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2,948,329

MICA PAPER

George L. Gaines, Jr., Scotia, and Arthur M. Bueche, Schenectady, N.Y., assignors to General Electric Company, a corporation of New York

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This invention relates to the preparation of mica paper. More particularly, this invention relates to sheets of mica paper which are characterized by improved tensile strength and moisture resistance and to the process by which these improved products are obtained.

Heretofore, the preparation of mica paper has been known in the art. For example, mica paper preparation is described in Patents 2,549,880—Bardet, 2,614,055—De Senarclens and 2,709,158—Bouchet. Mica paper prepared by the methods of these patents as well as by other known methods is gaining commercial acceptance because of the excellent electrical properties of the mica paper and because of its inertness at elevated temperatures. However, despite the excellent electrical and thermal properties of mica paper, mica paper has not gained universal acceptance because of its relatively low tensile strength and also because of the fact that mica paper disintegrates rapidly and completely on contact with water.

It is an object of the present invention to provide an improved mica paper.

A further object of the invention is to provide a mica paper of improved tensile strength and moisture resistance.

These and other objects of our invention are accomplished by (1) impregnating mica paper with an anhydrous alkyl orthosilicate, (2) hydrolyzing the impregnated paper under acidic conditions, and (3) removing the volatile hydrolysis products from the impregnated mica paper.

The term "mica paper" in this application is used in its usual sense to refer to a sheet-like aggregate of mica particles which has been prepared by any of the general methods described in the three patents mentioned above or by any other method. In general, mica paper is prepared by forming a slurry of finely divided mica platelets in water and forming a sheet of paper from the platelets in the slurry by conventional paper making techniques. The mica employed in preparing the paper can comprise phlogopite, lepidolite, or preferably muscovite.

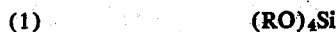
The slurry of the mica platelets in water may be prepared by any suitable means. One usual method of preparing this slurry is by first heating or firing the mica at a temperature of about 800° C., e.g., from about 750 to 850° C., for a time of about 10 minutes, e.g., from about 5 to 20 minutes. This heating step causes a loss in weight of the mica equal to about 2 percent by weight of the original weight of the mica. The heating also has the effect of softening the mica while at the same time delaminating and increasing the bulk volume of the mica. This heat treated mica is then added to the aqueous medium, generally plain water, and agitated by any suitable device, such as by a high speed comminuter or mixer to convert the mica into small particles or platelets. In addition to heat treating the mica flakes prior to dispersing them in the aqueous medium, the mica flakes can also be ground up in an aqueous medium without the firing step. This grinding again is accomplished by means

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of high speed comminuters or mixers or may also be accomplished by impinging high velocity jets of water against the mica flakes. Usually, the comminution of the mica takes place in a suspension containing about 1 percent, by weight, of mica. This results in a pulp-like slurry of mica in which the particle size of the mica flakes has a wide distribution. The extra-fine and extra-coarse particles in this comminuted aqueous suspension can then be removed and the resulting slurry is formed into sheets of mica paper on conventional paper making apparatus. In alternative methods of making mica paper, the aqueous medium, instead of being pure water, is sometimes acidic or basic in nature. Thus, the fired mica flakes are sometimes ground up in an alkaline carbonate solution and the solution is then neutralized by a suitable acid, such as, for example, hydrochloric acid.

Regardless of the method of preparation of the wet sheets of mica paper, the wet sheets are then dried by evaporation with or without the application of external heat and the dried sheets are then sometimes pressed or calendered at elevated temperatures to form the final mica paper.

It is the mica paper prepared by the process described above or by any analogous process which is the starting material in the process of the present invention. This mica paper is impregnated with an anhydrous alkyl orthosilicate such as an orthosilicate having the formula



where R represents alkyl radicals, as well as the partial hydrolysis products of these orthosilicates. The term "anhydrous" as used in this application excludes the presence of uncombined water in the orthosilicate, but does not exclude the presence of silicon-bonded hydroxyl groups when the orthosilicate is partially hydrolyzed.

Among the preferred alkyl orthosilicates of the present invention are those in which the four R groups of Formula 1 are alkyl radicals containing a maximum of five carbon atoms. Illustrative of the alkyl orthosilicates employed in the present invention are methyl orthosilicate, ethyl orthosilicate, propyl orthosilicate, butyl orthosilicate, t-butyltriethyl silicate, t-amyltriethyl silicate, di-t-amyl-diethyl silicate, di-n-butyl-diethyl silicate, butyltriethyl silicate, methyltributyl silicate, methyltripropyl silicate, methyltriisopropyl silicate, etc.

