United States Patent Office 2,948,640 Patented Aug. 9, 1960

2,948,640

METHOD OF IMPREGNATING MICA PAPER WITH AN ALKYL ORTHOTITANATE, AND PRODUCT PRODUCED THEREBY

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No Drawing. Filed Aug. 9, 1956, Ser. No. 603,162

6 Claims. (Cl. 117—119)

This invention relates to the preparation of mica paper. More particularly, this invention relates to sheet products of mica which are characterized by improved physical properties 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 2,709,158—Bouchet; 2,614,055—De Senarclens; 2,549,880—Bardet. Mica paper prepared by the methods of these patents as well as by other known methods has gained commercial acceptance because of the good electrical properties of the mica paper and because of its utility at elevated temperatures. However, the relatively low tensile strength, low tear resistance, and low crease resistance of mica paper limit the applications to which it may be put.

One object of the present invention is to provide a mica paper of superior physical properties.

A further object of the present invention is to provide mica paper which has improved physical properties while retaining the electrical properties and thermal properties characteristic of prior art materials.

These and other objects of my invention are obtained by a process which comprises impregnating mica paper with an alkyl orthotitanate, hydrolyzing the impregnated product, and heating the hydrolyzed product to remove volatile hydrolysis products.

Mica paper which may be employed in the process of my invention may be prepared by any of the methods described in the three patents mentioned above. The term "mica paper" is used herein to refer to a product which is generally prepared by heating mica, which may comprise phlogopite, 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 have 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.

This mica paper may then be converted to the improved product of the present invention by impregnating the paper with an alkyl orthotitanate, hydrolyzing the impregnated product, and heating the hydrolyzed product to remove volatile hydrolysis products. The alkyl orthotitanates which may be employed in the practice of the present invention may be described as compounds containing a titanium atom to which are bound four alkoxy groups. The particular alkyl orthotitanate employed in the practice of my invention is not critical and satisfactory results can be obtained employing orthotitanates in which the alkyl groups contain from 1 to 18 or more carbon atoms. However, I prefer to employ orthotitanates in which the alkyl groups contain from about 2 to 6 carbon atoms with the preferred specific alkyl orthotitanate being tetrabutyl titanate. The orthotitanates can have a variety of different types of alkoxy groups attached to the same titanium atom and mixtures of several orthotitanates can be employed. Specific alkyl orthotitanates which are useful in my invention include, for example, tetrapropyl titanate, tetrabutyl titanate, tetraoctyl titanate, tetramethyl titanate, diethyldibutyl titanate, octadecyltripropyl titanate, etc.

Where the alkyl orthotitanates are liquids at room temperature, they can be used in pure form to impregnate the mica paper. In addition, even though the orthotitanates are liquid at room temperature, they can be diluted with suitable inert solvents. Where the alkyl orthotitanates are solids at room temperature, they are also dissolved in suitable inert solvents and used in solution for the impregnation step. Suitable inert solvents for use in the impregnation step include, for example, aromatic hydrocarbons such as, for example, benzene, toluene, xylene; aliphatic hydrocarbons such as, for example, n-heptane, hexane, octane, etc.; petroleum hydrocarbon fractions, such as, for example, gasoline, kerosene, mineral, spirits, etc. Where a solution of the alkyl orthotitanate in an inert solvent is used, the concentration of the alkyl orthotitanate can vary within very broad limits. Thus, satisfactory impregnation can be obtained employing solutions containing as low as 10 percent by weight of the alkyl orthotitanate in the solvent. The concentration can then vary anywhere from this lower limit of about 10 percent up to 100 percent of the alkyl orthotitanate in the case of those orthotitanates which are liquid at room temperature.

