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METHOD OF RENDERING MICA PAPER MOISTURE RESISTANT AND ARTICLE PRODUCED THEREBY

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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, 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, there are two serious drawbacks to the universal acceptance of mica paper in many applications. These drawbacks are the relatively low tensile strength of the paper and the fact that the mica paper disintegrates completely on contact with water.

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

A further object of my invention is to provide a mica paper which is moisture resistant.

These and other objects of my invention are accomplished by contacting mica paper with a chlorosilane or a mixture of chlorosilanes having the formula

$$(1) \qquad (R)_nSi(Cl)_{4-n}$$

where R is a hydrocarbon radical, e.g. an alkyl radical, for example, methyl, ethyl, propyl, butyl, octyl, etc. radicals, an aryl radical, e.g. phenyl, naphthyl, diphenyl, tolyl, ethylphenyl, etc. radical, an aralkyl radical, e.g. benzyl, phenylethyl, etc.; substituted alkyl radicals, e.g. chloromethyl, β-fluoroethyl, etc. radicals, substituted aryl radicals, e.g. chlorophenyl, dichlorophenyl, etc. radicals; and n has a value of from 0.8 to 1.9, inclusive.

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. In general, mica paper is prepared by heating mica which may comprise phlogophite, lepidolite, or preferably muscovite, at a temperature and time sufficient to partially "dehydrate" the mica. In general, the heating of the mica is carried out at a temperature of about 800° C., e.g., from about 750–850° C. for a time of about 10 minutes, e.g., from 5–20 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 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 an aqueous medium, generally plain water, and agitated by any suitable device, such as, a high speed comminuter or mixer, to convert the mica into small particles or platelets. 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 suspension 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 are then removed and the resulting slurry is formed into sheets of paper on conventional paper-making apparatus. In alternative methods of making mica sheet, 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.

Mica paper prepared by any of these processes or by analogous processes may be employed in the practice of the present invention. In addition, mica paper which has been treated subsequent to formation may also be employed in my process. Thus, mica paper may be employed which has been treated with an alkyl orthotitanate as described in the copending application of Myron L. Corrin, Serial No. 603,162, filed concurrently herewith and assigned to the same assignee as the present invention. In the aforementioned Corrin application, which is hereby incorporated by reference into the present application, mica paper is impregnated with a solution of an alkyl orthotitanate such as, for example, tetrapropyl titanate or tetrabutyl titanate, and the impregnated sheet is then hydrolyzed by contacting the sheet with water vapor and the resulting hydrolyzed sheet is then dried at an elevated temperature to remove volatile hydrolysis products. The mica sheet of this Corrin application is characterized by improved tensile strength, tear resistance and crease resistance over prior art materials. However, despite the excellent physical properties of mica paper treated by the method of this Corrin application, the resulting paper is still subject to complete disintegration when brought into contact with water.

The chlorosilanes within the scope of Formula 1 which are employed in the practice of my invention are well known in the art. Specific chlorosilanes within the scope of Formula 1 include, for example, methyltrichlorosilane, ethyltrichlorosilane, β-chloroethyltrichlorosilane, phenyltrichlorosilane, benzyltrichlorosilane, naphthylchlorosilane, etc. Among the various specific chlorosilanes within the scope of Formula 1, I prefer to employ methyltrichlorosilane. It should be understood, however, that in addition to using specific chlorosilanes within the scope of Formula 1, mixtures of various chlorosilanes may be employed so long as the average composition of the mixture falls within the scope of the formula. Thus, mixtures of two or more compounds within the following formula

$$(2) \qquad (R)_aSiCl_{4-a}$$

where R is as previously defined and a has a value of from 0 to 3, may be mixed to form a mixture of materials having an average composition within the scope of Formula 1. Specific compounds within the scope of Formula 2 include, for example, silicon tetrachloride, methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, ethyltrichlorosilane, methylethyldichlorosilane, butyltrichlorosilane, diphenyldichlorosilane, benzyltrichlorosilane, dibutyldichlorosilane, chloromethyltrichlorosilane, etc. In the preferred embodiment of my invention, the R radicals of all of the specific materials within the scope of Formula 2 are methyl radicals.

