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[54] **POLYAMIDE PAPER PRODUCT AND METHOD OF MAKING**  
**34 Claims, 7 Drawing Figs.**

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 32.6N; 264/343; 174/110(.43)

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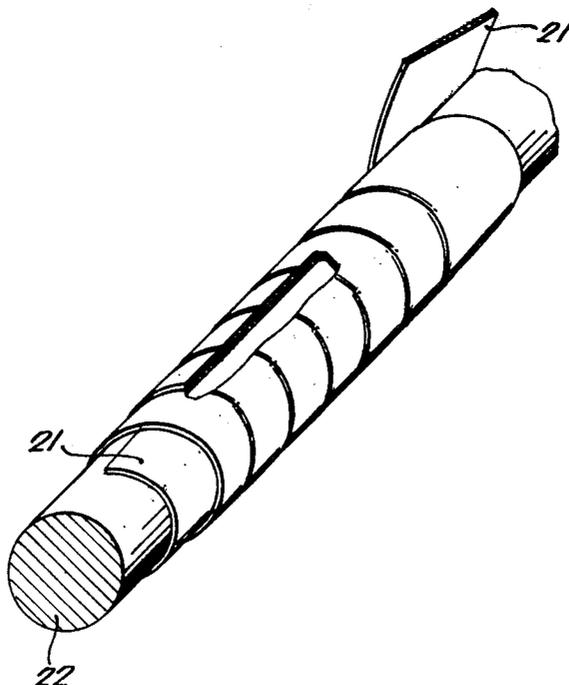
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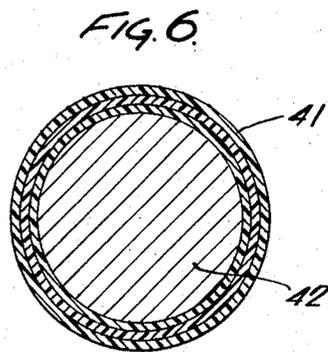
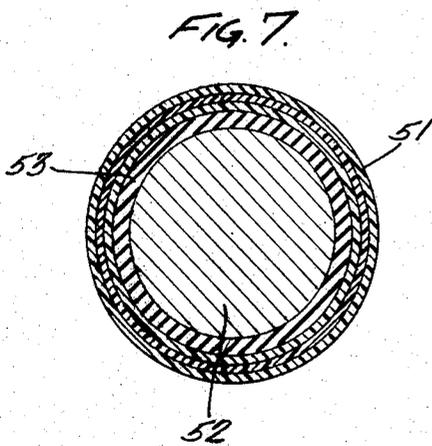
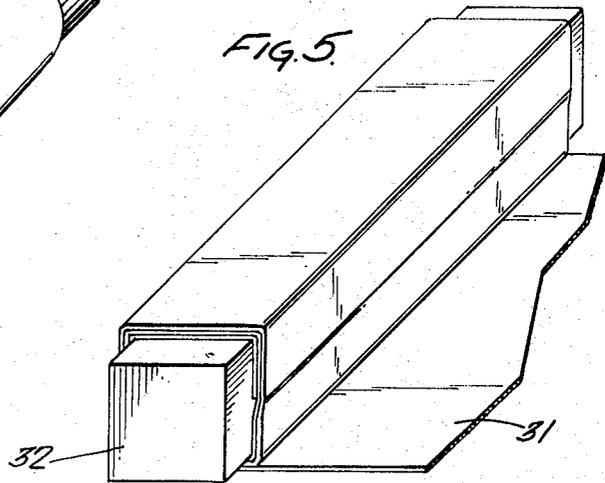
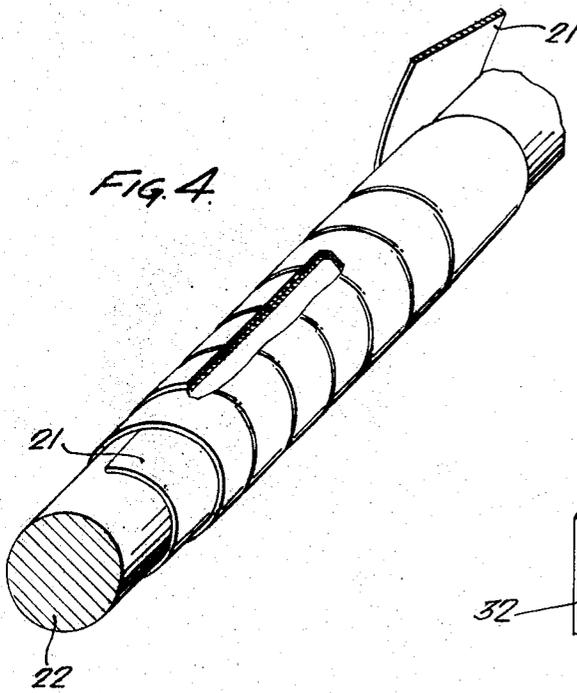
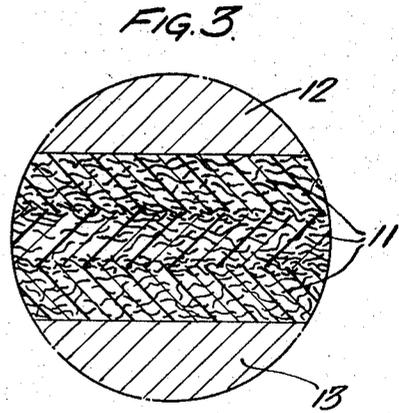
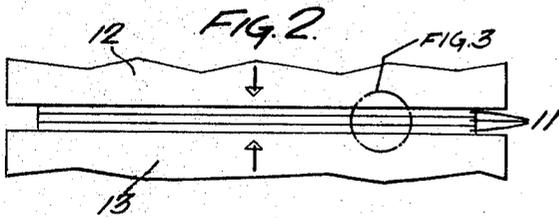
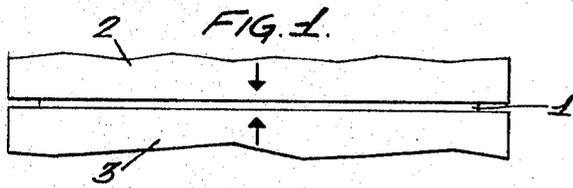
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**ABSTRACT:** A paper web composed of fibers and fibrils of a high temperature resistant aromatic polyamide is impregnated with a solvating liquid which solvates and swells the surfaces of the fibers and fibrils without destroying them and the solvating liquid is thereafter evaporated, providing improved electrical and mechanical properties in the paper web. A plurality of such paper webs, impregnated with the solvating liquid is superposed in laminar relation and the solvating liquid is evaporated from the plies while in said superposed relation to provide an improved laminate.





