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WATER-RESISTANT INDURATED FIBER AND METHOD OF MAKING THE SAME

Duncalf W. Hollingworth, Newark, Del., assignor to Continental-Diamond Fibre Company, Newark, Del., a corporation of Delaware

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The present invention relates to a water-resistant indurated fiber and to the method of making the same, and more particularly it relates to an improved indurated fiber which possesses very low water-absorptive qualities and at the same time is characterized by the mechanical and electrical properties which render such products of value in the industries.

The principal object of the present invention is to provide an indurated fiber product of remarkable resistance to water, in contradistinction to the previously manufactured indurated fiber products known as vulcanized fiber whose application in the industries is limited by the absence of said property.

Another object of the present invention is to furnish an indurated fiber which, with respect to its mechanical and electrical properties, is comparable to products of this type previously manufactured, but which is water-resistant, and, therefore, may be employed in the field of electrical insulation under high humidities, a field not open previously to products of this class.

Still another object of the present invention is to provide processes by which indurated fiber of the desired characteristics may be economically manufactured.

Other objects will be apparent from a consideration of the specification and claims.

Heretofore vulcanized or indurated fiber has been manufactured from various types of cellulose, such as alpha cellulose or cotton ray paper by treatment of the sheets with suitable hydrolyzing agents such as zinc chloride, aluminum chloride, sulphuric acid, phosphoric acid, mixtures of sulphuric and phosphoric acid, and mixtures of sulphuric acid, phosphoric acid, and acetic acid, the last named agent being described in Patent No. 1,894,907, dated January 17, 1933. The partially hydrolyzed sheets are superposed one above the other to obtain the desired thickness of the product, and are then subjected to a washing process known as "puring" which removes the chemicals therefrom. After puring, the sheets are dried by subjecting the fiber product to heat, after which various finishing operations are carried out, such as rolling, calendering, pressing and the like.

The vulcanized fiber products are characterized by high strength, especially impact, good dielectric qualities when dry, extreme toughness, easy machinability, and ability to flow or be formed under heat when wet. Due to these properties, vulcanized fiber has been largely manufactured and used in this country. In addition to these properties, indurated fiber manufactured in accordance with Patent No. 1,894,907 has the ability of flowing or being formed when dry. Attempts have been made to reduce the water-absorption of vulcanized fiber, but these have not been successful due to the nature of the materials sought to be incorporated in the vulcanized fiber. Certain of these materials failed to penetrate the fibers, while others placed a coating on the fibers, preventing proper gelatinization by the hydrolyzing agent. The highly water-absorptive character of the vulcanized fiber has prevented its acceptance by the Underwriters Laboratories, due to the fact that its value as a dielectric material is destroyed for all practical purposes under high humidities.

