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PROCESS FOR PRODUCING DIELECTRIC SHEETS

William J. Lies, Williamstown, Mass., assignor to
Sprague Electric Company, North Adams,
Mass., a corporation of Massachusetts

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1

This invention relates to dielectric materials and more specifically refers to processes for producing very thin dielectric sheets which predominate in high dielectric constant ceramic materials.

It has been known for many years that titanium dioxide possesses a dielectric constant far exceeding most other common dielectric materials of both organic and inorganic nature. For this reason its use as a dielectric material in certain types of electrical condensers has been extensive. One type which has been produced for high voltage applications consists of a disc of titanium dioxide of thickness of about .010 to about .100 inch. The diameter generally is provided with a collar to give it rigidity and to increase the flash over voltage. Condensers of this type are generally of quite low capacity and are usually employed in series for high voltage applications. Another type which has been produced in quantity is the cylindrical or tubular type condenser wherein a very thin walled tube of titanium dioxide is extruded and fired to produce a rigid cylindrical body which can be provided with electrodes on the inner and outer surface. Condensers of this type have been used to replace mica condensers for low voltages, low capacity applications. Up until this time no practical method has been suggested for producing dielectric sheets of thickness less than about .010 inch. The thinner sheets are required for high capacity, minimum volume and maximum efficiency in high or low voltage condensers.

Another method suggested for making thin films is described in U. S. Patent No. 2,360,479. In this patent is disclosed a method of producing relatively thin dielectric sheets by firing a preliminary film which is obtained by casting a suspension of titanium dioxide in a water solution of a water soluble polyvinyl resin, as represented by polyvinyl alcohol. Upon drying, the preliminary film contains from about 5% to about 6% of the polyvinyl alcohol. In order to make possible the manufacture of flat films, the casting is done upon a flat base which must be of plastic such as polystyrene. When the film is dry, the whole assembly, that is, film and base, is placed in a furnace and fired at a temperature sufficient to sinter the particles of titanium dioxide together. At the same time the polyvinyl alcohol binder and the base section are decomposed and removed from the titanium dioxide, leaving only inorganic materials. While thin dielectric sheets may be obtained by this procedure, it is awkward and expensive since the polystyrene base is completely

2

used up without recovery and the furnace volume required is increased. More serious is the difficulty that the dielectric sheet resulting from the process is no longer flat and uniform. Unfortunately, the titanium dioxide particles apparently move somewhat during the removal of the resin in the firing process and as a result no longer have the smooth flat surface dimensions obtained when the preliminary film is compacted in a press. If the polystyrene base is not employed, although this procedure is not suggested, it has been found that the strength of the preliminary film per se is not sufficient to allow it to be fired in a furnace without special supplemental elements.

It is an object of this invention to overcome the foregoing and related disadvantages. A further object is to produce improved dielectric films and sheets. A further object is to produce thin dielectric sheets by new and improved processes. A still further object is to produce new and improved electrical condensers. Additional objects will become apparent from a consideration of the following description and claims.

These objects are attained in accordance with the invention wherein I employ a method for producing dielectric sheets which comprises firing a film consisting of a major portion of a compound selected from the class containing titanium dioxide and meta-titanates and a minor portion of a hydrophilic condensation resin. In a still more restricted sense this invention is concerned with a method for producing dielectric sheets which comprises firing at a temperature in excess of 1000° C. a film consisting of a major portion of titanium dioxide and a minor portion of a hydrophilic melamine-formaldehyde resin. In a limited sense this invention is concerned with a method for producing thin dielectric sheets which consists of firing at a temperature from about 1250° C. to about 1360° C. a film consisting of a predominant portion of titanium dioxide and a minor portion of a hydrophilic condensation resin. In one of its preferred embodiments this invention is concerned with a method for producing thin dielectric sheets which comprises firing at a temperature between about 1250° C. to 1360° C. a cast film of thickness less than about .010 inch, said film consisting of a predominant portion of titanium dioxide and a minor portion of a hydrophilic melamine-formaldehyde condensation resin. The invention is also concerned with electrical condensers utilizing the dielectric sheets produced as indicated above.

According to my invention I have discovered

that hydrophilic condensation resins exhibit unusual properties as binders for particles of inorganic dielectric materials, particularly in casting slips. In contrast to other binders for dielectric materials, resins of this type do not have to be used with swellable gums, peptizing agents, electrolytes or other modifying agents. They impart to the preliminary film extremely desirable physical properties and can be introduced in high concentrations. The preliminary dielectric films of the invention, with a major portion of dielectric particles and a minor portion of the resinous binder, are relatively tough and rigid and may be fired, without special support, at elevated temperatures to remove the binder without deformation, warping etc. of the resultant dielectric sheet. This desirable characteristic is in direct contrast with natural gums and rosins and polyvinyl alcohol, since films employing these binders require modifying agents and then support during firing.