The mica paper is treated according to the process of the present invention by first impregnating the mica paper with the alkyl orthosilicate by any suitable means. The simplest method of impregnating the sheet is by dipping the mica sheet in the anhydrous alkyl orthosilicate. The mica sheet is allowed to remain immersed in the orthosilicate until uniform impregnation is accomplished. The time required for this uniform impregnation is relatively short and satisfactory impregnation can be obtained in times as low as 30 seconds with 2 mil sheets. In general, we increase the time of immersion as the sheet thickness increases. No particular disadvantage is observed in allowing the mica sheet to remain in the alkyl orthosilicate for extended periods of time. In operation, we prefer to allow from about 1 to 5 minutes immersion of the mica paper in the orthosilicate to insure complete and uniform impregnation of the sheet. Instead of immersing the sheet in the alkyl orthosilicate, the impregnation step may also be accomplished by placing the mica paper on a suitable porous sheet or screen and drawing the alkyl orthosilicate solution through the mica sheet. However, this method offers certain disadvantages in that the use of fairly complicated equipment is required. The impregnation can also be accomplished by spraying the orthosilicate onto the mica paper.

After impregnating the mica paper with the anhydrous alkyl orthosilicate, the orthosilicate is hydrolyzed under

acidic conditions to form a mica paper which contains the hydrolysis products of the orthosilicate permanently unified with the mica paper. Acidic conditions are required for the hydrolysis since we have found that the alkyl orthosilicates will not hydrolyze under neutral conditions and no satisfactory basic hydrolysis system has been found. Acid conditions for the hydrolysis may be provided by one of two methods. The first method comprises incorporating an acid forming substance into the alkyl orthosilicate which will yield an acid on contact with moisture in the air. When this method is employed, the acid forming ingredient is mixed with the alkyl orthosilicate prior to incorporation of the orthosilicate in the mica paper. Thus, during the impregnation of the mica paper, both the orthosilicate and the acid forming substance are incorporated into the mica sheet. After impregnation of the sheet, contact of the sheet with the minor amount of moisture found in the air is sufficient to provide moisture for generating the acid and also for hydrolyzing the orthosilicate. In carrying out this first type of hydrolysis, any suitable acid forming ingredient may be incorporated into the anhydrous alkyl orthosilicate. However, the preferred acid forming substance incorporated in the orthosilicate is an acid forming salt, particularly a metal halide which yields a hydrohalic acid on contact with moisture. The preferred metal halides are ferric chloride, cupric chloride, aluminum chloride, stannic chloride, etc. The amount of the acid forming metal halide which is incorporated into the alkyl orthosilicate may vary within extremely wide limits. Satisfactory hydrolysis of the orthosilicate has been accomplished employing amounts of the metal halides which vary from about 0.1 to 10 percent by weight of the acid halide based on the weight of the alkyl orthosilicate. Preferably, we employ from about 2 to 8 percent by weight of the metal halide based on the weight of the orthosilicate. When impregnating the mica paper with the orthosilicate containing the metal halide, the sheet is merely dipped into the mixture of the orthosilicate and metal halide for sufficient time to allow impregnation of the mica paper. The impregnated mica paper is then removed from the impregnating solution and allowed to stand in air for a few seconds to allow hydrolysis of the orthosilicate. During this few seconds, moisture in the air reacts with the metal halide yielding a hydrohalic acid which acts as a catalyst for the hydrolysis of the alkyl orthosilicate by means of additional moisture in the air. This entire acid forming and hydrolysis step may be accomplished in times as short as 5 to 10 seconds. However, we prefer to allow at least one minute to insure relatively complete hydrolysis of the orthosilicate.

In the second method of hydrolyzing the alkyl orthosilicate impregnated mica paper, the acid is supplied by means external to the impregnated sheet. This is accomplished by subjecting a mica sheet which has been impregnated with an alkyl orthosilicate to the action of vapors of an acid. One convenient method of accomplishing this type of hydrolysis is to place the alkyl orthosilicate impregnated mica paper above an aqueous solution of the acid and vapors of the acid and of the water in the solution act to provide both the small amount of moisture necessary for the hydrolysis and the small amount of acid desirable to catalyze the hydrolysis. Where this method of hydrolysis is employed, complete hydrolysis of the alkyl orthosilicate can again be accomplished in a matter of seconds. However, we prefer to allow at least one minute and preferably from about 2 to 5 minutes to insure complete hydrolysis of the alkyl orthosilicate. Among the preferred acids employed for this external type of acid catalyzed hydrolysis are the hydrohalic acids, with hydrochloric acid being the specific preferred acid.