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## POLYAMIDE PAPER PRODUCT AND METHOD OF MAKING

There is available a paper composed of aromatic polyamide (nylon) fibers and fibrils which is unusually resistant to high temperatures and has good electrical and mechanical properties. Its combination of electrical properties; mechanical toughness and strength and long useful life at temperatures above 180° C. (it retains 60 percent of its room temperature tensile strength at 250° C., does not melt, and will not burn independently at temperatures above 500° C.) has led to its use as electrical insulation and in other industrial applications.

This paper is composed of two different forms of the same aromatic polyamide polymer: short fibers (floc) and smaller fibrous binder particles (fibrils). It is made on conventional paper-making equipment and hence is an interfelted web of the stated fibers and fibrils. However, bonding of the fibers and fibrils is accomplished by heat and pressure, and no additives, like binders, fillers, or the like, are used (see U. S. Pat. No. 2,999,788 and "Properties and Performance of 'Nomex' High Temperature Resistant Nylon Paper," Technical Information Bulletin N-195, Sept. 1965, E. I. du Pont de Nemours & Company, Inc.). The paper is available in thicknesses ranging from about 2 mils to about 40 mils, and has a specific gravity from about 0.3 to about 1, depending upon thickness and degree of calendaring.

The stated paper is very resistant to flow at elevated temperatures and, therefore, presents problems in making laminates thereof and in molding in laminate form. In order to laminate the paper, according to the technical literature, the plies have to be heated to a temperature of 540° F. under 300 p.s.i., degassed frequently and then pressed at 1,000 p.s.i. with further degassing or "breathing." (See "Properties and Processing of 'Nomex' High Temperature Resistant Nylon Paper," Technical Information Bulletin NP-31, Sept., 1963, E. I. du Pont de Nemours & Company, Inc.). The laminates so made are generally limited to flat or substantially flat, relatively simple shapes.

It is the principal object of the present invention to provide a novel method for improving the electrical properties of the described paper.

It is a further principal object of the present invention to provide a novel method of laminating the described paper.

It is another object of the present invention to provide a novel method of laminating the described paper whereby the laminate has enhanced electrical properties, such as dielectric strength.

It is a further object of the present invention to provide a method of laminating the described paper whereby complex laminated shapes, such as tubes, insulating jackets, and the like, may be prepared.

Another object of the present invention is to provide improved paper of the type described.

Still another object of the present invention is to provide a new and improved laminate of the described paper.

Other object objects will become apparent from a consideration of the following specification and claims.

The method of the present invention broadly comprises impregnating the described paper with at least one solvating agent selected from the group consisting of dimethylsulfoxide, N,N-dimethylformamide, N,N-dimethylacetamide and N-methyl-2-pyrrolidone, removing said solvating agent from said paper and subjecting said paper to compression normal to its plane.

The method of the present invention in preparing a laminate comprises superposing in laminar relation a plurality of plies of the described paper impregnated with the solvating agent, removing said solvating agent from said plies while in said superposed laminar relation and subjecting said plies to compression normal to the plane thereof.

The present process as applied to a single ply of the paper may take the form of any one of several typical embodiments: pressing a single ply of the impregnated paper, after evaporation of some or all of the solvating agent, between platens;

wrapping a single ply of the impregnated paper about a mandrel, and the like. The present process as applied to lamination may also take the form of any one of several typical embodiments: simple lamination of two or more individual impregnated sheets in a stack; lamination of plies of the same sheet as by winding the impregnated sheet about a mandrel followed by removing the laminate from the mandrel; formation of the laminate in situ as an insulating jacket as by winding the impregnated sheet about an electrical conductor, which may or may not have a covering of another insulating material thereon, and leaving the resulting laminate jacket in place, and the like.

The present invention maybe more readily understood from a consideration of the drawings in which:

FIG. 1 is a side elevational view of an embodiment wherein a single ply of paper is treated according to the present invention;

FIG. 2 is a side elevational view of the embodiment wherein individual sheets are laminated in a stack;

FIG. 3 is an enlarged section from FIG. 2;

FIG. 4 is a perspective view illustrating another laminating embodiment wherein a sheet, in tape form, is helically wound about a mandrel;

FIG. 5 is a perspective view illustrating still another laminating embodiment wherein a sheet is wrapped in nonspiral convolutions about a mandrel;

FIG. 6 is an end sectional view illustrating yet another embodiment wherein the laminate is formed about an electrical conductor; and

FIG. 7 is an end sectional view illustrating an embodiment similar to FIG. 6 wherein, however, the electrical conductor has a covering of another insulation thereon between the conductor and the laminate.