Among the condensation resins which are useful in accordance with my invention are hydrophilic types of melamine-formaldehyde resins, resorcinol-formaldehyde resins, phenol-formaldehyde resins and the like. In accordance with my invention these resins should be partially polymerized before use and must be hydrophilic in nature. As the suspending medium for the dielectric particles and as the solvent for the resin may be mentioned water and low molecular weight alcohols and glycols as well as mixtures thereof.

Excellent films of minimum thickness can be cast from suspensions of slips of the dielectric particles in a solution of the resinous material heretofore mentioned. The solvent may be removed from the film after casting by drying at elevated temperatures or by other means. It is preferable also to cure the resin to its full extent at a temperature above 100° C. The resultant cast and cured film may then be fired at elevated temperature to remove the resinous binder and sinter the particles of the dielectric material.

Among the dielectric materials particularly adapted to the process disclosed herein are titanium dioxide and the metatitanates. The firing temperature to which the cast film is subjected is dependent largely upon the nature of the inorganic dielectric used and should be sufficient to sinter the particles together to give a dense, rigid sheet.

The preparation of the casting slip consists generally of mixing the finely ground ceramic particles and the resinous binder in the suspending medium, for example, water. The sequence of steps is not too important since the ceramic particles can be mixed and suspended in the water before the resin is added. However, it is generally desirable to dissolve the resin in the water solvent before adding the titanium dioxide, since the resin decreases the viscosity of the water suspension to a great extent and the successful casting of very thin films is to some degree dependent upon this viscosity decrease. According to my invention I have thus found that the hydrophilic condensation resinous binder acts not only in its binding capacity but also as a peptizing agent. While I am not fully aware of the reason, however, it appears that this action is due to the fact that the partially polymerized molecules of the resin act somewhat as an electrolyte. For this reason, it is preferable to employ low molecule weight hydrophilic

condensation resins for the casting slip although the molecular weight is, of course, increased during the curing of the cast and dried film. As a general rule I prefer to keep within the ratio of 1 to 20 parts of inorganic dielectric material to 1 part of the resinous binder, based, of course, upon dry weight. For optimum results I have found that a concentration of about 7 parts of inorganic dielectric material to 1 part of resin is desirable. The amount of solvent and suspending material employed is generally between about 1 to about 10 parts to 1 part of resin. In order to obtain casting slips with low viscosity and to obtain thin cast films, it is not necessary to use very high concentration of water in conjunction with the novel binding materials of the invention.

The slip produced in accordance with the invention may be cast in the usual manner and any type of form or mold may be employed in the manufacture of thin dielectric sheets. In accordance with one of the preferred embodiments of this invention a polished and smooth flat base surface is desirable. For example, a stainless steel belt is useful. Other polished surfaces such as brass, glass and rubber may be used. If so desired a thin oil or grease film may be placed upon the casting surface before application of the slip thereto. However, this is not always necessary.

The casting may be accomplished simply by pouring the slip upon the smooth surface and allowing it to spread out by gravity. It is possible to accelerate the broadening by means of doctor blades and the like. Agitation of the base material during the casting process is also useful in obtaining films of minimum thickness. I have found also that extremely thin films may be obtained by maintaining the cast slip under reduced pressure during the agitation. The resultant film is free of bubbles and will possess a very smooth surface.

After casting of the film it is allowed to dry by convection of air or it may be subjected to elevated temperatures. After the drying is complete the film is subjected to elevated temperatures sufficiently high to complete the polymerization of the hydrophilic condensation resin binder. This temperature is generally above 100° C. and in the neighborhood of 150° C. for the preferred resins of the invention. If so desired a polymerization accelerator may be added to the suspension in order to speed the curing of the resin.

In accordance with one of the limited embodiments of the invention, it is possible to compact the film between heated platens in a press, in order to obtain maximum density of the preliminary film. This is generally unnecessary since the film is inherently smooth but may be incorporated in the process to replace the resin curing since, under pressure, the resin curing cycle is decreased. Likewise, polymerization catalysts may be added to the resin.

