Non brittle dielectric films are formed by blending a cyanoresin such as cyanoethyl hydroxyethyl cellulose (CRE) with a compatible, more crystalline resin such as cellulose triacetate. The electrical breakdown strength of the blend is increased by orienting the films by uniaxial or biaxial stretching. Blends of high molecular weight cyanoresin (CRE) with high molecular weight cyanoethyl cellulose (CRC) provide films with high dielectric constants.
Fig. 4.
Cyanoresin, cyanoresin/cellulose triacetate blends for thin film, dielectric capacitors

Origin of the invention
The invention described herein was made in the performance of work under a NASA contract, and is subject to the provisions of Public Law 96-517 (35 USC 202) in which the Contractor has elected not to retain title.

Technological field
This invention relates to advanced high energy density capacitors and, more particularly, this invention relates to such capacitors incorporating a thin film of cyanoresin or cyanoresin/cellulose triacetate blend having both a high dielectric constant and a high breakdown strength.

Background of the invention
Pulsed power capacitors are being developed as land based and space based weapons. There is an urgent need for a high energy density pulsed power capacitor with an energy density greater than 10 KJ/Kg and the ability to deliver energy in the milliseconds range for electro-magnetic gun applications. The highest energy density of current commercially available capacitors is 1.5 KJ/Kg.

The electrostatic energy which can be stored in any dielectric device is directly proportional to: (1) the effective capacitance of the device, and (2) the square of applied voltage. (1) is controlled by the effective dielectric constant and (2) is limited by the breakdown voltage of the dielectric material used in the device.

Polyvinylidene fluoride (PVDF) has the highest dielectric constant of any commercially available capacitor dielectric. A film of PVDF has a dielectric constant of 11 and a small area breakdown strength of 19 KV/mil. Experimental capacitors with energy densities of 2.5 KJ/Kg have been reported but are not yet commercially available.

In the last 10 years there has been a significant effort to develop new polymer films with higher dielectric constants and higher breakdown strengths than PVDF films.

Cyanoresin films have high dielectric constants (e=15) and are commercially available as film forming resins. Commercial-grade, high dielectric constant cyanoresins have been available since the late 1960's and have been widely used as a coating material for electroluminescent lamps. However, cyanoresin film has not been produced as a capacitor dielectric due to low electrical breakdown strength ~2 KV/mil and brittle nature of the material.

List of references

<table>
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</tbody>
</table>

Statement of the prior art
Caldwell discloses blends of cellulose triacetate (CTA) with a methacrylate polymer.

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Background of the invention
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Statement of the invention
The mechanical properties of cyanoresins as thin films for capacitors are improved by blending various cyanoresins, particularly high molecular weight cyanoethylated hydroxyethyl cellulose (CRE) with cyanoethyl cellulose (CRC). The electrical breakdown strength of the cyanoresin films is improved by blending the cyanoresin with a resin having a higher crystallinity such as cellulose triacetate.

The invention also relates to new methods for casting and fabricating thin films of the blended resins. The blended resins are dissolved in a common solvent. The common solvent systems contains a low vapor pressure, high boiling temperature, non-solvent. The non-solvent is the last to evaporate and helps to lift the very thin film from the casting drum surface. Uniaxial and biaxial orientation of the film increases crystallinity of the crystallized resin and thus further improves the electrical breakdown properties of the film.

Cellulose triacetate and the cyanoresins have a high oxygen-to-carbon ratio. Resins of this nature have self-healing characteristics. Self-healing is a local phenomenon during which a short circuit in a plate capacitor causes arcing and decomposition of the dielectric film in the path of the arc. Rather than permitting the decomposition to propagate, the hydrogen, carbon dioxide and water decomposition products locally passivate the adjacent metal film by vaporization or oxidation of the metal. The device is passivated before any significant current can flow into the fault side of the device. The capacitor returns to its operative mode almost instantly. Furthermore, the self-healing characteristic of the cyanoresin films are substantially improved by blends with improved mechanical properties. The higher Tg films provide better attachment to the metal localizing the decomposition fault action. Also the cellulose triacetate increases the oxygen to carbon ration of the blends. Higher reliability is provided by self-healing of the dielectric film.
These and many other features and attendant advantages of the invention will become apparent as the invention becomes better understood by reference to the following detailed description when considered in conjunction with the accompanying drawings.

**BRIEF DESCRIPTION OF THE DRAWINGS**

FIG. 1 is a cross-sectional view of a dielectric film of a cyanoresin having a metallized surface according to the invention;

FIG. 2 is a cross-sectional view of a capacitor including a cyanoresin dielectric film;

FIG. 3 is an x-ray diffraction (XRD) spectrum of a CRE/CTA film; and

FIG. 4 is a thermomechanical analysis (TMA) of a CRE/CTA film.