The amount of the alkyl orthotitanate used to impregnate the mica paper can vary within extremely wide limits, the only requirement being that the impregnation of the mica paper be uniform. In actual practice, I prefer to use, on a weight basis, a large excess of the orthotitanate to insure uniform impregnation. Satisfactory impregnation of mica paper has been obtained employing from 2 to 1000 or more parts by weight of the alkyl orthotitanate per part of mica paper. Preferably, from about 10 to 250 parts by weight of the orthotitanate are employed per part of the mica paper. This ratio is the same regardless of whether the orthotitanate is used in pure form or as a solution in an inert solvent. I have found that the impregnation is thorough and uniform when the impregnated mica sheet contains from about 4 to 40, and preferably about 20, parts by weight of the alkyl orthotitanate

per 100 parts of mica. However, it should be understood that mica sheets of improved properties are also obtained where the amount of the orthotitanate retained in the mica paper is outside of the range described. Although I do not wish to be bound by theoretical considerations, it is believed that the amount of the alkyl orthotitanate which is retained during the impregnation of the mica paper increases with increasing concentration of the orthotitanate in the impregnating solution. As the concentration of the orthotitanate in the solution increases, the amount of tetrabutyl titanate retained by the mica paper and available for hydrolysis also increases.

Thorough impregnation of the mica paper can be obtained by any suitable method. However, it should be understood that care must be taken to insure that impregnation is uniform. Uniform impregnation of mica paper is not obtained by merely soaking the mica paper in the orthotitanate or a solution of the orthotitanate. In this case the orthotitanate coats the surface of the paper but does not uniformly disperse in the interior of the sheet. A convenient method of insuring thorough and uniform impregnation of the mica sheet is to support the mica paper on a suitable porous member and then pass the orthotitanate or orthotitanate solution through the supported paper. It should be obvious to one skilled in the art that the orthotitanate may be passed through the paper by applying positive pressure to the orthotitanate or by sucking the orthotitanate through the sheet. Another satisfactory method for insuring thorough impregnation of the mica sheet is to place the mica paper and the orthotitanate in a suitable closed vessel and then to evacuate the vessel to remove air or other entrained gases from the interior of the mica sheet. When the vessel returns to atmospheric pressure or superatmospheric pressures the orthotitanate will fill the voids in the mica sheet. It should be understood that even though large excesses of the orthotitanate may be used to impregnate the mica sheet the excess orthotitanate is not lost but may be collected and reused for impregnation of other mica paper.

After thoroughly and uniformly impregnating the mica sheet, excess orthotitanate is removed from the surfaces of the sheet and the impregnated sheet is then subjected to hydrolyzing conditions. Any suitable means for effecting the hydrolysis may be employed. However, since the impregnated mica sheet will disintegrate upon contact with liquid water, care should be taken that only water vapor comes into contact with the impregnated sheet. A convenient method for accomplishing hydrolysis of the impregnated sheet is to place the impregnated sheet in a gaseous atmosphere saturated with water vapor. The atmosphere may be water-saturated air or some other medium inert to the reactants. Thus, other satisfactory atmospheres include nitrogen, oxygen, hydrogen, carbon dioxide, helium, etc. The time required for the complete hydrolysis of the orthotitanate in the impregnated sheet may advantageously be accelerated by passing saturated air or other saturated gas through the impregnated sheet. This assures the presence of sufficient water vapor to prevent "starving" of the orthotitanate for water. In general, the hydrolysis of the impregnated sheet may be accomplished in times which vary from only a few minutes up to several hours or more depending upon the humidity of the hydrolyzing atmosphere.

Although I do not wish to be bound by theoretical considerations, it is believed that the hydrolysis of the impregnated sheet results in the formation of alkanols and intermediate titanium compounds containing hydroxyl groups bonded to titanium. These hydroxyl-titanium compounds subsequently condense to form molecules containing a plurality of titanium atoms, each of which is bonded to another through an oxygen atom.