Regardless of whether the hydrolysis is accomplished by means of an acid forming ingredient incorporated into the alkyl orthosilicate prior to impregnation or

whether the acid is supplied after impregnation, the mica paper containing the hydrolyzed alkyl orthosilicate is then heated at a temperature sufficient to remove volatile hydrolysis products. Generally, the temperature at which this heating step is carried out varies with the particular alkyl orthosilicate employed. However, we have found that satisfactory removal of volatile materials may be accomplished by heating the mica paper in a circulating air oven at a temperature greater than about 100° C., e.g., from about 110 to 150° C. Where these temperatures are employed, it is found that the volatile hydrolysis products are completely removed from the mica paper in several minutes, yielding a mica paper of improved tensile strength and improved moisture resistance.

In addition to using pure alkyl orthosilicates or alkyl orthosilicates containing acid forming ingredients for the impregnation step, we have also found that the impregnation step may be carried out in the presence of certain inert solvents although no particular advantage is accomplished by the use of such inert solvents. These alkyl orthosilicate solutions are sometimes employed, since there are presently available commercially alkyl orthosilicate solutions in solvents such as monohydric alcohols. Among the satisfactory inert solvents for use in our process are included, for example, methanol, ethanol, propanol, ethyl ether, methyl ethyl ether, etc. When the alkyl orthosilicate solution contains an inert solvent, it is preferred that the solution contain at least about 30 percent by weight of the orthosilicate. Where more than this amount of inert solvent is employed, the net effect is to diminish the amount of alkyl orthosilicate which is incorporated into the mica paper and thus decrease the resulting tensile strength of the treated mica paper.

Although the exact mechanism of the reaction of the present invention is not known, we believe that the effect of the reaction is to provide a silica-like structure containing alkoxy radicals attached to silicon which tends to cement together the mica particles in the mica sheet and thus increase the tensile strength of the sheet. The presence of the silicon-bonded alkoxy groups in the mica paper also tends to render the mica paper less susceptible to the deleterious effect of water. We have found that mica sheets treated by the method of the present invention are about twice as thick after the treatment as they were prior to treatment. The net effect of the treatment of the present invention is to increase the tensile strength of mica paper by a factor of two to four over the tensile strength of the untreated mica paper. In addition, untreated mica paper disintegrates completely as soon as it comes into contact with water. On the other hand, mica paper treated according to the process of the present invention may be immersed in water without any visible adverse effects.

The following examples are illustrative of the practice of our invention and are not intended for purposes of limitation.

In all of the examples the mica paper employed was prepared by firing flakes of muscovite mica at a temperature of about 800° C. for ten minutes. The fired sheets of mica were then added to water to form a slurry containing about one percent by weight of mica. This slurry was violently agitated to break up the mica into fine particles. The extra-fine particles and the extra-coarse particles were then separated from the slurry and the resulting material was formed into a paper-like sheet on a conventional paper making apparatus. The mica sheets were then calendered at a temperature of about 150° C. to remove all moisture from the sheet and to yield a uniform sheet of mica having a thickness of about 2 mils which had a metallic sheen.

Example 1

This example illustrates the preferred embodiment of our invention. A sheet of the mica paper described above

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was immersed in ethyl orthosilicate containing 6 percent by weight of ferric chloride based on the weight of the orthosilicate. After about two minutes this sheet was removed from the orthosilicate and allowed to stand in air for about 15 seconds. At this time the sheet was placed in a circulating air oven at 110° C. and allowed to remain in the oven for about 5 minutes, during which time all volatile hydrolysis products had been removed. The tensile strength of this treated sheet was about 2500 p.s.i. as compared with about 1050 p.s.i. for a control. The control had a thickness of about 1.9 mils as compared with a final thickness of about 4 mils for the treated sheet. When the control was immersed in water it disintegrated completely upon contact with the water while the treated sheet was unaffected by the water.

