
the dye bath the alkaline sulfid therein,
usually sodium sulfid, reacts with the soluble
salt with which the material has been im-
pregnated and converts it into the insoluble
hydroxid precipitates, and at the same time
carries into the apparently colloidal pre-
cipitate on the fibre the color base of the
dye-bath. In the case of alizarin, madder
and other dyes requiring alkaline baths, I
prefer to use caustic soda or sodium car-
bonate as the precipitating medium. These
precipitants, however, should not be used
for textile material impregnated with an
aluminum compound.

After dyeing cotton with an alkaline dye-
bath I sometimes (after washing the mate-
rial) treat it with a soap solution, for the
purpose of brightening and further fasten-
ing the color. In such case the soap reacts
with the metallic compound on the fibre, forming an insoluble soap which renders the fabric repellant to water. Preferably the metals selected for impregnating the fabric before dyeing are such as will also impart a degree of repellency to mildew and other fungous growth; as for example the rare earth metals, especially thorium, cerium, didymium and lanthanum.

In the case of dyes which cannot be applied from an alkaline bath but require a neutral or an acid bath, I first impregnate the textile material with a rare earth element, notably thorium, cerium, lanthanum or didymium, in the form of a compound (as for example an acetate) from which a compound can be precipitated which is insoluble but slightly soluble in dilute acids such as are used in acid dyeing, and in the subsequent dyeing of the impregnated material I include as a precipitant in the acid dye-bath a fluorid, phosphate, benzoate, salicylate, or other suitable salt of an alkali metal or alkaline earth metal. Then as a result of the reaction between the salt or salts just named and the rare earth salt the latter is converted into an insoluble compound—a fluorid, phosphate, etc., as the case may be, with the same effect as is produced in the case of dyes requiring alkaline baths as described above.

Cotton exhibits no basic properties, and hence cannot be dyed by means of certain acid colors which are available for animal fibres, and the choice of dyestuffs for use with cotton is therefore much more limited than in the case of animal fibres, for example wool and silk, which latter occupies an intermediate position between cotton and wool. In general, cotton dyeing is confined to the following classes of dyestuffs:

1. Basic colors (salts of organic bases), the dyeing power of which lies wholly in the basic portion of the salt and requires an acid or an acid salt to develop the color. These dyes require a mordant.

2. Direct colors, the characteristic feature of which is that they dye cotton directly, without mordanting. These colors fall into two distinct groups, which are known as direct cotton colors and sulfid colors. They are mostly alkali salts of sulfonated tetrizo bases, formed by diazotizing benzidine or dianido-stilbene, and then uniting the products with amines or phenols. Such dyes are thus already alkaline or at least are of the nature of alkaline salts and are not incompatible with other alkaline bases.

As an application of my invention to the dyeing of cotton with direct dyes the following example may be given:

The cotton is first impregnated with a rare earth salt or salts, as for example cerium acetate. The impregnating solution may also contain, for example, a soluble chromium salt, say chromium acetate, for the purpose of increasing fastness to light and washing. The impregnated cotton is preferably dried, after which it is passed through the dye bath, which may be of the composition:

Water, 1 gallon; dye (direct color or colors), 5 oz.; sodium fluorid, 6 oz.; sodium carbonate, 1/2 oz.

The amount of dyestuff is variable, especially since the absorption by the fabric is in inverse proportion to the amount of dye liquor in the dye bath. The sodium carbonate can be replaced by the same amount of soap.

When the impregnated material is passed into the dyeing and precipitating bath the sodium fluorid converts the rare earth metal salt on the fibres into an insoluble fluorid; and carries into the fibre, and into the fluorid precipitated thereon, a certain portion of the dyestuff. The sodium fluorid may be replaced by any other salt capable of producing a like effect, as for example sodium, potassium or ammonium phosphate, benzoate, salicylate, silicate, hydroxid (when not incompatible with the dyestuff), carbonate, cyanid, etc.

The sulfid colors can be applied only in a strongly alkaline bath, a circumstance that limits them, practically, to cotton, linen, jute, and other vegetable fibres. The usual solvent for the dye is a strong solution of sodium sulfid. In applying my invention with this class the textile material is first impregnated with soluble salt of one or more of the metals heretofore mentioned for a like purpose. Preferably, but not necessarily, the salt is one of an acid which has no tendering effect when dried, as for example an organic acid, say acetic or lactic. The impregnated fabric, preferably dried, is passed into the sulfid dye bath, thereby converting the soluble metallic salts of the impregnated fibre into insoluble compounds, as for example hydroxid. At the same time the color medium dissolved in the bath is released by the decomposition of the sulfid and appears intimately incorporated with the amorphous colloidal or quasi-colloidal hydroxid precipitated on and within the fibre. If desired, the conversion of the soluble salt into an insoluble compound can be effected before dyeing, in which case the dyeing operation may proceed exactly as with an unimpregnated fabric, but the incorporation of the dye is not likely to be as intimate or as uniform as when the insolubilization and the dyeing are effected simultaneously or by the same bath. The range of composition of the dyeing and insolubilizing or precipitating bath is wide, the composition depending largely upon the particular dyestuff to be used. In general, the color medium constitutes from five to fifteen per cent of the bath, with a variable
amount of sodium carbonate and a larger proportion of common salt. The sodium sulfid content may vary widely, say from five to thirty per cent.