The process of the present invention may be carried out in any suitable method. Two of the available methods for contacting mica paper with the chlorosilanes within the scope of Formula 1 are by dipping the mica

paper in the chlorosilane and by subjecting the mica paper to the vapors of the chlorosilane. In either case, the relative amounts of mica paper and chlorosilane are completely immaterial since only a very minor amount of the chlorosilane reacts with the mica paper. Where the treatment is effected by dipping the mica paper in the liquid chlorosilane, the only requirement is that there be present sufficient chlorosilane so that the mica paper is completely immersed in the liquid. When the treating process of the present invention is carried out with vapors of the chlorosilane or chlorosilane mixture, I prefer to carry out the treatment at the boiling point of the chlorosilane. By carrying out the treatment at the boiling point, there is assurance that sufficient chlorosilane comes into contact with the surface of the mica sheet so that some of it condenses on the surface of the sheet and is able to react with the sheet. The time required for the treatment of the mica sheet is only a few seconds whether immersion or vapor treatment is employed. Thus, the time required for immersing a sheet of mica paper into the liquid and withdrawing the sheet is sufficient to effect satisfactory treatment.

After contacting the mica paper with the chlorosilane, any unreacted chlorosilane is removed. This is accomplished by allowing the chlorosilane to evaporate at room temperature or by merely heating the treated sheet to a temperature above the boiling point of the chlorosilane for sufficient time to remove all volatile materials. The temperature suitable for evaporation of unreacted chlorosilanes from the surface of the mica sheet, of course, varies with the composition of the chlorosilane. Where the chlorosilane is a mixture of dimethyldichlorosilane and methyltrichlorosilane, the boiling point of the mixture is from 65–70° C. With this mixture, I prefer to employ a temperature of about 100° C. for evaporation. Where the chlorosilane mixture contains some silicon-bonded aryl radicals, the boiling point of the mixture is much higher, e.g., up to 150° C. or more. Where such high boiling chlorosilane mixtures are employed, I prefer to use a temperature of 200° C. or more to cause evaporation of volatile products.

Although the exact chemical mechanism involved in the present process is not fully understood, it is clear that a reaction takes place between the chlorosilane mixture and the mica paper. The speed and efficiency of this reaction depends to some extent on the reactivity of the silicon-bonded chlorine atoms in the chlorosilane. Thus, I prefer to employ chlorosilanes in which the R radicals attached to silicon are methyl since this type of chlorosilane contains the most reactive chlorine atoms. Where the silicon-bonded R radical is an aryl radical, for example, a phenyl radical, the reactivity of the silicon-bonded chlorine atoms are substantially reduced so that the rate of reaction of chlorosilane and the mica paper is retarded.

Unexpectedly, I have discovered that all chlorosilanes are not effective in the process of the present invention. Thus, where a sheet of mica paper is treated with a single chlorosilane consisting of trimethylchlorosilane, there is no improvement in either the tensile strength or moisture resistance of the mica paper. This result is quite surprising in view of the fact that trimethylchlorosilane is an effective surface coating agent for many materials. Similarly, dimethyldichlorosilane and diphenyldichlorosilane are completely ineffective, individually, in the process of the present invention. And, finally, a highly functional material such as, for example, silicon tetrachloride is also ineffective in the process of the present invention. However, it should be understood that although these particular chlorosilanes mentioned are ineffective when used alone in my process, when these materials are used in combination with other materials giving a mixture having an average composition within the scope of Formula 1, the resulting mixture imparts improved tensile strength and moisture resistance to mica paper. Thus, a mixture of silicon tetrachloride and trimethylchlorosilane, neither of which alone will improve mica paper, will both strengthen and give moisture resistance to mica paper if the mixture is selected so that the average composition is within the scope of Formula 1.

The following examples are illustrative of the practice of my 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 about 10 minutes. The fired sheets of mica were then added to water to form a slurry containing 1 percent by weight of mica. This slurry was violently agitated to break up the mica into fine particles. The ultra-fine particles and the coarse particles were then separated from the slurry and the resulting material was formed into a paper-like sheet of mica on a conventional paper-forming 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 paper having a metallic sheen.

