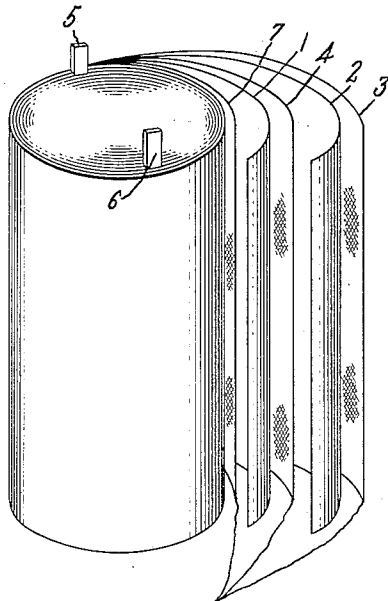


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FIBROUS DIELECTRIC COMPOSITIONS

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FIBROUS MATERIAL COMPRISING  
REACTION PRODUCT OF LIGNOCELLULOSE  
PULP AND ACRYLONITRILE

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## UNITED STATES PATENT OFFICE

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## FIBROUS DIELECTRIC COMPOSITIONS

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This invention relates to new fibrous lignocellulose derivatives and more particularly to new fibrous reaction products of lignocellulose pulps and acrylonitrile having a high dielectric constant rendering them especially suitable for use as dielectric materials in electric capacitors.

In the fabrication of capacitors of relatively small size, solid dielectric materials are generally desired. Various papers made from lignocellulose pulps, for example, kraft paper, commonly have been used as dielectric spacers in small capacitors. These fibrous dielectric spacers are generally impregnated with solid or liquid dielectric compositions such as, for example, petroleum hydrocarbons, including mineral oils or waxes, or one or more of the class of compositions generically termed askarels, which include chlorinated hydrocarbons such as chlorinated benzene, chlorinated diphenyl, chlorinated diphenyl oxide, chlorinated diphenyl methane, chlorinated diphenyl benzene, and alkyl derivatives thereof, castor oil and derivatives thereof, silicones, etc.

Since the fibrous material represents the major portion of the dielectric spacers, it is obviously desirable that the fibrous material have as high a dielectric constant as possible in order that the maximum capacitance per unit of size of capacitor can be obtained. We have found that by reacting lignocellulose pulp with acrylonitrile in an aqueous alkaline medium we can obtain fibrous materials having nitrogen contents of from about 0.3 percent to about 2.8 percent from which paper having substantially higher dielectric constants than ordinary kraft paper can be prepared.

It has been known for some time that acrylonitrile will react with cellulose pulps from which the lignin has been removed. However, the products of these prior art methods are cyanoethyl cellulose ethers or carboxyethyl cellulose ethers which are pastes or thermoplastic resins much like ethyl cellulose in their physical properties and have no fibrous structure. Our modified lignocellulose materials, on the other hand, only contain substituted cyanoethyl groups corresponding to a nitrogen content of from about 0.3 to about 2.8 percent by weight of the final product and retain substantially the same fibrous structure as that characterizing the original lignocellulose pulp prior to reaction with the acrylonitrile. Furthermore the fibrous reaction product may be hydrated, beaten into a paper making stock, and made into paper in accordance with well known paper making technique.

In preparing the fibrous material of our invention the lignocellulose pulp is first suspended in an aqueous alkaline medium such as, for example, a solution of sodium hydroxide or potassium hydroxide. The reaction may be carried out employing solutions of various degrees of alkalinity. However, we prefer to use solutions containing from about 6 percent to about 12 percent of the hydroxide. The ratio of pulp to the aqueous alkaline medium may be widely varied

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depending on the other conditions employed in the reaction. We have found that a ratio of about one part by weight of dry pulp to 20 parts by weight of the aqueous hydroxide solution affords suspensions of desirable consistency for carrying out the reaction. Various amounts of acrylonitrile may be added to the suspension of pulp depending on the length of time the reaction between the lignocellulose and the acrylonitrile is carried out. We have employed acrylonitrile in amounts varying from about 30 percent to about 70 percent by weight of the pulp. However, less acrylonitrile or more acrylonitrile may be employed if the reaction is continued for longer or shorter periods, respectively. During the addition of the acrylonitrile and during the reaction of the acrylonitrile with the pulp, the suspension is stirred continuously, maintaining a temperature of from about 0° C. to about 25° C., preferably from 7° C. to 18° C. The reaction is carried out until the resulting product has a nitrogen content of between about 0.3 percent and about 2.8 percent depending on the electrical and mechanical properties desired in the final product.