**DETAILED DESCRIPTION OF THE INVENTION**

The cyanoresins utilized in the invention can have an aliphatic, aromatic or aryloxy backbone. The resins have a nitrogen content based on CN groups of about 7 to 15% by weight, preferably from about 9-13% by weight and a viscosity (20% DMF solution at 20°C) typically from about 300 to 60,000 cp. The structure of the repeating unit of commercial cyanoresins are provided below.

**TABLE 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \epsilon )</th>
<th>tan( \delta )</th>
<th>Volume Resistance (Q - cm)</th>
<th>Breakdown Voltage V/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR-S</td>
<td>19.0</td>
<td>0.0015</td>
<td>( 4 \times 10^{12} )</td>
<td>2,100</td>
</tr>
<tr>
<td>CR-C</td>
<td>16.5</td>
<td>0.022</td>
<td>( 4 \times 10^{11} )</td>
<td>2,000</td>
</tr>
<tr>
<td>CR-V</td>
<td>19.7</td>
<td>0.064</td>
<td>( 1 \times 10^{12} )</td>
<td>1,800</td>
</tr>
<tr>
<td>CR-E</td>
<td>18.8</td>
<td>0.041</td>
<td>( 1 \times 10^{13} )</td>
<td></td>
</tr>
</tbody>
</table>

Dielectric Constant (\( \epsilon \)), Dissipation Factor (tan\( \delta \)), Resistivity (\( \rho \)) and Breakdown Strength (\( E_b \)) of Cyanoresins at 25°C.

Cyanoresins are generally soluble in acetone, acetonitrile, furfuryl alcohol, tetrahydrofurfuryl alcohol, nitromethane, N,N-dimethylformamide, N-methyl-2-pyrolidone, \( \gamma \)-butyrolactone and propylene carbonate. Some of the resins are soluble in halogenated solvents such as methylene chloride or chloroform.

Commercial cyanoresins are mainly used to coat the surface of electroluminescent layers of a lamp. The films are brittle and have low electrical breakdown strength. In order to optimize the mechanical properties and to increase electrical breakdown strength, cyanopolymers of different
molecular weights were blended with each other and in some cases with cellulose triacetate (CTA) as a matrix copolymer.

Films of the 4 cyanoresins having both high and low molecular weights were hand cast to evaluate the film forming properties for continuous film production. Small scale continuous 5" wide thin films with thicknesses ranging from 2 μm to 39 μm, and weighing about 100 g apiece, were produced with a 5" drum caster.

The film casting procedure described below was used for cyanoresin, cellulose triacetate (CTA) and cyanoresin/CTA blend films. A mixture of chloroform and dichloromethane was most often used as the solvent for film casting, especially the CTA blends, though acetone was also used for casting some of the cyanoresin blends.

The polymer or polymer blend was dissolved in 1500 ml of solvent mixture, using a ball mill with ½"x½" Burndum cylinders in a ½ gallon ball mill jar. The solution process was carried out overnight to ensure complete dissolution. The polymer concentration in solution ranged between 5% and 10% by weight, and yield a desirable viscosity for drum casting. The casting drum temperature was set at 30°C; the speed for film production was very slow (several feet per minute). The film was dried by passage through an electric oven after being lifted from the casting drum, and then wound on to a 6" drum under tension to induce orientation. The temperature of the oven ranged from 60°C to 190°C depending upon the nature of the polymer film.

A method of casting uniform films has been developed in accordance with the invention. The method is based on casting the resin solution onto a casting surface such as a drum from a solution in a solvent mixture containing a small amount of non-solvent having a low vapor pressure. Since the non-solvent is the last to evaporate, it lifts the film from out load. Crystallinity was calculated to be about 23.7%.

A preferred Thermomechanical analysis (TMA) was next performed on CTA films in order to assess thermal and dimensional stability. The CTA film is oriented and amorphous. The TMA indicates a glass transition temperature (Tg) of 185.8°C. At 207.5°C, the CTA started to crystallize. The melting temperature (Tm) of CTA is 271.4°C. The X-ray and TMA data suggest that the crystallinity of CTA film can be increased by biaxial stretching under stress, at a high temperatures of up to 250°C. The 13 μm CTA cast film gave a dielectric constant value of 3.6; dielectric loss of 0.016 and a DC electrical breakdown strength of 12.15 KV/mil.

In order to increase the electrical breakdown strength of CRE films, the CRE resin can be blended with weight of a compatible, semi-crystalline polymer such as cellulose triacetate. Solutions of 5–10% CRE resin and of a CRE/CTA blend in the chloroform-dichloromethane-DME solvent system were prepared and cast on the 5 inch drum caster to form a CTA film 13 μm thick and a CRE/CTA film 25 μm thick.