Example 1

A number of samples of mica paper were cut from a large sheet of mica paper 2 mils thick. Some of these samples of mica paper were treated with a mixture of dimethyldichlorosilane and methyltrichlorosilane having an average composition corresponding to the following formula

$$(CH_3)_{1.6}Si(Cl)_{2.4}$$

Some of the sheets were prepared by immersing the mica paper samples in the chlorosilane mixture while others were prepared by holding the mica paper over a vessel of the boiling chlorosilane (boiling point 65–70° C.) for about 30 seconds. The treated samples were then heated in an oven at about 110° C. for about 30 seconds to remove any unreacted volatile material. At the end of this time measurements were made of the tensile strength and the electrical characteristics of both the untreated mica paper and the treated mica paper. The untreated mica paper had a tensile strength of about 2000 pounds per square inch while the mica paper treated with the chlorosilane mixture either by immersion or by vapor treatment had a tensile strength of about 4000 pounds per square inch. The electrical strengths of both the untreated and treated mica paper remained about the same, with dielectric breakdown occurring at about 1000 volts per mil and with a D.C. resistance at 500 volts of about 10^{10} ohm centimeters. When the untreated mica paper was placed under a stream of water, it disintegrated completely in a few seconds. The treated samples of mica paper were completely unaffected by a stream of water or by being immersed in water.

Example 2

A sample of 4 mil mica paper was treated by immersing it in methyltrichlorosilane for about 4 seconds. At the end of this time the treated sheet was placed in an oven at 110° C. for about 1 minute to remove volatile materials. The resulting treated mica sheet had a tensile strength about twice as great as the tensile strength of the untreated sheet and was completely unaffected by immersion in water.

Example 3

Following the procedure of Example 2, a sheet of mica paper was treated by immersion in phenyltrichlorosilane. After heating this treated sample at a temperature of about 200° C. to remove volatile products, the tensile strength was about 1.5 times as great as the tensile strength of the untreated material. In addition, this treated mica sheet was unaffected by water.

Example 4

This example illustrates the treatment of mica paper with individual chlorosilanes outside of the scope of the present invention. Four mil samples of mica sheet were treated with trimethylchlorosilane, diphenyldichlorosilane, and silicon tetrachloride by the method of Example 2. In each case, the treatment with the chlorosilane with subsequent heating of the treated sheet failed to improve either the tensile strength or moisture resistance of the mica paper.

Example 5

This example illustrates the treatment of mica paper with a mixture of two chlorosilanes, neither of which alone will improve the properties of mica paper. Following the procedure of Example 2, a sheet of 4 mil mica paper was treated with a mixture of silicon tetrachloride and trimethylchlorosilane having an average composition corresponding to the following formula:

$$(CH_3)_{1.2}Si(Cl)_{2.8}$$

This treated sheet had a tensile strength over twice as great as an untreated sample and did not disintegrate when immersed in water.

Example 6

Following the procedure of Example 2 a sheet of 4 mil mica paper was treated with a mixture of phenyltrichlorosilane, silicon tetrachloride, dimethyldichlorosilane, methyltrichlorosilane, and diphenyldichlorosilane having an average composition corresponding to the following formula:

$$(CH_6H_5)_{0.5}(CH_3)_{0.5}Si(Cl)_3$$

This treated sheet had a tensile strength about 70 percent greater than the tensile strength of an untreated sample and did not disintegrate when immersed in water.

Example 7

Following the procedure of Example 1, a sheet of 4 mil mica paper was treated with a mixture of dimethyldichlorosilane and methyltrichlorosilane having an average composition corresponding to the formula

$$(CH_3)_{1.2}Si(Cl)_{2.8}$$

This treated sheet exhibited a tensile strength over two times as great as the tensile strength of the untreated sheet and was completely unaffected by immersion in water, while the untreated sheet disintegrated completely upon immersion.