The present method appears to be unique in its action on the state stated fibers and fibrils and, in the preparation of laminates, on the consequent bond between the plies in the laminate. The stated solvating liquids do not dissolve or destroy the fibers or fibrils or any part thereof, and there is no formation of a sticky, tacky, adhesive phase. Rather, it appears that the liquid solvates at least the surfaces of the fibers and fibrils causing them simply to swell while retaining their integrity as individual fibers and fibrils. This swelling, however, causes individual fibers and fibrils, initially not in contact or, at most, only in contact at space spaced points, to expand and crowd to where there is markedly enhanced surface-to-surface contact and fit over relatively large interfaces resulting in molecular attraction between the engaged surfaces. Subsequent evaporation of the solvating liquid does not reverse the action causing the individual fibers and fibrils to separate and withdraw back to their initial position. Instead, the molecular attractions, believed to be due to the intermolecular attraction or cohesive forces arising from the close proximity of polymer molecules, and nitrogen and hydrogen atoms, in adjacent fibers and fibrils, is retained upon evaporation of the solvating liquid causing the structure as a whole to consolidate and shrink, as the fibers and fibrils contract back to the original size, and hence become more dense. While, however, the fibers and fibrils are in their swollen and solvated state the material may be shaped, the removal of the solvating liquid while maintaining the material in the desired shape resulting in a final compact, consolidated, dense product in which the fibers and fibrils are firmly bonded together. The stated shrinkage is a great advantage, not only in providing the improved properties, but especially where the material is shaped about a form, like a mandrel, and wherein shrinkage of the material causes it to assume a tight fit about and a faithful reproduction of the form and imposes the desired compression. Upon the evaporation of the solvating liquid, the product is composed essentially of the original polymer, since no appreciable extraneous material, like binder, filler, etc., is used in the making of the described paper sheet and none is left behind following the present treatment, and the individual fibers and fibrils are distinguishable as in the original paper, although in a more consolidated state.

What has been said in the preceding paragraph applies to a single ply as well as to laminates prepared according to the present invention. Referring specifically to the laminated product, although the individual fibers and fibrils are distinguishable, as stated, the individual plies are difficult to distinguish. It appears that the aforementioned swelling and bonding causes fibers and fibrils on the surface of one ply to intertwine and mingle with fibers and fibrils on the surface of the adjacent ply and to remain united in that position upon evaporation of the solvating liquid.

Referring further to the aromatic polyamide paper sheet utilized in accordance with the present invention, this has been described above and in the herein-mentioned publications and patents to which further reference may be made. As stated, the paper is available in thicknesses ranging from about 2 to about 40 mils. However, the paper used in accordance with the present invention, preferably has a thickness of from about 2 to about 5 mils. As also stated, the paper is available in specific gravities ranging from about 1, for calendered material, down to about 0.3 for uncalendered material. The preferred paper used in accordance with the present invention has a specific gravity of at least about 0.7. As an example of a high temperature resistant aromatic polyamide of which the fibers and fibrils in the paper may be composed is polymetaphenyleneisophthalamide, substantially in the beta form, as disclosed in U. S. Pat. No. 3,287,324.

As is apparent from what has been said above, the solvating liquid with which the paper is impregnated in accordance with the present invention, is one which is capable of solvating the aromatic polyamide of which the fibers and fibrils of the paper are composed. By solvating is meant the formation of a complex between one or more molecules of the liquid and aromatic polyamide molecules resulting in swelling of fibers and fibrils without dissolving or destroying them. Liquids like dimethylsulfoxide, N,N-dimethylformamide, N,N-dimethylacetamide and N-methyl-2-pyrrolidone, and combinations thereof, like a 2:1 (by volume) combination of N-methyl-2-pyrrolidone and N,N-dimethylacetamide, have been found suitable as solvating agents in accordance with the present invention. The foregoing solvating liquids are illustrative and do not represent an exhaustive study of all possible solvating liquids — although it can be stated that acetone, toluene, methyl ethyl ketone, methyl cellosolve, phenol, formamide, acetic acid, 72 Be' zinc chloride and 1-nitropropane have been found to be unsuitable — and hence reference herein to the stated solvating liquids will be understood to include equivalent materials. The solvating liquid may be, and in some cases preferably is diluted with an inert liquid diluent like toluene, acetone and methyl ethyl ketone. In such mixtures, however, the diluent is advantageously present in an amount no greater than about 65 percent, preferably no more than about 50 percent, by weight, of the mixture.

As stated, the paper will be impregnated with the solvating liquid, and this may be accomplished by immersing the paper in a body of the solvating liquid, by brushing, spraying or rolling the solvating liquid onto the paper, or the like. The purpose and effect of impregnation with the solvating liquid is simply to swell and crowd the fibers as stated, and thus removal of solvating liquid will be begun before deterioration of the paper's structure occurs as might happen, for example, should the paper remain immersed for extended periods of time in the solvating liquid.

In treating a single ply of the described paper in accordance with the present invention, the sheet is impregnated with the solvating liquid and then the solvating liquid is removed from the sheet as by evaporation. As stated, this in itself causes consolidation of the fibers in the paper. Further consolidation of the fibers, and enhanced further improvement in mechanical properties, is achieved by subjecting the paper to compression normal to its plane. This may be done after substantially all of the solvating agent has been removed. Preferably, however, this is accomplished while there is at least some solvating agent remaining in the paper, that is before substantially complete removal of the solvating agent. This means that at

least during the final stage of the removal of the solvating agent, for example when the content of solvating agent in the sheet is preferably no less than about 5 percent, and preferably no less than about 10 percent, by weight, of the sheet, the sheet is held under compression normal to its plane at least until the content of solvating agent has been reduced to the point where no further substantial shrinkage will occur under the existing conditions.