Example 2

This example illustrates the treatment of mica sheet with a solution of ethyl orthosilicate in ethyl alcohol. A number of solutions were prepared, each containing ethyl orthosilicate, ethyl alcohol, and 6 percent, by weight, of ferric chloride based on the weight of the orthosilicate. The table below lists the percent of ethyl orthosilicate in the treating solution based on the total weight of the orthosilicate and the ethyl alcohol, the thickness of the sheet and the tensile strength observed on the sheet. In each case, the treated sheet was prepared by dipping untreated mica paper into the orthosilicate-alcohol solution for about 1 minute, allowing the treated sheet to stand in air for about 15 seconds, and drying the hydrolyzed sheet for about 10 minutes at 110° C.

Percent Orthosilicate	Thickness, mils	Tensile Strength, p.s.i.
None (control).....	1.9	1050
73.5.....	3.9	2500
41.5.....	3.3	3900
13.5.....	3.4	700

As is shown by the table above, the mica paper impregnated with orthosilicate-alcohol solutions containing 73.5 percent and 41.5 percent of the orthosilicate had markedly improved tensile strengths as compared with the control. The sheet impregnated with the solution containing only 13.5 percent orthosilicate, which concentration is outside of the preferred range of the present invention, had a tensile strength which was inferior to the tensile strength of the control. When the sheets treated with the 73.5 percent and the 41.5 percent orthosilicate solutions were immersed in water they were completely unaffected by the water.

Example 3

This example illustrates the use of an external source of acid for the hydrolysis of the orthosilicate. A sheet of mica paper which had been immersed in ethyl orthosilicate for about one minute, was allowed to stand over an open container of concentrated aqueous hydrochloric acid for about one minute. At the end of this time the sheet was placed in a circulating air oven at 110° C. and allowed to dry for about five minutes. At the end of this time the resulting sheet had a tensile strength of about 3000 p.s.i., and was completely unaffected by immersion in water. When this same procedure was repeated except that the sheet after impregnation was not contacted with acid vapors, the resulting sheet had a tensile strength below that of an untreated control and disintegrated completely upon contact with water. This shows that the hydrolysis must be accomplished under acidic conditions.

Example 5

This example illustrates the necessity for treatment

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with anhydrous alkyl orthosilicate. A sheet of mica paper was immersed in a solution containing equal parts by weight of ethyl orthosilicate and water. As soon as this sheet came into contact with the solution, the sheet disintegrated completely forming a slurry of mica particles in the orthosilicate-water solution.

Although the foregoing examples have not illustrated all of the possible embodiments of our invention, it should be understood that our invention may be carried out with any of the orthosilicates within the scope of Formula 1. In addition, any type of inert solvent may be used as a diluent for the alkyl orthosilicate employed during the impregnation. Similarly, acid forming substances other than ferric chloride may be incorporated into the orthosilicate solution prior to impregnating the mica paper.

The improved mica paper prepared by the process of the present invention can be employed in all of those applications in which prior art mica paper can be used. In addition, the improved mica paper of this invention can also be employed in those applications where a product having increased physical properties is desirable in combination with a product which is resistant to moisture. Thus, this mica paper can be employed as a dielectric medium in capacitors, can be employed as insulation in dynamoelectric machines, for example, as slot insulation in electric motors, can be employed as insulation in high temperature apparatus such as in electron tubes, etc.

What we claim as new and desire to secure by Letters Patent of the United States is:

1. The method of obtaining a mica paper having improved tensile strength and moisture resistance which comprises the essential steps of (1) impregnating the mica paper with an anhydrous alkyl orthosilicate, (2) subjecting the alkyl silicate in the mica paper for the first time to acidic conditions generated by externally derived moisture to effect hydrolysis of the alkyl silicate, and (3) heating the mica paper containing the hydrolyzed alkyl silicate at a temperature sufficient to remove the volatile hydrolysis products and to leave behind a hydrolyzed alkyl silicate containing silicon-bonded alkoxy groups.

2. The method of claim 1 in which the alkyl orthosilicate is ethyl orthosilicate.

3. The method of obtaining a mica paper of improved tensile strength and moisture resistance which comprises the essential steps of (1) impregnating the mica paper with an anhydrous solution of ethyl orthosilicate containing anhydrous ferric chloride, the ethyl orthosilicate comprising, by weight, at least 30% of the total weight of the solvent and the orthosilicate, (2) hydrolyzing the ethyl orthosilicate in the mica paper by subjecting the ethyl orthosilicate and ferric chloride to externally derived moisture, and (3) heating the mica paper containing the hydrolyzed ethyl orthosilicate at a temperature sufficient to volatilize the hydrolysis products from the impregnated mica paper and to obtain a hydrolyzed ethyl orthosilicate containing silicon-bonded ethoxy groups.

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