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COATED FIBROUS SHEET MATERIALS

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This invention relates to the coating and filling of fibrous, sheet materials, such as paper, textiles and the like; and it relates more particularly to the coating or filling of paper or textiles with water-resistant materials to impart thereto a water resistant finish which is very durable, which is highly resistant to decomposition and to high temperatures, etc. Textiles, such as cotton fabrics, filled or coated in accordance with the invention, are water resistant to the extent that the coating or filling composition is not readily removed by water as in washing, and the coating or filling is highly resistant to deterioration because of exposure to the weather. Such textiles, properly treated in accordance with the invention, may be highly water absorptive and have advantages over previously known filled or coated textiles for certain purposes where high water absorption is desired; or the textiles may be highly resistant to water penetration, i. e. quite waterproof.

In accordance with the present invention, paper, textiles and the like including such fabrics as cotton fabrics and glass cloth, are filled or coated with a composition including a water-swellaible colloidal hydrous silicate of aluminum, calcium, or magnesium, or a complex water-swellaible colloidal hydrous silicate of more than one of these metals, and an emulsified synthetic resin, the water-swellaible hydrous silicate and the resin being applied in the form of an aqueous slurry or suspension, containing the emulsified resin, and the suspended silicate. The compositions may, of course, include other materials commonly used in the coating or filling of textiles and paper, such as adhesives including starch, casein, or the well known casein substitutes, or added minerals, including the various clays, calcium carbonates, calcium sulfates, etc. In some cases the water-swellaible hydrous colloidal silicate may naturally occur in admixture with minerals such as carbonates which are sufficiently soft to permit pulverization to impalpable fineness, and in such cases the water-swellaible silicates may be used without separation of the admixed mineral.

The water-swellaible silicate-synthetic resin emulsion compositions have important advantages for the back filling of fabrics of open weave where washability or resistance to heat and moisture is desired, as in shoe linings, etc. Closely woven fabrics are ordinarily finished by "starching" instead of filling, and the silicate-resin emulsion compositions have outstanding advantages for such finishing of fabrics, because, when applied to fabrics, they do not readily wash out and they impart to the cloth a finished or "feel" which is free from the objectionable clamminess of fabrics finished with starch. Glass textiles are more or less widely used for electrical insula-

tion purposes; but it has not been found possible to weave a fabric sufficiently tight to prevent current leakage through the interstices of the fabric. It has been proposed to prevent such current leakage by filling between the threads of the fabric with varnish, but the varnish melts and carbonizes at the temperatures to which such insulating material is commonly heated. Glass fabrics filled with the silicate-resin composition show greatly improved properties for electrical insulation, because of the great resistance to decomposition at high temperatures, glass fabrics so filled showing no decomposition or deterioration at temperatures up to 500° F. or higher. For certain purposes, such as bandages and the like, fabrics are desired which are entirely water absorbent; and for such purposes, fabrics may be filled with water-swellaible silicate-resin compositions which have important advantages, both because they retain the natural porosity of the cloth and because the water-swellaible silicate has the property of absorbing substantial amounts of water.

Textiles or paper filled or coated in accordance with this invention are quite flexible and pliable and are not harsh and stiff to the extent that they crack where folded. The filling or coating is not brittle, and does not fall out when the material is bent, nor readily fall out on repeated folding of the material.

The water-swellaible silicates used in preparing the coating, filling and finishing compositions may be obtained from various sources. In general, they belong to the Montmorillinite group of minerals, which includes Montmorillinite, Beidellite, Nontronite and Saponite. They occur in nature in admixture with various other mineral products, and in some cases it is important to remove some of the other mineral products before using the water-swellaible hydrous silicates, whereas in other cases, such removal is unnecessary. Where the water-swellaible hydrous calcium-magnesium-aluminum silicates, which occur in bentonite, are used, it is important to separate and discard the gritty material with which such silicates are usually associated; and this separation may be readily obtained centrifugally, with the subjection of a slurry or suspension of bentonite in water containing from around 4 to 15% or more of solids to a centrifugal force ranging from about 400 to 1500 or more times the force of gravity, as described in the application of William H. Alton, Serial No. 174,859, filed November 16, 1937. Where the water-swellaible silicates used occur naturally in admixture with carbonates, etc., it may be desirable to separate the carbonates from the silicates by a similar process, as described in the application of William H. Alton, Serial No. 228,682, filed September 6, 1938, so that a product