5 Mordant colors possess the property of combining with metallic oxids and other compounds, the combination in general producing the tint, which varies with the particular oxid or compound employed. Others of this class possess, within themselves, the property of dyeing, irrespective of their ability to form color lakes with metallic oxids. The chemical explanation of this class characteristic is found in the fact that the members of the class all contain hydroxyl groups while others contain both hydroxyl and carboxyl groups. It is not, however, necessary that the metallic base exists in the textile material in the form of oxid or hydroxid, inasmuch as the color media of the class under consideration have the power of combining with oleats, tannates, silicates, etc., to form the "lake" on or within the fibre. In applying my invention with mordant colors the textile material is, as in the case of the dyes already described, first-impregnated with the desired metallic salt, preferably an acetate, and is then dried or tightly squeezed between rollers to eliminate at least the major portion of the moisture. The dyed or squeezed fabric is next passed through the dye bath, which latter contains in addition to the color medium or media a chemical agent capable of precipitating and rendering insoluble the metallic salt or salts with which the material was impregnated. Among the precipitating or insolubilizing agents usable for the purpose, I may mention hydrates and carbonates of the alkali metals, alkaline silicates, oleats, tannates, borates, oxalates, fluorids, phosphates, etc. In this way the necessary mordanting, that is, the formation of the color lake, is effected, and at the same time, as in the other cases hereinafter described, a substance is introduced into the textile material, in or upon the fibres thereof, which renders the latter repellent to water or mildew or both.

Developed colors include a group of colors which are developed upon the fibres by the successive application of their constituent parts, one of which is usually of an acid character. In applying my invention with a dye of this class the metallic compound which is precipitated upon or in the fibre must be of such nature that it will not readily dissolve in dilute acids. Such compounds are well illustrated by the phosphates of the rare earth metals (including hypophosphates, pyrophosphates, etc.) and the fluorids of the same group, as well as silicates and, to a lesser extent, the dried hydroxids. The latter are, as a rule, very soluble in the freshly precipitated wet state, but many, as for instance thoriun and cerium hydroxids, are rendered relatively insoluble by drying. Zirconium hydroxid precipitated from a hot solution is almost insoluble in dilute acid solutions, although the hydroxid formed by cold precipitation is easily soluble in such solutions. The acids used to develop the colors in the dyeing operation are quite dilute and hence there is little or no danger of dissolving the metallic compound with which the textile material has been impregnated; and especially is this true when the impregnating compound is a phosphate, oxalate, or fluorid of the rare earth elements. "Developed colors" fall into three general classes:

(a) Insoluble azo colors.—These are formed by the addition of a dissolved diazo compound to an alkaline solution of a phenol or to an acid solution of an amido compound. The most striking example of this sub-group is the well known paranitranilin red.

(b) Developed direct colors.—These are developed from primuline or from direct colors containing free amido compounds by passing the dyed material into a solution of an amine or a phenol.

(c) Benzo-nitrol colors.—With these the material is dyed by means of certain direct colors which are developed by passing the textile material into a solution of diazo compounds, as for instance diazotized paranitranilin. The process is similar to the development of the insoluble azo colors.

In dyeing operations in which the actual dyeing is conducted in an alkaline bath, the fixing or precipitating agent required for insolubilizing the water-repellant or mildew-repellant compound or compounds may be in general directly incorporated with the dye-bath and the insolubilizing operation is then carried on simultaneously with the dyeing of the textile material. When the dye-bath is of a neutral character the insolubilizing can also be effected simultaneously with the dyeing, but for this purpose a neutral precipitant must be used, as for example a fluorid, phosphate, oleate, silicate, etc. With the exception of the developed dyes, such as the insoluble azo dyes and their related groups, nearly all cotton dyeing is effected with neutral or alkaline dye-baths. With silk and wool the case is different, these materials being usually dyed in an acid bath, and in this case the fixing or precipitating agent for insolubilizing the water-repellant or mildew-repellant compound or compounds must be such that the compound so produced shall be relatively insoluble in the dilute acidity of the acid dye bath. These conditions are met by the rare earth element compounds, which in general confer mildew-repellancy as well as affording a basis for building up water-repellancy. Typical examples of precipitated compounds (of rare earth elements)
which are relatively insoluble in dilute acids are fluorids, phosphates, oxalates, silicates, oleates, stannates and tannates, and in some cases the dried hydroxids, especially cerium and thorium hydroxids; and zirconium hydroxid precipitated by caustic alkali from a hot solution.