Compression may be accomplished in the case of an individual sheet, as illustrated schematically in FIG. 1, by pressing the sheet, 1, between platens 2 and 3. This may also be accomplished in the case of a single ply wound about a mandrel through shrinkage of the sheet itself in situ causing the sheet to assume a tight fit about the mandrel and, hence, providing the desired compressive forces. Of course, a combination of such means may be employed. In continuous running lengths of sheet material, belts, rolls or the like may be employed to provide the desired compression.

Evaporation of the solvating liquid can be aided by the use of heat, and suitable conditions, including temperature and pressure applicable to the treatment of a single ply, are set forth hereinafter in connection with the discussion concerning preparation of laminates.

In forming a laminate in accordance with the present invention, a plurality — that is, two or more — of plies of the paper, impregnated with the stated solvating liquid, is superposed in laminar relation. This mechanical step may be accomplished using any of the techniques common in laminating. For example, as shown in FIG. 2, individual impregnated sheets 11 may be stacked and pressed between platens 12 and 13. This could be done in a continuous manner as by passing sheets, from individual parent rolls, continuously through baths or coating rolls of solvating liquid and thereafter through the nip between the pressing rolls. Also, the laminate need not be flat as shown in FIG. 2, since platen 12 could represent, for example, a male mold member and platen 13 a female mold member.

FIG. 3 illustrates the fibrous nature of the plies of paper 11 in the final laminate of the invention, and, somewhat exaggerated, the mingling and intertwining of fibers from adjacent plies.

The formation of laminates in tubular form — having cross sections which are circular or elliptical, square, rectangular, or the like — is illustrated in FIGS. 4—7. In FIG. 4 a relatively long narrow sheet (tape) of impregnated paper 21 is wound in helical fashion about a mandrel 22. Enough tension is applied during winding to provide a snug fit between the paper and the mandrel and between the plies of paper built up by winding. Additional pressure may also be applied as by passing a roll, or rolls, the axis of which is parallel to that of mandrel 22, about the periphery of the tube. Following removal of the solvating liquid, the tubular laminate may be removed from the mandrel.

FIG. 5 illustrates essentially the same procedure as in FIG. 4 wherein, however, a relatively long sheet of the paper 31 is simply wrapped or wound around a mandrel 32. In this case, for purposes of illustration, the mandrel 32 selected has a square cross section. Otherwise, the procedure may be as in connection with that of FIG. 4. In accordance with one common method of making flat laminates, the laminate may be slit longitudinally, especially when mandrel 32 is substantially circular in cross section.

FIG. 6 illustrates an embodiment wherein the laminate 41 is formed about an electrical conductor 42 in a manner as discussed in connection with FIGS. 4 and 5. However, in this case the laminate 41 is to serve as an insulating jacket around conductor 42, and is, therefore, not removed therefrom. Otherwise, the electrical conductor 42 acts, in the formation of the laminate, as a mandrel.

FIG. 7 illustrates a modification of the embodiment shown in FIG. 6 wherein the laminate 51 serves as a tough outer insulating jacket there already being an insulating covering 53 on conductor 52. Insulating cover 53 may be, for example, the polyimide of pyromellitic dianhydride and 1,4-diamino

diphenyl ether; resin-bonded mica flakes; mica paper, and the like.

Although FIGS. 4-7 show laminates, it will be obvious from what has been said that similar procedures and structures would be applicable employing a single ply of the described paper instead of a laminate thereof.

Once the impregnated plies of paper have been superposed in laminar relation in the desired position and number of plies, the solvating liquid is removed by evaporation from the laminate. Evaporation of the solvating liquid, as will be apparent, will present no problem since the liquids are relatively volatile. Hence simple standing at room temperature will result eventually in substantially complete evaporation of the solvating liquid. Circulating dry — and preferably warm — air aids in evaporation, as does reduced pressure. Elevated temperatures hasten evaporation. Thus, in accordance with preferred practice, the impregnated laminate is heated to evaporate the solvating liquid at a rate no greater than that at which the vaporized solvating liquid can pass through the laminate to the surrounding atmosphere without disrupting the bonds between plies, such as blistering. Thus, the laminate may be heated to a temperature above room temperature and up to the boiling point of the solvating liquid until most of the solvating liquid has evaporated. Thereafter, the laminate may be, and preferably is, heated to a higher temperature, say from about 135° to about 290° C., depending, for example, upon the boiling point of the solvating liquid to remove remaining solvating liquid. Removal of the last trace of solvating liquid stabilizes the product.

Mechanical pressure (compression) is applied normal to the plane of the plies, either after substantially complete removal of the solvating liquid or, preferably as stated, at least during the final portion of evaporation. When the laminate is formed by wrapping the plies around a mandrel, including an electrical conductor, shrinkage of the laminate upon evaporation of the solvating liquid results in such pressure. Even in this embodiment additional or auxiliary mechanical pressure may be applied to remove air from between the plies and to press the plies into closer contact, as by the use of pressure rolls about the periphery. Flat laminates and laminates of other simple shapes can be pressed between platens as illustrated in FIG. 1. The amount of pressure may be dictated by the particular laminate structure and the properties desired therein, and pressures up to several thousand psi. might be used especially with material from which the solvating liquid has been substantially completely removed. The amount of pressure may also depend upon the amount of solvating liquid remaining in the material at the time pressure is applied. For example, when the material still contains no less than about 5 percent, by weight, of the solvating liquid, the pressure may be as low as about 100 p.s.i. whereas, higher pressures may be necessary when less solvating liquid is present.