After hydrolysis of the impregnated mica sheet, the sheet is then heated at an elevated temperature to remove the volatile products resulting from the hydrolysis. As previously explained, it is believed that these volatile products consist of aliphatic alcohols plus water. Conditions under which the volatile products may be removed from the hydrolyzed sheet may vary within wide limits. However, it is preferred that the heating step take place at a temperature greater than 100° C., and preferably at a temperature of from about 150–300° C. At these elevated temperatures, the rate of devolatilization of the hydrolyzed sheet is very rapid. The heating step may be carried out in a conventional air circulating oven, or any other type of suitable heating apparatus. In addition, the heating step may be combined with a pressure step by pressing the hydrolyzed mica sheet in a heated press of any desired design. When the pressure heating step is to be applied to remove hydrolysis products, it should be understood that this pressure step may be used in place of the pressure step employed in the preparation of the original unimpregnated mica sheet. At any rate, it is found that maintaining the hydrolyzed mica sheets at a temperature of about 200° C., for 1–5 minutes is sufficient to remove all volatile materials from the sheet. The product resulting from this hydrolysis and heating step advantageously contains from about 1 to 10 parts and preferably about 5 parts, by weight, of hydrolyzate per 100 parts of mica, although treated mica sheets having improved properties are also obtained with amounts of hydrolyzate outside of this range.

The improved mica paper prepared by the method of the present invention may be described as a mica paper having incorporated therein a substantially carbon-free hydrolyzate of an alkyl orthotitanate. This improved mica paper is similar in appearance to that of conventional mica paper not containing the hydrolyzate. That is, the mica paper is somewhat similar in appearance to conventional paper formed from wood fibers except that it is silver in color. This mica paper differs from the prior art mica paper in its much higher tensile strength. Thus, the mica paper of my invention has tensile strengths from 2 to 10 or more times greater than the tensile strength of the original mica paper. In addition, both the tear resistance and the crease resistance of this improved mica paper is superior to that of prior art materials. This improvement in physical properties has been accomplished without any sacrifice of the other properties which make mica paper desirable for high temperature electrical applications. This improved mica paper is stable at very high temperatures, for example, temperatures of the order of 300–500° C. or more, and at the same time has a high dielectric strength and exhibits low electrical losses.

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

In all of the following examples the mica sheet employed was a 2 mil sheet which had been prepared by firing flakes of muscovite mica at a temperature of about 800° C. for about 10 minutes. At the end of this time the mica flakes were added to water which was violently agitated. The violent agitation caused disintegration of the fired mica into fine particles. Both the extra-fine particles and the extra-coarse particles were separated from the slurry and a sheet was formed from the slurry on a conventional paper-making apparatus. This sheet was then dried by calendering at elevated temperatures. Except where otherwise indicated in the examples, an alkylorthotitanate or alkylorthotitanate solution was drawn through the mica sheet which was supported on a porous surface, employing from about one-half to three minutes to pull all of the orthotitanate through the sheet. All parts are by weight.

Example 1

A sheet of mica paper was cut up into a number of samples, each sample being equal to one part by weight. A number of these samples were then impregnated with about 180 parts of solutions of tetrabutyl or tetrapropyl

titanate in benzene and also with pure tetrabutyl titanate. Several of the samples were then hydroylzed by allowing them to stand in air which had a relative humidity of about 50 percent at room temperature and then pressed at 500 pounds per square inch at 200° C. for about one minute. Other samples were hydroylzed by placing them in a closed vessel saturated with water vapor at room temperature for 22 hours. Some of these samples were then dried in an oven at 150° C. without pressure while others were heated in a press at 500 pounds per square inch at a temperature of 100° C. or 200° C. for about one minute. The table below lists the treatment which each of these samples was given and the tensile strength in pounds per square inch observed in each sample. In addition, the table also lists the dielectric dissipation factor (tan loss angle) and the dielectric constant observed on some of the samples. The letters TBT in the table are an abbreviation for tetrabutyl titanate. The namenclature 22% TBT in the table indicates a 22 weight percent solution of tetrabutyl titanate in benzene. Similarly, the initials TPT are an abbreviation for tetrapropyl titanate.