The reaction may be stopped by adding sufficient dilute acetic acid to make the mixture slightly acid and subsequently filtering and washing the pulp with water until neutral. However, the reaction is preferably stopped by filtering the pulp from the reaction mixture and washing the pulp with dilute acetic acid and water until neutral. The pulp is then beaten in a paper beater of the conventional type and is made into paper of the desired thickness by any of the well known methods familiar to those skilled in the art.

As the number of cyanoethyl groups substituted in the lignocellulose pulp is increased, the dielectric constant of papers made from the resulting pulps is increased. However, if the number of cyanoethyl groups is increased to any appreciable extent above that corresponding to a nitrogen content of about 2.8 percent, the resulting product tends to become resinous or pasty rather than fibrous in character and therefore cannot be readily beaten and made into paper. Furthermore, these resinous materials have relatively high power factors which render them unsuitable for use as dielectric materials, particularly for use in capacitors. We have also found that in order to obtain an appreciable improvement in dielectric constant over that of ordinary kraft pulp, it is necessary that the reaction between the acrylonitrile and lignocellulose pulp be carried out sufficiently to substitute cyanoethyl groups corresponding to a nitrogen content of at least about 0.3 percent.

The fibrous materials of our invention are most advantageously employed as dielectric materials for use in capacitors when impregnated with dielectric compositions such as, for example, the compositions described above as having been employed with ordinary kraft paper.

The accompanying drawing shows somewhat conventionally a capacitor embodying the dielectric materials of our invention.

The capacitor comprises armatures 1 and 2 of suitable metal, for example, aluminum foil, and interposed sheets of the fibrous material of our invention 3, 4 and 7. A single sheet of fibrous material separating the armature is shown to render the drawing as simple as possible but it should be understood that more than one sheet may be employed if desired. Terminals 5 and 6 for external electrical connection are provided for the armatures. In order to obtain as much capacitance per unit volume as possible, the spacer sheets 3, 4 and 7 are preferably impregnated with a dielectric composition as hereinbefore described.

In order that those skilled in the art better may understand how the present invention may be carried into effect, the following examples are given by way of illustration and not by way of limitation. All parts are by weight.

#### Example 1

|                                        | Parts |
|----------------------------------------|-------|
| Lignocellulose pulp                    | 3     |
| Sodium hydroxide solution (10 percent) | 60    |
| Acrylonitrile                          | 1     |

The pulp was placed in the sodium hydroxide solution in a vessel equipped with a stirrer and open to the atmosphere. The pulp was maintained in suspension in the alkaline solution by means of the stirrer. The acrylonitrile was added slowly. During this addition and throughout the subsequent reaction period of about three hours, the vessel was maintained at a temperature of about 2° C. by means of a water bath and the pulp was maintained in suspension by means of the stirrer. In order to stop the reaction after three hours, the reaction mass was neutralized with dilute acetic acid, and the neutralized mass was allowed to stand for about 12 hours in order to leach all of the alkaline solution from the pulp. The pulp was then filtered with a fine screen and washed thoroughly to remove all soluble electrolytes. The resulting pulp, which contained 2.6 percent nitrogen, was then beaten in a paper beater of the conventional type and made into paper.

#### Example 2

|                                        | Parts |
|----------------------------------------|-------|
| Lignocellulose pulp                    | 3     |
| Sodium hydroxide solution (10 percent) | 60    |
| Acrylonitrile                          | 1     |

The pulp and sodium hydroxide solution were placed in a nickel kettle equipped with a stirrer. The pulp was maintained in suspension in the solution by means of the stirrer and the suspension was cooled to 9° C. The acrylonitrile was added to the suspension over a period of one-half hour, and the reaction was carried out for two hours longer at 10° C. The reaction mixture was then neutralized with dilute acetic acid and the neutralized mass was allowed to stand for about 12 hours to leach the remaining sodium hydroxide from the pulp. The pulp was filtered from the solution and was then washed thoroughly and beaten in a pulp beater. Paper made from the resulting pulp contained 1.28 percent nitrogen.