Since removal of the solvating agent involves conversion of the agent to the gaseous state such gaseous agent must escape. Common expedients may be employed for this purpose, where necessary. For example in a press as shown in FIGS. 1 and 2, the faces of the platens may be provided with means to permit escape of any evaporating solvating agent. Such means include, for example, providing holes in the platens, providing platen faces with foraminous faces like screening or absorbent material, and the like. "Breathing," which involves releasing the pressure for a brief period or periods, may also be helpful.

The final, dry laminate is hard and tough, and may be subjected to mechanical shaping and finishing operations, such as sanding, grinding, sawing, drilling, stamping, punching, milling, swaging, turning on a lathe, and the like.

The following examples are given for the purpose of illustration and are not intended to limit the scope of the invention in any way.

## EXAMPLE 1

Three sheets of paper, composed of fibers and fibrils of an aromatic polyamide ("Nomex" high temperature resistant Nylon paper of E. I. du Pont de Nemours & Company, Inc.), 6 inches wide by 24 inches long by 3 mils thick are impregnated with a solvating liquid composed of six parts, by volume, of N-methyl-2-pyrrolidone, three parts of N,N-dimethylacetamide and four parts of toluene by brushing the liquid onto the surface of the paper sheet. The impregnated sheets are then wrapped around a ½ inch by ½ inch steel mandrel to form a tube 6 inches long and a square internal cross section one half inch by one half inch. During wrapping, additional solvating liquid is brushed onto the outer surface of each wrap of paper sheet. After the three sheets are so wrapped about the mandrel, the paper appears to be uniformly impregnated and the outer edges and sides are rounded to provide an outer elliptical cross section. After standing at room temperature for 2 hours, the wrapped paper has a uniform light, grayish-white color indicating that the solvating liquid has partially evaporated. The structure is then heated at 135° C. for about 10 hours and then at 180° C. for about 5 hours.

After the heat treatment, the tube has a substantially square outer cross section, the change from elliptical to square being due to the shrinkage of the paper during heating.

The tube is then sanded and removed from the mandrel.

From photomicrographs of a cross section of the tube it is impossible to distinguish the individual plies, but the fibrous structure of the paper is still evident.

## EXAMPLE 2

Four sheets of the polyamide paper used in example 1, 6 inches wide by 24 inches long by 3 mils thick, are brushed with the solvating liquid used in example 1 and wrapped around a cylindrical steel mandrel 2 3/16 inches in diameter. During wrapping, additional solvating liquid is brushed onto each ply as in example 1. The structure is then permitted to stand at room temperature for about 3 hours, then heated at 135° C. for about 10 hours, then at 180° C. for about 5 hours and finally at 200° C. for about 1 hour.

The resulting tube, upon grinding to a smooth finish and removal from the mandrel, is well laminated. During heating it has shrunk in length from 6 inches to 5-½ inches. The tube's wall thickness is 1/32 inches.

## EXAMPLE 3

In this example flat laminates, of two-, and three- and four plies, respectively, are prepared by brushing, onto sheets of the polyamide paper used in example 1, each sheet being 6 inches by 6 inches by 3 mils thick, a solvating liquid composed of 6 parts, by volume, of N-methyl-2-pyrrolidone, three parts of N,N-dimethylacetamide, four parts of toluene and thirteen parts of methyl ethyl ketone. The laminates are prepared by building up the stated number of plies, alternating machine and cross directions of the sheet. A glass rod is used to remove air and excess solvating liquid from the wet laminates and each laminate is air dried for 3 hours and then heated at 110° C. for 18 hours. Each laminate is then pressed between steel plates at about 170° C. and 1,100 p.s.i. for about 10 minutes. The press platens are cooled before removing the finished laminates.

The resulting two-ply laminate is somewhat translucent, has a slightly glossy surface and a mottled grayish-yellow color. It is 0.0059 inch thick.

The three-ply laminate has a higher resistance to tear than the two-ply laminate, and is 0.0089 inch thick.

The four-ply laminate is very tough and resilient and is 0.0118 inch thick.

These laminates can be used for chemical and electrical applications; for example, as battery separators.

EXAMPLE 4

This example illustrates the in situ preparation of a laminate as an insulator for electrical conductors.

A copper armature, 0.440 inch wide by 0.170 inch thick (with rounded corners), is spirally wound with an impregnated tape one half inch wide of the aromatic polyamide paper used in example 1. The thickness of the winding is three plies. The solvating liquid is composed of six parts, by volume, of N-methyl-2-pyrrolidone, three parts of N,N-dimethylacetamide and 4 parts of toluene. The swollen structure forms immediately after impregnating causing the paper in contact with the copper to bond thereto, and causing each ply of paper to bond to each other. The structure is then heated at 135° C. for about 8 hours. The resulting insulated coil can be bent and twisted without destroying the laminated insulation.