Sample No.	Treatment	Tensile Strength, p.s.i.	Tan Loss Angle	Dielectric Constant
1	None (control)	2,870	0.33	3.5
2	11% TBT (no hydrolysis, no press.).	3,130		
3	11% TBT (5 hr. air hydrolysis 200° C Press.).	5,600	0.25	3.3
4	11% TBT (22 hr. air hydrolysis, 200° C Press.).	7,500	0.25	2.8
5	11% TPT (22 hr. sat. air, No Press.).	4,200		
6	11% TPT (22 hr. sat. air, 100° C. press.).	7,600		
7	11% TPT (22 hr. sat. air, 200° C. press.).	14,000		
8	11% TBT (22 hr. sat. air, No press.).	9,370		
9	11% TBT (22 hr. sat. air, 200° C. press.).	13,000		
10	22% TBT (22 hr. sat. air, No Press.).	10,300		
11	22% TBT (22 hr. sat. air, 200° C. press.).	17,000		
12	100% TBT (22 hr. sat. air, 200° C. press.).	5,600		

The above table shows (samples 1, 5 and 6) that when mica paper is impregnated with tetrapropyl titanate and the impregnated sheet is hydrolyzed for 22 hours in saturated air, the tensile strength is one and one-half times as great as the tensile strength of a control even without pressing the final sheet. When the sheet is pressed at 100° C., the tensile strength is almost three times as great as the control. Similarly, the table shows that merely impregnating mica paper with tetrabutyl titante (sample 2) has little effect on its tensile strength. However, impregnating and then hydrolyzing better than triples the tensile strength (sample 8) even though the sample is dried without pressure. Where the same treatment is given except that the sheet is pressed at 200° C., the resulting sheet has better than four times the tensile strength (sample 9) of the control. Similarly, the table shows that sheets prepared from 22 percent by weight tetrabutyl titanate solutions in benzene are superior to those prepared with only 11 percent solutions and both solutions are much stronger than the control. Finally, the table shows (samples 3 and 4) that the electrical properties of the mica paper are not adversely effected by the orthotitanate treatment.

Example 2

This example illustrates the effect of treating mica paper with various concentrations of tetrabutyl titanate solution. A number of samples (one part each) were prepared from a 2 mil sheet of mica paper and these sheets were treated with about 130 parts of various benzene solutions of tetrabutyl titanate. The treatment was effected by sucking the benezene solution through the mica paper in about 30 seconds. The impregnated sheets were then exposed to saturated air for about 24 hours and the sheets were then pressed at 500 pounds per square inch and 200° C. for 1 minute. The tensile strength of each of the sheets was measured and the weight gain of each sheet was also measured. The following table lists the concentration of the treating solution, the weight gain of the final sheet in parts per hundred parts of mica sheet and the average tensile strength observed. The weight gain is due to the devolatilized hydrolyzate in the mica paper.

Sample No.	TBT Concentration, Wt. Percent	Weight Gain. Parts/100 parts Mica	Tensile Strength, p.s.i.
13	0 (control)	0	1,200
14	11	1.8	2,500
15	22	4.2	3,000
16	32	4.6	6,000
17	42	4.9	7,500

Example 3

This example illustrates the use of various amounts of the alkyl orthotitanate solutions in the impregnation of mica paper. A number of samples of mica paper were cut from a sheet of mica paper and these sheets were treated with various amounts of various concentrations of tetrabutyl titanate in benzene solution. In each case the tetrabutyl titanate solution was sucked through the mica paper in about 15–30 seconds. The 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 at 200° C. for 1 minute. The table below lists the number of parts of benzene solution of tetrabutyl titanate employed per part of mica paper, the concentration in weight percent of the tetrabutyl titanate in benzene, the weight gain observed during the treatment of the mica paper, and the tensile strength observed in the final product.