consisting substantially entirely of water-swellable, hydrous colloidal silicate is used in preparing the coating, filling and finishing compositions, particularly where a highly absorptive composition is desired. On the other hand, for many, if not most, purposes, the presence of such extraneous minerals as calcium carbonate or magnesium carbonate is unobjectionable, because these minerals are soft, may be readily pulverized to an extremely finely divided state, and do not abrade or wear machinery as do the gritty particles which occur in commercial bentonite.

It is important and advantageous to use a water-swellable silicate of a light, advantageously white, color. Some silicates, derived from available sources, are not well suited for use in accordance with the present invention because of their dark color, particularly where it is desired to obtain white or light colored paper or textiles. Coloring materials may, of course, be included in the compositions.

A wide range of synthetic resins may be used in forming the resin emulsions used in the coating, filling and finishing compositions. Advantageously the resins are used by forming an aqueous emulsion of the resin, and admixing such aqueous emulsion with a slurry or suspension of the water-swellable silicate. The resulting aqueous composition, containing the emulsified resin and the suspended silicate, thus being a composite suspension and emulsion, is extremely stable, and shows practically no tendency to settle out, providing the relative proportions of the silicate and the resin are properly adjusted. It is important that the amount of resin in the composition does not greatly exceed the amount of bentonite, in order to produce satisfactory coatings or finishings, and to have proper stability of the composition.

Among the synthetic resins which may be emulsified with water for use in carrying out the invention are the alkyd resins, that is, the resins derived from a polyhydric alcohol, a polybasic acid and a modifying agent, such as a fatty acid, particularly the fatty acids derived from drying oils, the acrylic acid and acrylic acid ester resins, obtained by the polymerization of acrylic acid or acrylic acid esters, the cumar resins, the vinyl resins, obtained by polymerization of vinyl compounds, the phenol resins, the modified phenol resins, such as the resins obtained from phenol resins and ester gum, copal or the like, the urea- or thiourea-formaldehyde resins, etc. Of course, mixtures of the various resins, such as mixtures of the alkyd resins and the phenol resins, or the alkyd resins and the urea-formaldehyde resins, or other mixtures of compatible resins may be used. In general, the resins should be of a light color, advantageously as colorless and transparent as possible, particularly where light or white paper or textiles are desired.

The resin emulsions are readily produced by the emulsification of the resins with water with the aid of an alkaline emulsifying agent, such as ammonia, triethanolamine, morpholine, sodium carbonate, etc. The emulsion is prepared by placing the resin, together with water and the emulsifying agent in a suitable mixer, usually a high speed mixer, and agitating until suitable emulsification takes place. Ordinarily, the mixture is warmed to promote emulsification, except where an emulsifying agent which is highly volatile, such as ammonia, is used, in which case the emulsification is usually carried out in the

cold. Methods of producing emulsions of the various resins are well known, and need not be further explained here. In general, ordinary glyptal resins, that is, the glycerin-phthalic anhydride resins, unmodified by other agents such as fatty acids or the like, do not have properties which make them useful because they do not form emulsions with alkaline emulsifying agents and form films which soften in water and dissolve in dilute alkaline solution and hence are not resistant to laundering operations or the like. Nevertheless, for the coating of paper, and for other purposes where washability is not required, even these resins may be used in carrying out the invention, particularly when used in admixture with other resins, such as rosin, ester gum, copal, phenolic resins, either straight or modified, urea-formaldehyde resins, etc.

In forming the water emulsions, there is no critical range of proportions of solids to water. It is convenient to prepare the emulsions with a solid content of about 25%, although they may be varied over a wide range, as is understood in the art.