#### Example 3

|                                       | Parts |
|---------------------------------------|-------|
| Lignocellulose pulp                   | 2.41  |
| Sodium hydroxide solution (6 percent) | 44.40 |
| Acrylonitrile                         | 1.00  |

The pulp was suspended in the sodium hydroxide solution in a vessel equipped with a stirrer and open to the atmosphere. The acrylonitrile was added slowly to the suspension and the reaction was continued for four hours with stirring, maintaining the temperature of the suspension between 10° C. and 15° C. At the end of four hours the reaction was stopped by drowning in a large volume of water, filtering out the pulp, and washing the pulp with dilute acetic acid and finally with water until the pulp was neutralized. The nitrogen content of this pulp was 0.90 percent.

#### Example 4

|                                        | Parts |
|----------------------------------------|-------|
| Lignocellulose pulp                    | 2.41  |
| Sodium hydroxide solution (12 percent) | 44.40 |
| Acrylonitrile                          | 1.00  |

The above ingredients were mixed and the reaction was carried out as described in Example 3. The resulting modified lignocellulose pulp had a nitrogen content of 2.32 percent.

#### Example 5

|                                        | Parts |
|----------------------------------------|-------|
| Lignocellulose pulp                    | 1.55  |
| Sodium hydroxide solution (10 percent) | 30.6  |
| Acrylonitrile                          | 1.0   |

The pulp was suspended in the sodium hydroxide solution in a vessel open to the atmosphere and equipped with a stirrer. The acrylonitrile was added slowly to the pulp suspension with stirring. After the acrylonitrile had been added the reaction was continued for four hours at a temperature of 15° C. to 20° C. with stirring. The reaction was stopped by neutralizing the reaction mass with dilute acetic acid. After the treated pulp had been filtered and washed free of electrolytes it was found to have a nitrogen content of 2.48 percent.

#### Example 6

|                                        | Parts |
|----------------------------------------|-------|
| Lignocellulose pulp                    | 2.41  |
| Sodium hydroxide solution (10 percent) | 46.20 |
| Acrylonitrile                          | 1.00  |

The pulp was suspended in the sodium hydroxide solution in a vessel open to the atmosphere and equipped with a stirrer. The acrylonitrile was added slowly and the reaction was continued for four hours after all of the acrylonitrile had been added, maintaining the temperature of the suspension between -1° C. and 3° C. The suspension was stirred constantly during the addition of the acrylonitrile and during the subsequent reaction period. After four hours the reaction was stopped by neutralizing the reaction mass with dilute acetic acid. When filtered and washed free of electrolytes, the resulting pulp had a nitrogen content of 1.69 percent.

As hereinafore indicated, we have found that the reaction of acrylonitrile with lignocellulose pulp is most readily carried out at temperatures of between about 7° C. and about 18° C. At temperatures within this range the cyanoethyl groups are substituted in the lignocellulose structure at the maximum rate consistent with a minimum of hydrolysis of the resulting product. This readily may be seen from the following examples in which the same proportions of ingredients were employed as those described in Example 6 and all of the reaction conditions were the same as in Example 6 except for the tempera-

tures employed. The variation in the nitrogen content of the resulting pulps with the reaction temperatures employed was as follows:

| Example | Temperature Range, Degrees Centigrade | Percent Nitrogen in Treated Pulp |
|---------|---------------------------------------|----------------------------------|
| 7       | 7 to 8                                | 2.06                             |
| 8       | 12 to 13                              | 2.46                             |
| 9       | 17 to 18                              | 2.01                             |
| 10      | 21 to 22                              | 1.91                             |
| 11      | 28 to 29                              | 0.35                             |

As has been indicated above, papers prepared from the modified lignocellulose pulps of our invention are characterized by substantially higher dielectric constants than papers prepared from ordinary lignocellulose pulps, such as, for example, kraft pulp. To illustrate the increased dielectric constant of our material, the dielectric constants of ordinary kraft paper and papers prepared from pulps of our invention have been determined by comparison with dielectric compositions of known dielectric constants. Results of these measurements are as follows:

| Frequency Kilocycles | Kraft Pulp | Modified Lignocellulose Pulp |                |
|----------------------|------------|------------------------------|----------------|
|                      |            | 2.3% Nitrogen                | 0.77% Nitrogen |
| 1                    | 6.33       | 7.91                         | 6.97           |
| 50                   | 6.40       | 7.42                         | 6.86           |
| 1,000                | 5.90       | 6.85                         | 6.44           |

The advantages in employing the pulps of our invention in dielectric spacers for capacitors are realized as over-all increases in capacitance as compared with capacitors of the same dimensions in which the spacers comprise ordinary kraft paper. For example, at 1,000 cycles, the total dielectric constant of kraft paper and pentachlorodiphenyl is 5.32 while the total dielectric constant of our modified lignocellulose pulp having a nitrogen content of 0.77 percent and pentachlorodiphenyl is 5.65. This represents a 6 percent increase in capacitance.