The 13 μm CTA film was dried at 160°C under tension, and its thermal, morphological and electrical properties were evaluated. This particular film was also used to establish the experimental conditions required to induce CTA crystallinity. X-ray diffraction (XRD) data, not shown, indicates that the CTA film is oriented and amorphous. This film can be subsequently crystallized at 250°C after 30 minutes without load. Crystallinity was calculated to be about 23.7%.

Thermomechanical analysis (TMA) was next performed on CTA films in order to assess thermal and dimensional stability. The CTA film is oriented and amorphous. The TMA indicates a glass transition temperature (Tg) of 185.8°C. At 207.5°C, the CTA started to crystallize. The melting temperature (Tm) of CTA is 271.4°C. The X-ray and TMA data suggest that the crystallinity of CTA film can be increased by biaxial orientation under stress, at high temperatures of up to 250°C. The 13 μm CTA cast film gave a dielectric constant value of 3.6; dielectric loss of 0.016 and a DC electrical breakdown strength of 12.15 KV/mil.

A small roll (~100 gm) of 5 inch wide, 25 μm thick blend film was produced with a drum caster. The film was dried at 150°C under tension. X-ray diffraction data (XRD) shown in FIG. 3 indicates that the film is amorphous but oriented. The TMA data for this film, shown in FIG. 4, show a Tg of 157.7°C. The film started to crystallize at 184°C, and its melting point was ~245.5°C. The TMA data indicates that this film should be able to withstand temperatures up to 150°C. For purposes of comparison, the electrical properties of all four matrix polymer films are summarized in Table 2.

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Film Thickness (μm)</th>
<th>Dielectric Constant (KHz)</th>
<th>Dielectric Loss (KHz)</th>
<th>Avg. Breakdown Strength DC (KV/mil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTA</td>
<td>13</td>
<td>3.60</td>
<td>0.016</td>
<td>12.15</td>
</tr>
<tr>
<td>CRE</td>
<td>39</td>
<td>16.24</td>
<td>0.050</td>
<td>3.0</td>
</tr>
<tr>
<td>CRE (80)</td>
<td>25</td>
<td>16.16</td>
<td>0.040</td>
<td>4.6</td>
</tr>
<tr>
<td>CRE (50)</td>
<td>35</td>
<td>7.87</td>
<td>0.031</td>
<td>9.42</td>
</tr>
</tbody>
</table>
The oriented amorphous CRE/CTA film (~35 mm thick) gave dielectric constant of 7.87 (1 kHz), a dielectric loss of 0.031 (1 kHz) and an average DC breakdown strength of 9.42 KV/mil. If the morphology of this cast film is optimized with biaxial orientation (by inducing crystallinity to the cast film), the film should display a breakdown strength exceeding 15 KV/mil. The thickness of the film will decrease during stretching.

The present invention represents the first synthesis of a capacitor film with both a high dielectric constant and a high breakdown strength. Its thickness ranges from 2 µm to 30 µm. This film can be made from commercial high dielectric constant cyanoresins and cyanoresin/cellulose triacetate CTA blends. A continuous solution process for casting of the thin films of cyanoresins has been developed. The very high oxygen to carbon ratio of the film contributes to self-healing of dielectric films when used in capacitors providing high reliability devices.

It is to be realized that only preferred embodiments of the invention have been described and that numerous substitutions, modifications and alterations are permissible without departing from the spirit and scope of the invention as defined in the following claims.

We claim:
1. A capacitor comprising in combination:
   a dielectric layer formed of a blend of a cyanoresin with
   a compatible second resin having at least 20% crystallinity; and
   a metal film adjacent a surface of the layer.
2. A capacitor according to claim 1 in which the blend comprises 10%-90% by weight of a first high molecular weight cyanoresin and 10%-90% by weight of a second high molecular weight cyanoresin.
3. A capacitor according to claim 2 in which the first cyanoresin is cyanoethyl hydroxyethyl cellulose.
4. A capacitor according to claim 3 in which the second high molecular weight cyanoresin in the blend is selected from the group consisting of cyanoethyl cellulose and cyanoethyl pullulan.
5. A capacitor according to claim 1 in which the second compatible resin is cellulose triacetate.
6. A capacitor according to claim 1 in which the cyanoresin has a nitrogen content from 5-20% by weight.
7. A capacitor according to claim 6 in which the cyanoresin is a cyano-lower-alkylated resin selected from the group consisting of pullulan, polyvinyl alcohol, cellulose and hydroxyethyl cellulose.
8. A capacitor according to claim 1 in which the crystallinity of the compatible second resin is effected by uniaxial or biaxial orientation of the layer.

* * * * *