The coating compositions containing the water-swellable hydrous silicate and the emulsified resin for most filling, finishing and coating purposes should contain in the neighborhood of 3 to 5% of the water-swellable silicate, and equal or smaller amounts of the resins, and may contain other admixed materials, such as other minerals, including those which may occur in natural admixture with the silicates, starch, clays, casein or casein substitutes, etc. In general, compositions containing more than 4 to 5% of the water-swellable silicates present difficulties in application, because of their viscosity, as the silicates form a viscous paste with water, particularly where the proportion of the silicate to water is in excess of 4 or 5%. The other ingredients, such as the emulsified resins, etc., do not greatly effect the viscosity of the compositions in the proportions used.

The relative proportions of resin and water-swellable silicates in the compositions may be varied over a relatively wide range, and the relative proportions used will depend to a large extent on the nature of the material coated or filled, and the characteristics desired. For example, for filling cloth intended for window shades and the like, a relatively high proportion of resin will be used, so that the filled fabric will be resistant to water penetration. For such purposes, the resin and water-swellable silicate may be used in about equal proportions, or the amount of resin may be somewhat in excess of the amount of silicate, for example, about twice as much. Where a water-absorbent product is desired, the resin should be used in smaller amounts, for example in amounts ranging from $\frac{1}{10}$ to $\frac{1}{4}$ the amount of the water-swellable silicate; that is, in amounts just sufficient to prevent the silicate from being readily removed by washing, exposure to water, etc. For coating paper, substantially the same considerations apply. If the paper is to be highly resistant to penetration by water, a relatively large proportion of resin should be used, for example, an amount equal to, or a little greater than the amount of water-swellable silicate. On the other hand, use of smaller proportions of resin results in the production of coated papers having less resistance to penetration by water, but having high resistance to penetration by oil and oily materials, with the coating having

excellent adhesion. In no case should the resin be used in amounts such that the water-swella-
 ble silicate is a minor constituent of the composi-
 tion, for example, in amounts ranging from 5 to
 10 times the amount of silicate, as compositions
 containing such proportions of resin and silicate
 in effect "varnish" the textile or paper, and give
 a product quite different in nature from the prod-
 ucts of this invention.

The invention will be further illustrated by the
 following specific examples, although it is not
 limited thereto.

Example 1.—A fabric intended for shoe linings
 is filled with a composition consisting of an aque-
 ous suspension or emulsion containing about 4%
 of bentonite freed from gritty materials by cen-
 trifugal treatment as described and about 3 to
 4% of an acrylic acid resin or a methyl or ethyl
 acrylate resin, the resin being formed into an
 emulsion containing about 25% solids and this
 emulsion being added to a bentonite suspension,
 with dilution of the resulting composition if re-
 quired. The resulting filled fabric has the proper
 stiffness and a desirable texture for shoe linings,
 has no clammy feel, and does not decompose or
 mold because of heat or moisture.

Example 2.—An open-weave fabric is back-
 filled with a composition made from about 110
 parts of a 7% suspension of potato flour, about
 50 parts of an emulsion of an acrylate or acrylate
 ester resin containing about 25% solids and about
 40 parts of a 13% suspension of bentonite freed
 from grit in water, with dilution of the resulting
 composition to the desired consistency for back-
 filling with available equipment. Fabric so back-
 filled has an excellent finish, and is highly re-
 sistant to removal of the filling by washing or
 exposure to weather.

Example 3.—A closely woven fabric is finished
 with the use of an aqueous composition contain-
 ing about 3% of a water-swella-ble silicate having
 a white color, from 2 to 3% of a synthetic resin,
 such as an acrylate or acrylic acid ester resin, or
 an alkyd resin, or a phenol-formaldehyde resin,
 or a cumar resin, or a urea-orthiourea-formalde-
 hyde resin, or a mixture of two or more of these
 resins, or a mixture of one or more of these re-
 sins with a product such as ester gum, rosin or
 copal. The composition may also contain up to
 3 or 4% of finely divided mineral matter, such
 as calcium or magnesium carbonate, which may
 be introduced into the combination as a naturally
 occurring mixture with the water-swelling sili-
 cate. The fabric so finished is washable, is free
 from any clammy or disagreeable feeling on con-
 tact with the body, and has an excellent appear-
 ance.