EXAMPLES 5—30

In these examples, two-ply laminates are prepared from 6 inches by 6 inches by 2 mils paper of the same type as used in example 1 using various solvating liquids as set forth in the following table. The bond between the plies in each laminate is noted and the dielectric strength is measured using a ¼ inch electrode. The laminates are prepared by dipping two sheets in each of the enumerated solvating liquids, removing excess liquid with scraper bars and laying one wet sheet over the other with nominal rolling to eliminate excess solvating liquid and air. Each wet laminate is then placed between two screens; the resulting sandwich is placed between two sheets of asbestos paper; the resulting structure is placed between two layers of paper padding; and this structure in turn is placed between two steel platens. Each laminate, in this arrangement, is then pressed at 350° F. for 15 minutes at a pressure of 250 p.s.i. and then at 1,000 p.s.i. for about an hour. After removal from the press, each laminate is heated for one hour at each of the following temperatures: 135° C., 165° C., 180° C., and 260° C. Each laminate is then pressed between steel platens at about 180° C. and at a pressure of about 1,800 p.s.i. for about 15 minutes. The results are tabulated below:

TABLE I

| Ex. | Solvating liquid   | Bond | Dielectric strength (volts/mil) |
|-----|--|------|---------------------------------|
| 5   | 6 pts./v. N-methylpyrrolidone                                    |      |                                 |
|     | 3 pts./v. dimethyl acetamide                                     |      |                                 |
|     | 4 pts./v. toluene  | Good | 1,541                           |
| 6   | 80 pts./w. Ex. 5 liquid plus 10 toluene                          | do.  | 1,455                           |
| 7   | 80 pts./w. Ex. 5 liquid plus 20 toluene                          | do.  | 1,409                           |
| 8   | 70 pts./w. Ex. 5 liquid plus 30 toluene                          | do.  | 1,378                           |
| 9   | 60 pts./w. Ex. 5 liquid plus 40 toluene                          | Fair | 1,442                           |
| 10  | 50 pts./w. Ex. 5 liquid plus 50 toluene                          | do.  | 1,232                           |
| 11  | 90 pts./w. Ex. 5 liquid plus 10 acetone                          | Good | 1,444                           |
| 12  | 80 pts./w. Ex. 5 liquid plus 20 acetone                          | do.  | 1,527                           |
| 13  | 70 pts./w. Ex. 5 liquid plus 30 acetone                          | do.  | 1,377                           |
| 14  | 60 pts./w. Ex. 5 liquid plus 40 acetone                          | Fair | 1,254                           |
| 15  | 50 pts./w. Ex. 5 liquid plus 50 acetone                          | do.  | 1,359                           |
| 16  | 90 pts./w. dimethyl sulfoxide plus 10 toluene                    | Good | 1,683                           |
| 17  | 70 pts./w. dimethyl sulfoxide plus 30 toluene                    | Fair | 1,043                           |
| 18  | 80 pts./w. dimethyl sulfoxide plus 20 acetone                    | Good | 1,052                           |
| 19  | 70 pts./w. dimethyl sulfoxide plus 30 acetone                    | Fair | 1,152                           |
| 20  | Dimethyl formamide   | Good | 1,595                           |
| 21  | 80 pts./w. dimethyl formamide plus 20 toluene                    | Fair | 1,403                           |
| 22  | 60 pts./w. dimethyl formamide plus 40 toluene                    | Good | 1,007                           |
| 23  | 50 pts./w. dimethyl sulfoxide plus 50 pts./w. dimethyl formamide | do.  | 1,303                           |
| 24  | N,N-dimethyl acetamide   | do.  | 1,142                           |
| 25  | N-methyl-2-pyrrolidone   | do.  | 1,513                           |
| 26  | 80 pts./w. N-methyl-2-pyrrolidone plus 20 acetone                | do.  | 1,340                           |
| 27  | 70 pts./w. N-methyl-2-pyrrolidone plus 30 acetone                | do.  | 1,379                           |
| 28  | 60 pts./w. N-methyl-2-pyrrolidone plus 40 acetone                | do.  | 1,211                           |
| 29  | 80 pts./w. N-methyl-2-pyrrolidone plus 20 toluene                | do.  | 1,162                           |
| 30  | 60 pts./w. N-methyl-2-pyrrolidone plus 40 toluene                | do.  | 1,126                           |

\*Undue delay in removing solvating liquid, resulting in some deterioration of structure in Example 20.

NOTE.—The untreated polyamide paper used in these examples has a dielectric strength of about 650 volts/mil.

EXAMPLES 31 AND 32

Two sets of laminates are prepared by the procedure used in examples 5—30, using sheets of the polyamide paper 9 inches by 9 inches. In one set of laminates, 20 sheets of polyamide paper, each 2 mils thick, are laminated to provide a laminate one thirty-secondths inch thick (example 31) and in the other set of laminates 25 sheets of the polyamide paper, each 3 mils thick, are laminated to provide a laminate one sixteenth inch thick (example 32). The sheets are all laid in the same relation with respect to machine direction ("MD") and cross machine direction ("CD").

Various physical and electrical properties are measured for each set, and these are tabulated below:

TABLE II

| Property  | Example 31            | Example 32            |
|---|-----------------------|-----------------------|
| Flexural strength, ASTM D-790, cond. A, p.s.i.:               |                       |                       |
| MD-1  | 25,300                | 25,400                |
| MD-2  | 25,900                | 23,600                |
| Average   | 25,600                | 24,500                |
| CD-1  | 19,100                | 20,500                |
| CD-2  | 19,700                | 20,800                |
| Average   | 19,400                | 20,650                |
| Modulus in flexure, ASTM D-790, cond. A:                      |                       |                       |
| MD-1  | 0.735×10 <sup>6</sup> | 1.00×10 <sup>6</sup>  |
| MD-2  | 0.665×10 <sup>6</sup> | 0.869×10 <sup>6</sup> |
| Average   | 0.700×10 <sup>6</sup> | 0.935×10 <sup>6</sup> |
| CD-1  | 0.555×10 <sup>6</sup> | 0.781×10 <sup>6</sup> |
| CD-2  | 0.589×10 <sup>6</sup> | 0.806×10 <sup>6</sup> |
| Average   | 0.572×10 <sup>6</sup> | 0.794×10 <sup>6</sup> |
|   | Example 35            | Example 36            |
| Impact edge, Izod, E-48/50 ASTM D-229, ft. lb./inch of notch: |                       |                       |
| MD-1  |                       | 10.50                 |
| MD-2  |                       | 6.82                  |
| Average   |                       | 8.66                  |
| CD-1  |                       | 7.28                  |
| CD-2  |                       | 7.28                  |
| Average   |                       | 7.28                  |
| Are resistance, sec. ASTM D-495                               | 12.3                  | 14.5                  |
| Dielectric strength, v./mil, ASTM D-149 (2" Electrode in Oil) | 1,050                 | 1,165                 |
|   | 1,300                 |                       |
| Average   | 1,172                 |                       |
| Density, g./cm. <sup>3</sup>                                  | 1.298                 | 1.315                 |
| Rockwell hardness "M"   | 65-73                 | 89                    |
| Dissipation factor, 10 <sup>6</sup> c.p.s., ASTM D-150        | 0.0219                | 0.024                 |
| Dielectric constant, 10 <sup>6</sup> c.p.s., ASTM D-150       | 4.83                  | 4.30                  |
| Dissipation factor 60 c.p.s., ASTM D-150                      | 0.015                 | 0.019                 |
| Dielectric constant, 60 c.p.s., ASTM D-150                    | 5.92                  | 5.24                  |
| Insulation resistance, C96/35/90, megohms                     | 8.5×10 <sup>6</sup>   | 1.5×10 <sup>7</sup>   |
| Water absorption, 24 hours, percent.                          | 0.828                 | 0.492                 |
| Abrasion resistance, mg./1,000 cycles Taber <sup>1</sup>      |                       | 0.3403                |

<sup>1</sup> Taber=Full vacuum 1,000 gm. weights—1,000 cycles, H 18 wheels.

EXAMPLE 33

A 5 mil thick mica sheet, prepared from no. 5 mica splittings and a silicone resin binder, is bonded, by heating, to one side of a 1—2 mil glass fiber cloth. This composite sheet is then wrapped around a copper bar, with the cloth next to the bar, and heated to 150°—175° C. Upon cooling, three plies of polyamide paper as used in example 1, but 2 mils thick and impregnated with the solvating liquid used in example 1, are wrapped around the covered bar. The composite is then heated as in example 1. The treated paper covering forms a tight insulating jacket having high mechanical and wear resistant properties.

The same procedure may be followed but using a single ply of polyamide paper providing, however, a thinner outer jacket.

## EXAMPLE 34

The procedure of example 33 is followed except that the copper bar is first covered with a mica paper formed from mica splittings and polyester fibers bonded with silicone resin instead of the mica sheet — glass fabric laminate used in example 33.

## EXAMPLE 35

The procedure of example 33 is followed except that the initial covering on the copper bar is two plies of a ¼ mil film of the polyimide of pyromellitic dianhydride and 1,4-diamino diphenyl ether instead of the mica sheet — glass fabric laminate as used in example 33.

## EXAMPLES 36 - 37

This example illustrates the improvement even in a single ply of the polyamide paper treated in accordance with the present invention.

Single 9 inches by 12 inches sheets of calendered polyamide paper of the type used in example 1 but varying in thickness; namely, 7 mils and 10 mils, respectively, are dipped in a bath of the solvating liquid used in example 1 until saturated. Upon removal from the bath and air drying, they are heated in an oven at 135° C. for 13 minutes and then heated in a press at about 180° C. at 333 p.s.i. for 15 minutes. The tensile strength, dielectric strength (using a ¼ inch electrode) and density of each treated sheet is determined and compared with those values for the untreated sheet.

|                | Thick-ness (mil) | Tensile strength (p.s.i.) |        | Dielectric strength (volts/mil) | Density (g./cc.) |
|----------------|------------------|---------------------------|--------|---------------------------------|------------------|
|                |                  | MD                        | CD     |                                 |                  |
| Example 36:    |                  |                           |        |                                 |                  |
| Untreated..... | 7                | 17,300                    | 9,695  | 944                             | 0.981            |
| Treated.....   | 7                | 20,050                    | 11,770 | 1,323                           | 1.153            |
| Example 37:    |                  |                           |        |                                 |                  |
| Untreated..... | 10               | 14,600                    | 9,450  | 707                             | 1.001            |
| Treated.....   | 10               | 21,100                    | 12,450 | 1,041                           | 1.162            |

## EXAMPLE 38

This example further illustrates the improvement in a single ply of the polyamide paper treated in accordance with the present invention. In this example, the solvating liquid has been substantially completely removed before pressing.

A 2-½ inch by 6 inch sheet of aromatic polyamide paper of the type used in example 1 (0.00235 inch thick) is passed through a bath of solvating liquid as used in example 1. Excess liquid is removed from the sheet with a glass rod and the impregnated paper is air dried for 3 hours, heated at 135° C. for 2 hours and then heated at 155° C. for 5 hours. The resulting dry sheet shows evidence of shrinkage and cockling. The sheet is then passed three times through calender rolls heated to about 330° F., the pressure being increased after each pass.

The resulting product has a light yellowish color, is translucent and has a glossy surface. The comparative data are as follows:

Initial thickness—0.00235 inch average.

Final thickness—0.00208 inch average.