Example 8

This example illustrates the process of the present invention applied to "titanized" mica paper prepared by the method of the aforementioned Corrin application. A sheet of 2 mil mica paper was cut into a number of samples and these samples were "titanized" by taking 1 part by weight of the mica paper and sucking 180 parts by weight of a 22 percent by weight tetrabutyl titanate solution in benzene through the paper in about 15–30 seconds. These sheets were then exposed to saturated water vapor in a closed container for approximately 24 hours and were then pressed at 500 pounds per square inch pressure at 200° C. for 1 minute. Several of these titanized sheets were then treated with the mixture of dimethyldichlorosilane and methyltrichlorosilane described in Example 1. The treatment consisted of immersing the "titanized" mica sheet in the liquid chlorosilane mixture and then heating the mixture at about 120° C. until all volatile materials had evaporated. The tensile strength and moisture resistance of the untreated mica paper, the "titanized" mica paper and the "titanized" and chlorosilane-treated mica paper were investigated. The untreated mica sheet had a tensile strength of about 1600 pounds per square inch, the "titanized" sheet had a tensile strength of about 4000 pounds per square inch, while the mica sheet which was both "titanized" and treated with the chlorosilane mixture had a tensile strength of about 4200 pounds per square inch. Neither the untreated nor the "titanized" mica paper had any water resistance. The mica paper which was both "titanized" and treated with the chlorosilane mixture was completely unaffected by immersion in water.

Although the foregoing examples have illustrated the use of specific chlorosilanes or chlorosilane mixtures without the use of solvents, it should be understood that the chlorosilane or chlorosilane mixtures may be dissolved in any suitable inert solvent in carrying out the process of the present invention. However, it should be understood that no particular advantage is gained by the use of such solvents. In fact, the use of solvents presents the additional problem of having to remove the solvent from the mica paper after the chlorosilane treatment. This removal may be effected by evaporating the solvent during the evaporation of the volatile unreacted chlorosilanes. The following example illustrates the use of solvents in the process of the present invention.

Example 9

A solution of chlorosilanes was prepared by adding 1 part of a mixture of dimethyldichlorosilane and methyltrichlorosilane having an average composition corresponding to the formula

$$(CH_3)_{1.6}Si(Cl)_{2.4}$$

to 4 parts of benzene. A sample of 4 mil mica paper was immersed in this solution for about 10 seconds and then heated at a temperature of about 120° C. for about 2 minutes. The resulting treated sheet had a tensile strength about 60 percent greater than the tensile strength of the untreated mica sheet and was completely unaffected by immersion in water.

Although the foregoing examples have illustrated the process of the present invention in connection with mica paper prepared only by one process, it should be understood that the chlorosilane treatment of the present invention is independent of the method by which the mica paper is formed. Thus, the process of the present invention is applicable to mica paper prepared by any of the methods described in the three patents previously enumerated as well as to mica paper prepared by any other analogous method.

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

1. The method of preparing mica paper of improved tensile strength and moisture resistance which comprises (1) impregnating mica paper with monomeric tetrabutyl orthotitanate, (2) hydrolyzing the impregnated product, (3) heating the hydrolyzed product to remove volatile hydrolysis products, (4) and treating the resultant product with a mixture of dimethyldichlorosilane and methyltrichlorosilane having the average composition

$$(CH_3)_nSi(Cl)_{4-n}$$

where n is a value from 0.8 to 1.9.

2. The method of preparing mica paper of improved tensile strength and moisture resistance which

comprises (1) impregnating mica paper with a monomeric alkyl orthotitanate, (2) hydrolyzing the impregnated product, (3) heating the hydrolyzed product to remove volatile hydrolysis products, (4) and treating the resultant product with a chlorosilane composition having the average formula

$$(R)_nSi(Cl)_{4-n}$$

where R is a member selected from the class consisting of alkyl, aryl, and aralkyl radicals and n has a value of from 0.8 to 1.9.

3. The method as in claim 2 in which the monomeric alkyl orthotitanate is monomeric butyl orthotitanate.

4. The product prepared by the method of claim 2.

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