If modified pulp of higher nitrogen content, for example, a modified pulp containing 2.3 percent nitrogen is employed in a dielectric spacer with pentachlorodiphenyl, the over-all dielectric constant becomes at least 6, representing an 11.5 percent gain in capacitance. If a dielectric liquid, such as tetrachloro-ortho-nitrodiphenyl, having a dielectric constant of about 20 is used as an impregnant, the over-all constant increases from 7.90 with kraft paper to at least 9.52 with a paper prepared from our modified pulp containing 2.3 percent nitrogen, representing a gain in capacitance of 20.5 percent.

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

1. A material comprising the fibrous product of reaction of a lignocellulose pulp with acrylonitrile in an aqueous alkali metal hydroxide medium, said fibrous material having a nitrogen content of from about 0.3 percent to about 2.8 percent.

2. A material comprising the fibrous product of reaction of a lignocellulose pulp with acrylonitrile in an aqueous alkaline medium containing from about 6 percent to about 12 percent of an alkali metal hydroxide, said fibrous material hav-

ing a nitrogen content of from about 0.3 percent to about 2.8 percent.

3. A material comprising the fibrous product of reaction of kraft pulp with acrylonitrile in an aqueous alkali metal hydroxide medium, said fibrous material having a nitrogen content of from about 0.3 percent to about 2.8 percent.

4. A dielectric material comprising the fibrous reaction product of a lignocellulose pulp and acrylonitrile in an alkali metal hydroxide solution said fibrous material having a nitrogen content of from about 0.3 percent to about 2.8 percent.

5. A dielectric sheet material comprising the fibrous reaction product of a lignocellulose pulp and acrylonitrile in an aqueous alkali metal hydroxide medium, said fibrous material having a nitrogen content of from about 0.3 percent to about 2.8 percent and a dielectric composition comprising a halogenated hydrocarbon

6. A dielectric sheet material comprising the fibrous reaction product of a lignocellulose pulp and acrylonitrile in an aqueous alkali metal hydroxide medium, said fibrous material having a nitrogen content of from about 0.3 percent to about 2.8 percent, and a dielectric composition comprising a petroleum hydrocarbon.

7. A dielectric sheet material comprising the fibrous reaction product of a lignocellulose pulp and acrylonitrile in an aqueous alkali metal hydroxide medium, said fibrous material having a nitrogen content of from about 0.3 percent to about 2.8 percent, and a dielectric composition comprising castor oil.

8. A dielectric sheet material comprising the fibrous reaction product of a lignocellulose pulp and acrylonitrile in an aqueous alkali metal hydroxide medium, said fibrous material having a nitrogen content of from about 0.3 percent to about 2.8 percent, and a dielectric composition comprising pentachlorodiphenyl.

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#### REFERENCES CITED

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

#### UNITED STATES PATENTS

| Number    | Name        | Date           |
|-----------|-------------|----------------|
| 2,015,104 | Dreyfus     | Sept. 24, 1935 |
| 2,075,410 | Thompson    | Mar. 30, 1937  |
| 2,190,018 | Del Mar     | Feb. 13, 1940  |
| 2,212,836 | Kohman      | Aug. 27, 1940  |
| 2,232,041 | Webb        | Feb. 18, 1941  |
| 2,281,602 | Ruben       | May 5, 1942    |
| 2,332,048 | Bock et al. | Oct. 19, 1943  |
| 2,332,049 | Bock et al. | Oct. 19, 1943  |
| 2,349,797 | Bock et al. | May 30, 1944   |
| 2,360,367 | Ruben       | Oct. 17, 1944  |
| 2,375,847 | Houtz       | May 15, 1945   |
| 2,391,687 | McLean      | Dec. 25, 1945  |

#### OTHER REFERENCES

"Cellulose as an Insulating Material," by G. T. Kohman, Industrial and Engineering Chemistry, July 1939, pp. 807-817.

"Electrical Insulating Papers," by H. H. Race et al., The Paper Industry and Paper World, Nov. 1940, pp. 792-796.

"A New Kraft Capacitor Paper" by H. F. Miller, General Electric Review, Dec. 1941, pp. 20-24.