Sample No.	Parts of TBT solution/ part of mica paper	TBT Concentration, Wt. Percent	Wt. gain, Parts/100 Parts Mica	Tensile Strength, p.s.i.
18	0 (control)			1,200
19	127	11	1.8	2,500
20	635	11	1.0	4.000
21	130	42	4.9	7,500
22	650	42	5.6	6,000

Sample 20 was analyzed for carbon to determine the extent of hydrolysis of the tetrabutyl titanate. This analysis showed that the final product contained only about 1.3 parts of carbon per 1000 parts of mica paper, indicating that the hydrolysis of the tetrabutyl titanate was substantially complete and that the resulting product is substantially free from carbon.

Example 4

This example illustrates the effect of different solvents for the alkyl orthotitanates employed in the practice of the present invention and also illustrates the effect of various atmospheres in the hydrolysis of the orthotitanate. A number of samples of mica paper were cut from a sheet of mica paper and each of these sheets, equivalent to one part of mica, were treated with 140 to 180 parts of various solutions of tetrabutyl titanate in various solvents. These sheets were then hydrolyzed by placing them in a container filled with saturated air or saturated hydrogen for a 24 hour period. The sheets were then heated at 500 pounds per square inch and 200° C. for 1 minute and the weight gain of the sheets and the ten-

sile strength were measured. The table below lists the results of these runs.

Sample No.	Solvent	TBT Concentration, Wt. Percent	Atmosphere	Wt. gain, Parts/100 Parts Mica	Tensile Strength, p.s.i.
23	Control				1,200
24	Benzene	22	Air	4.2	3,000
25	do	22	H_2	3.3	4,500
26	Hexane	27	Air	3.8	6,500

While the foregoing examples have illustrated many of the variations of the process and product of the present invention, it should be understood that other variations not specifically illustrated may also be used. In addition to employing tetrapropyl and tetrabutyl titanate as the alkyl orthotitanate, other orthotitanates of the class described may be employed in my process. Thus, alkyl orthotitanates in which the alkyl group contains from 1–18 or more carbon atoms may be employed. Similarly, solvents for the orthotitanates other than those specifically illustrated may be employed and hydrolysis atmospheres other than those specifically illustrated may be employed.

Although the present invention has been described in terms of impregnating the mica paper with specific alkyl orthotitanates, it should be understood that partial hydrolyzates of these orthotitanates can also be employed. The partial hydrolyzates may be used in pure form or as solutions in an inert solvent. After impregnating with the hydrolyzate, the impregnated mica paper is then hydrolyzed in the manner previously described with water vapor.

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 papers may be used. In addition, the improved mica paper of the present invention can also be employed in those applications where a product having improved physical properties is desirable. Thus, this mica paper can be employed as a dielectric medium in capacitors, 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 physical properties which method comprises impregnating the mica paper with a composition consisting essentially of an alkyl orthotitanate in monomeric form, hydrolyzing the alkyl orthotitanate in the mica paper, and heating the mica paper.

2. The method of claim 1 in which the alkyl orthotitanate is employed as a solution in an inert solvent, said solution containing more than about 10 percent by weight of the alkyl orthotitanate, the solvent for said solution being selected from the class consisting of liquid aromatic and aliphatic hydrocarbons.

3. Mica paper obtained in accordance with the method of claim 1.

4. The method of preparing mica paper of improved physical properties which comprises impregnating the mica paper with a composition consisting essentially of an alkyl orthotitanate in the monomeric form, hydrolyzing the alkyl orthotitanate in the mica paper by subjecting it to an inert atmosphere saturated with water vapor, said atmosphere being inert under the conditions of the reaction, and heating the mica paper.

5. The method of preparing mica paper of improved physical properties which comprises impregnating the mica paper with a composition consisting essentially of tetrabutyl titanate in the monomeric form, hydrolyzing the tetrabutyl titanate in the mica paper with water vapor, and heating the mica paper.

6. The method of preparing mica paper of improved physical properties which comprises impregnating the mica paper with a solution consisting essentially of tetrapropyl titanate in the monomeric form in an inert solvent selected from the class consisting of liquid aromatic and aliphatic hydrocarbons, hydrolyzing the tetrapropyl titanate in the mica paper and heating the mica paper.

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