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 absorbent 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-swellable colloidal hydrosilicate of aluminum, calcium, or magnesium, or a complex water-swellable colloidal hydrosilicate of more than one of these metals, and an emulsified synthetic resin, the water-swellable hydrosilicate 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, casin, or the well-known casein substances, or added minerals, including the various clays, calcium carbonates, calcium sulfates, etc.

In some cases the water-swellable hydrosilicate 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-swellable silicates may be used without separation of the admixed mineral.

The water-swellable 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 insulation 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-swellable silicate-resin compositions which have important advantages, both because they retain the natural porosity of the cloth and because the water-swellable 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 when 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-swellable silicates used in preparing the coating, filling and finishing compositions may be obtained from various sources. In general, they belong to the Montmorillonite group of minerals, which includes Montmorillonite, Beldellite, 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-swellable hydrosilicates, whereas in other cases, such removal is unnecessary. Where the water-swellable hydrosilicate of 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. 174,639, filed November 16, 1937. Where the water-swellable 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. 228,692, 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, etc., in the various natural silicates, make them unacceptable, 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 resin is dissolved 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 acryllic acid ester resins, obtained by the polymerization of acryllic 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-phthallic anhydride resins, unmodified by other agents such as fatty acids or the like, do not have properties which make them suitable 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 resins, ester gum, copal, pheonolic 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 fillings, 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, the compositions contain a large proportion 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 proportion 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 ½ to ¾ 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-swellable silicate be a minor constituent of the composition, 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 product 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 aqueous suspension or emulsion containing about 4% of bentonite freed from gritty materials by centrifugal 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 required. 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 backfilled 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 backfilling with available equipment. Fabric so backfilled has an excellent finish, and is highly resistant 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 containing about 3% of a water-swellable silicate having a white color, from 2 to 3% of a synthetic resin, such as an acrylic or acrylic acid ester resin, or an aliphatic resin, or a phenol-formaldehyde resin, or a cumar resin, or a urea- or thiourea-formaldehyde resin, or a mixture of two or more of these resins, or a mixture of one or more of these resins with a product such as ester gum, resin 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-swellable silicate. The fabric so finished is washable, is free from any clammy or disagreeable feeling on contact with the body, and has an excellent appearance.

**Example 4.**—A white paper is coated with an aqueous composition containing about 4% of a water-swellable hydrous colloidal silicate, about the same amount of extremely finely divided 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 electrical insulation, is filled with the use of an aqueous composition containing about 3 to 5% of a water-swellable mixed calcium and magnesium silicate and about 2% of emulsified alkyd resin. The filled fabric has excellent electrical insulating properties and resistance to decomposition at high temperatures.

The coating and filling compositions may contain dyes, 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 materials which comprises applying thereto an aqueous composition comprising a water-swellable colloidal silicate and an emulsified synthetic resin, the proportion of resin to water-swellable silicate not exceeding about two.
2. The process of treating fibrous sheet materials which comprises applying thereto an aqueous composition comprising a water-swellable colloidal silicate and an emulsified synthetic resin, the amount of water-swellable silicate in such composition being at least as great as the amount of resin.
3. The process of treating fibrous sheet materials which comprises applying thereto an aqueous composition comprising a water-swellable colloidal silicate from the group consisting of water-swellable aluminum, calcium and magnesium silicates and an emulsified synthetic resin, the proportion of resin to water-swellable silicate not exceeding about two.
4. The process of treating fibrous sheet materials which comprises applying thereto an aqueous composition comprising a water-swellable colloidal mixed calcium and magnesium silicate and an emulsified synthetic resin, the proportion of resin to water-swellable silicate not exceeding about two.
5. The process of treating fibrous sheet materials which comprises applying thereto an aqueous composition comprising a water-swellable colloidal silicate from the group consisting of water-swellable aluminum, calcium and magnesium silicates, calcium and magnesium carbonate, and an emulsified synthetic resin, the proportion of resin to water-swellable silicate not exceeding about two.
6. Fibrous sheet material having applied thereto a composition including a water-swellable colloidal silicate and a synthetic resin, the proportion of resin to water-swellable silicate not exceeding about two.
7. Fibrous sheet material having applied thereto a composition comprising a water-swellable silicate and a synthetic resin, the amount of resin not exceeding the amount of water-swellable silicate.
8. Fibrous sheet material having applied thereto a composition comprising a water-swellable silicate from the group consisting of water-swellable aluminum, calcium and magnesium silicates and a synthetic resin, the proportion of resin to water-swellable silicate not exceeding about two.
9. Fibrous sheet material having applied thereto a composition comprising a water-swellable colloidal mixed calcium and magnesium silicate and a synthetic resin, the proportion of resin to water-swellable silicate not exceeding about two.
10. Fibrous sheet material having applied thereto a composition comprising a water-swellable colloidal mixed calcium and magnesium silicate and a synthetic resin, the proportion of resin to water-swellable silicate not exceeding about two.

WILLIAM H. ALTON.