The preliminary film thus obtained is tough, flat, self-supporting and adapted to the firing operation. The thickness of the film is generally less than .010 and may be lower than .005 inch. The following example is representative of the process described herein. 350 grams of titanium dioxide powder of fineness greater than 325 mesh was mixed with 100 cc. of water to give a very thick paste. 50 grams of a water-soluble, partially polymerized melamine-formaldehyde resin

(sold commercially under the trade name "Melmac M-405") was added to the paste, upon further agitation went into solution and the viscosity of the paste decreased markedly to give a fluid slip. 5 grams of glycerin was added, to lower the drying rate. The free-flowing casting slip thus prepared was poured upon a stainless steel plate which had been coated with a thin layer of beeswax. The cast film was carefully dried. After most of the solvent had been removed by air drying, the film was cured for 30 minutes at 150° C. The film which was then removed from the stainless steel base, was tough and retained the flat, smooth surface of the base material. It was placed in a furnace which was heated to a temperature of 1360° C. where it was held for 30 minutes. The film was removed from the furnace after it had cooled to 1200° C. Upon cooling to room temperature a rigid, flat thin sheet of titanium dioxide was obtained. The thickness of this sheet was .007 inch. A portion of each side of the sheet was provided with a fired silver electrode surface, producing a simple electrical condenser. This condenser was tested at 1 megacycle and gave a "Q" value of 820. From the known area of the silver electrode and thickness of the dielectric sheet, it was possible to calculate the dielectric constant of the material. This was found to be 108.

While my invention has been directed particularly to the preparation of dielectric sheets utilizing hydrophilic condensation resin binders, I also contemplate that other binding materials can be used, if they are available with such molecular weights and such chemical structure that they will exhibit the peptizing properties described herein. Polyvinyl alcohol, for example, does not fall within this category and films employing it as a binder are not satisfactory in many respects.

To obtain films of minimum thickness, it is advisable to treat the cast film before it is dried by a special process which combines agitation with reduced pressure. Thereby, it is possible to remove all traces of bubbles and to obtain a uniform plane surface on the upper side of the film.

While my invention has been particularly directed to the production of thin dielectric sheets, the casting slips which employ the resins described herein are useful in many other fields in which slip casting is generally employed.

For example, it is possible to slip cast intricate shapes in metal, plastic, or rubber molds. Heretofore, plaster of Paris molds were used to absorb the water from the slip. As a result numerous molds were required and the surface of the cast object reflected the many imperfections in the relatively delicate surface of the plaster of Paris. After casting, the mold can be heated carefully to remove the moisture from the slip, after which time the dried object may be removed from the mold and fired in the usual manner.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope hereof, it is to be understood that the invention is not limited to the specific embodiments hereof except as defined in the appended claims.

What I claim is:

1. In a method of producing dielectric sheets having thicknesses of the order of 10 mils, the steps of casting a thin film from a slip of finely divided dielectric particles of a compound selected from the class consisting of titanium dioxide and titanates, which slip includes a partially polymerized hydrophilic condensation resin in an amount of from 5 to 50 per cent by weight of the dielectric particles, drying and curing the cast film to substantially completely polymerize the resin, and then firing the cured film to burn off the resin and sinter the dielectric particles together.
2. The method as defined by claim 1 in which the cast film, before curing, is agitated and subjected to reduced pressure to smoothen its upper surface.
3. A method for producing thin dielectric sheets which comprises firing a thin film of about 20 parts to about 1 part by weight of finely divided particles of the class consisting of titanium dioxide and titanates, said particles being bonded together by about one part by weight of a cured hydrophilic condensation resin, and continuing the firing till said particles are sintered together and the resin is burnt away.
4. A method for producing thin dielectric sheets which comprises firing a thin film of about 1 to 20 parts by weight of titanium dioxide particles bonded together by about 1 part by weight of a cured hydrophilic melamine-formaldehyde resin to burn away the resin and sinter said particles together.
5. A method for producing thin dielectric sheets which comprises casting a thin film from a slip containing a predominant portion of finely divided titanium dioxide particles, a minor portion of a partially polymerized hydrophilic condensation resin and water, drying the film, curing the resin in the dried film substantially completely and then firing the film to burn off the resin and sinter the titanium dioxide particles together.
6. A method for producing thin dielectric sheets which comprises casting a thin film from a slip containing a predominant portion of finely divided titanium dioxide, a minor portion of a partially polymerized hydrophilic melamine-formaldehyde resin and water, drying the film, curing the dried film to substantially completely polymerize the resin and form a self-sustaining plate and firing the plate at a temperature of about 1250° C. to about 1360° C. for about 30 minutes to remove the resin therefrom and sinter the titanium dioxide particles together.

WILLIAM J. LIES.

REFERENCES CITED

- The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,266,637	Hauser	Dec. 16, 1941
2,360,479	Detrick et al.	Oct. 17, 1944
2,434,236	Verwey et al.	Jan. 6, 1948