Of the foregoing fabrics I consider it preferable to effect the fixation or insolubilization of the water-repellant or bacterial-resistant material simultaneously with the actual dyeing, for the reason that the penetration of the color medium of the dye is much more thorough, approximating in fact the thorough penetration so characteristic of yarn or stock dyeing, and the result is therefore relatively faster to light and washing. Nevertheless, where the simultaneous method is not practicable on account of the incompatibility of the insolubilizing media and the dye-bath, the fabric or other textile material can be made water-repellant or mildew- or bacteria-resistant before dyeing and may then be dyed by any of the well known methods.

It is important, however, where the dyeing is to be carried out with an acid bath, to take precautions that the compound (deposited upon or within the fibers) by which the resistant or repellant properties are imparted to the material, be of such nature that it is readily insoluble in dilute acids. Although the simultaneous method is to be preferred, the subsequent dyeing method is equally efficacious in preventing the staggering of colors which is almost inevitable in former processes in which an already dyed material or fabric is subjected to treatment for the purpose of rendering it repellent to water or resistant to bacterial attack.

I do not claim herein the use of water-soluble salts or other compounds as media for protecting textile material from tendering products resulting from the action of atmospheric or other agencies on the coloring agent; nor do I claim for such purposes the use of compounds of elements (as for example calcium, strontium, barium, and zinc) which are capable of forming sulfids in the wet way. Such compounds in solution react to form sulfids when the textile material is treated with alkaline sulfid, and the sulfids so produced in the textile material not only have no protective effect but may even in some cases be themselves a source damage to the material.

It is to be understood that the invention is not limited to the specific details herein described but can be carried out in other ways without departure from its spirit as defined by the following claims.

I claim:

1. The method of coloring textile material and rendering the same repellent to subsequent tendering products, comprising coloring the textile material with a metallic sulfid and depositing in the textile material, for neutralizing acid products resulting from the action of atmospheric or other agencies on the said metallic sulfid, an insoluble basic compound of an element incapable of forming a sulfid in the wet way.

2. The method of coloring textile material and rendering the same repellent to subsequent tendering products, comprising simultaneously coloring the textile material with a metallic sulfid and depositing in the textile material, for neutralizing acid products resulting from the action of atmospheric or other agencies on the said metallic sulfid, an insoluble basic compound of an element incapable of forming a sulfid in the wet way.

3. The method of coloring textile material and rendering the same repellent to fungous growth, bacterial attack, or tendering products, comprising impregnating the textile material with a soluble compound of a metal capable of reacting with an alkaline sulfid to form an hydroxid, and with a soluble compound or another group capable of reacting with an alkaline sulfid to form a sulfid which is capable of coloring the material, and thereafter treating the impregnated material to convert the first mentioned soluble compound into an insoluble compound and the other soluble compound into a sulfid.

4. The method of coloring textile material with mineral colors and simultaneously rendering the same repellent to fungous growth, bacterial attack, or tendering products, comprises impregnating the textile material with soluble metallic salts capable of reacting with alkaline sulfid, one producing thereby an insoluble hydroxid and another a metallic sulfid of suitable color, and treating the impregnated material with an alkaline sulfid solution.

5. The method of coloring textile material with mineral colors and simultaneously rendering the same repellent to fungous growth, bacterial attack, or tendering products, comprising impregnating the textile material with a rare earth metal compound and a compound of a metal of another group, and treating the impregnated material with an alkaline sulfid solution whereby the first named compound is converted into an insoluble hydroxid and the second into a sulfid.

6. The method of coloring textile material with mineral colors and simultaneously rendering the same repellent to fungous growth, bacterial attack, or tendering products, comprising impregnating the textile material with salts of a rare earth metal and a metal of another group, and treating the impregnated material with an alkaline sulfid to precipitate on the textile material an insoluble hydroxid of the rare earth metal and a colored sulfid of the other metal.

7. Textile material colored with sulfid and
containing a neutralizing compound of an element incapable of forming a sulfid in the wet way.

8. Textile material colored with sulfid and containing a neutralizing hydroxid of an element incapable of forming a sulfid in the wet way.

9. Textile material colored with metallic sulfid and containing a neutralizing compound of an element incapable of forming a sulfid in the wet way.

In testimony whereof I hereto affix my signature.

CLARENCE B. WHITE.