Decrease in thickness—11.5%.

Dielectric strength ¼ inch electrode (volts per mil):

  Before treatment—about 650.

  After treatment—1884 average.

Modification is possible in the selection of solvating liquid and in the techniques and procedural details without departing from the scope of the present invention.

I claim:

1. The method of improving electrical insulating properties of an interfelted paper web consisting essentially of high temperature resistant aromatic polyamide fibers and fibrils which comprises impregnating said paper with at least one solvating liquid for such fibers and fibrils selected from the group consisting of dimethylsulfoxide, N,N-dimethylformamide, N,N-

dimethylacetamide and N-methyl-2-pyrrolidone, evaporating said solvating liquid from said paper and subjecting said paper to compression normal to its plane.

2. The method of claim 1 wherein said paper is heated to aid in the evaporation of said solvating liquid.

3. The method of claim 1 wherein said solvating liquid has mixed therewith an inert liquid diluent in an amount no more than about 65 percent, by weight, of the mixture.

4. The method of claim 3 wherein said inert liquid diluent is in an amount no more than about 50 percent, by weight, of the mixture.

5. The method of claim 3 wherein said inert liquid diluent is at least one of those selected from the group consisting of toluene, acetone and methyl ethyl ketone.

6. The method of improving electrical insulating properties of an interfelted paper web consisting essentially of high temperature resistant aromatic polyamide fibers and fibrils which comprises impregnating said paper with at least one solvating liquid for such fibers and fibrils selected from the group consisting of dimethylsulfoxide, N,N-dimethylformamide, N,N-dimethylacetamide and N-methyl-2-pyrrolidone, and thereafter evaporating said solvating liquid from said paper, at least the final portion of said evaporation being conducted while said paper is held under compression normal to its plane.

7. The method of claim 6 wherein said paper is heated to aid in the evaporation of said solvating liquid.

8. The method of claim 6 wherein said paper is wrapped about a mandrel during evaporation of said solvating liquid.

9. The method of claim 8 wherein the mandrel comprises an electrical conductor.

10. The method of claim 9 wherein said electrical conductor has a covering of electrical insulation thereon.

11. The method of claim 6 wherein said solvating liquid has mixed therewith an inert liquid diluent in an amount no more than about 65 percent, by weight, of the mixture.

12. The method of claim 11 wherein said inert liquid diluent is in an amount no more than about 50 percent, by weight, of the mixture.

13. The method of claim 11 wherein said inert liquid diluent is at least one of those selected from the group consisting of toluene, acetone and methyl ethyl ketone.

14. The method of making a laminated structure of interfelted paper consisting essentially of high temperature resistant aromatic polyamide fibers and fibrils which comprises superposing, in laminar relation, a plurality of plies of such paper, said plies being impregnated with at least one solvating liquid for such fibers and fibrils selected from the group consisting of dimethylsulfoxide, N,N-dimethylformamide, N,N-dimethylacetamide and N-methyl-2-pyrrolidone, evaporating said solvating liquid from said plies while in said superposed laminar relation and subjecting said plies to compression normal to their plane.

15. The method of claim 14 wherein said plies represent individual sheets of said paper which are arranged in a stack.

16. The method of claim 14 wherein the plies are heated to aid in the evaporation of said solvating liquid.

17. The method of claim 14 wherein said solvating liquid has mixed therewith an inert liquid diluent in an amount no more than 65 percent, by weight, of the mixture.

18. The method of claim 17 wherein said inert liquid diluent is in an amount no more than about 50 percent, by weight, of the mixture.

19. The method of claim 17 wherein said inert liquid diluent is at least one of those selected from the group consisting of toluene, acetone and methyl ethyl ketone.

20. The method of making a laminated structure of interfelted paper consisting essentially of high temperature resistant aromatic polyamide fibers and fibrils which comprises superposing, in laminar relation, a plurality of plies of such paper, said plies being impregnated with at least one solvating liquid for such fibers and fibrils selected from the group consisting of dimethylsulfoxide, N,N-dimethylformamide, N,N-

dimethylacetamide and N-methyl-2-pyrrolidone and thereafter evaporating said solvating liquid from said plies while in said superposed laminar relation, at least the final portion of said evaporation being conducted while said plies are held under compression normal to the plane thereof.

21. The method of claim 20 wherein said plies represent individual sheets of said paper which are arranged in a stack; and wherein said stack is pressed during at least said final portion of said evaporation.

22. The method of claim 20 wherein said plies are provided by wrapping said paper about a mandrel.

23. The method of claim 22 wherein said paper is wrapped helically about said mandrel.

24. The method of claim 22 wherein the laminate, after evaporation of said solvating liquid, is removed from said mandrel to provide the laminate in tubular form.

25. The method of claim 22 wherein said mandrel comprises an electrical conductor.

26. The method of claim 25 wherein said electrical conductor has a covering of electrical insulation thereon.

27. The method of claim 20 wherein said co solvating liquid has mixed therewith an inert liquid diluent in an amount no more than 65 percent, by weight, of the mixture.

28. The method of claim 27 wherein said inert liquid diluent is in an amount no more than about 50 percent, by weight, of the mixture.

29. The method of claim 27 wherein said inert liquid diluent is at least one of those selected from the group consisting of toluene, acetone and methyl ethyl ketone.

30. A paper product provided by the method of claim 1.

31. A laminate provided by the method of claim 14.

32. A tubular laminate provided by the method of claim 24.

33. A laminate-covered electrical conductor provided by the method of claim 25.

34. A laminate-covered electrical conductor provided by the method of claim 26.

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