Example 4.—A white paper is coated with an
 aqueous composition containing about 4% of a
 white water-swella-ble hydrous colloidal silicate,
 about the same amount of extremely finely divid-
 ed calcium and magnesium carbonate, and about
 3 to 4% of emulsified alkyd resin. The paper
 produced is smooth and has an excellent finish,
 with a coating which adheres well, even when
 the paper is folded or bent.

Example 5.—A glass fabric, intended for elec-
 trical insulation, is filled with the use of an aque-
 ous composition containing about 3 to 5% of a
 water-swella-ble mixed calcium and magnesium
 silicate and about 2% of emulsified alkyd resin.
 The filled fabric has excellent electrical insulat-

ing properties and resistance to decomposition
 at high temperatures.

The coating and filling compositions may con-
 tain dyestuffs, pigments, etc. compatible with the
 other ingredients to color the textile or paper, as
 well as other modifying agents, such as latex, etc.

I claim:

1. The process of treating fibrous sheet ma-
 terials which comprises applying thereto an aque-
 ous composition comprising a water-swella-ble
 colloidal silicate and an emulsified synthetic resin,
 the proportion of resin to water-swella-ble sili-
 cate not exceeding about two.

2. The process of treating fibrous sheet ma-
 terials which comprises applying thereto an aque-
 ous composition comprising a water-swella-ble
 colloidal silicate and an emulsified synthetic resin,
 the amount of water-swella-ble silicate in such
 composition being at least as great as the amount
 of resin.

3. The process of treating fibrous sheet ma-
 terials which comprises applying thereto an aque-
 ous composition comprising a water-swella-ble
 colloidal silicate from the group consisting of
 water-swella-ble aluminum, calcium and magne-
 sium silicates and an emulsified synthetic resin,
 the proportion of resin to water-swella-ble sili-
 cate not exceeding about two.

4. The process of treating fibrous sheet ma-
 terials which comprises applying thereto an aque-
 ous composition comprising a water-swella-ble col-
 loidal mixed calcium and magnesium silicate and
 an emulsified synthetic resin, the proportion of
 resin to water-swella-ble silicate not exceeding
 about two.

5. The process of treating fibrous sheet ma-
 terials which comprises applying thereto an aque-
 ous composition comprising a water-swella-ble
 colloidal mixed calcium and magnesium silicate,
 calcium and magnesium carbonate, and an emul-
 sified synthetic resin, the proportion of resin to
 water-swella-ble silicate not exceeding about two.

6. Fibrous sheet material having applied there-
 to a composition including a water-swella-ble col-
 loidal silicate and a synthetic resin, the propor-
 tion of resin to water-swella-ble silicate not ex-
 ceeding about two.

7. Fibrous sheet material having applied there-
 to a composition comprising a water-swella-ble
 silicate and a synthetic resin, the amount of resin
 not exceeding the amount of water-swella-ble sili-
 cate.

8. Fibrous sheet material having applied there-
 to a composition including a water-swella-ble col-
 loidal silicate from the group consisting of water-
 swella-ble aluminum, calcium and magnesium sili-
 cates and a synthetic resin, the proportion of
 resin to water-swella-ble silicate not exceeding
 about two.

9. Fibrous sheet material having applied there-
 to a composition comprising a water-swella-ble
 colloidal mixed calcium and magnesium silicate
 and a synthetic resin, the proportion of resin to
 water-swella-ble silicate not exceeding about two.

10. Fibrous sheet material having applied
 thereto a composition comprising a water-swella-
 ble colloidal mixed calcium and magnesium sili-
 cate, calcium and magnesium carbonate, and a
 synthetic resin, the proportion of resin to water-
 swella-ble silicate not exceeding about two.

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