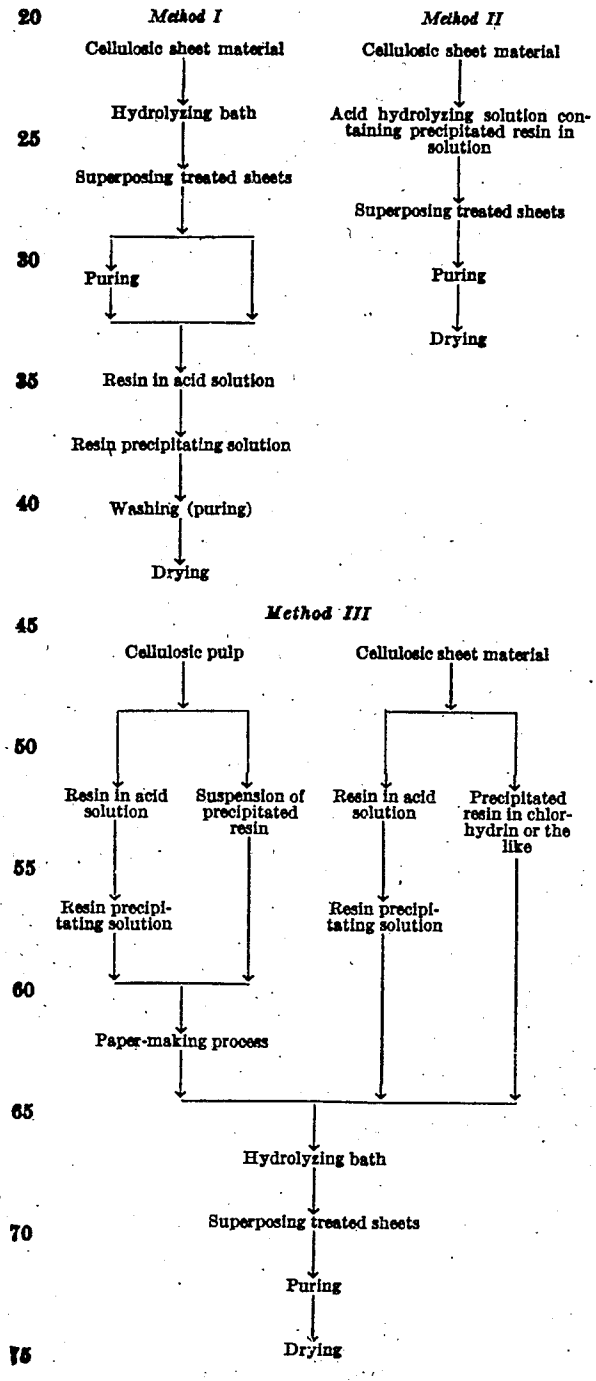
The indurated fiber of the present invention is characterized by a surprising resistance to water and is, therefore, applicable as an insulation material even under high humidities. The product of the present invention is in addition comparable in all respects with the desirable mechanical and electrical properties found in the vulcanized fiber products usually manufactured.

The product of the present invention is an indurated fiber characterized by low water-absorption comprising a plurality of sheets of partially hydrolyzed cellulose joined together and containing a primary aromatic amine-formaldehyde resin, preferably an infusible, insoluble, thermoplastic aniline-formaldehyde resin within its pores and upon its surfaces associated with said partially hydrolyzed cellulose. The product depending upon its method of manufacture may have the resin homogeneously distributed throughout the sheets of partially hydrolyzed cellulose, or it may have greater amounts of resin at the surfaces of the product than is present in the interior thereof. In fact in some instances, at the center of the product there may be practically no resin associated with the partially hydrolyzed cellulose.

The process of the present invention comprises broadly the association of a primary aromatic amine-formaldehyde resin, preferably an infusible, insoluble, thermoplastic aniline-formaldehyde resin with cellulosic material in a process which in general comprises the steps of subjecting cellulosic sheet material to the action of a hydrolyzing agent to hydrolyze the sheets partially, superposing a plurality of said treated sheets one above the other, puring, and drying said superposed material. The association of the resin with the cellulosic material may take place either during or after the fabrication of the sheet material, or before, with, or after the partial hydrolyzing step; as will hereinafter fully appear. The process regardless of the order of the specific steps employed will result in an indurated fiber product characterized by low water-absorption in which the plurality of sheets of partially hydrolyzed cellulose are joined together, and in which a primary aromatic amine-formaldehyde resin is associated with the partially hydrolyzed

cellulose. The joining of the partially hydrolyzed superposed sheets of the present invention is brought about primarily by the action of the hydrolyzed cellulose, although in some instances the binding action of the resin will be found to cooperate with the binding action of the hydrolyzed cellulose. The various processes of the present invention are herein grouped into three general methods designated as Methods I, II and III.

Method I is characterized by associating the resin with the cellulose sheets after the hydrolyzing step; Method II by associating the resin with the acid hydrolyzing agent during the hydrolyzing step; and Method III by the association of the resin with the cellulosic material prior to the hydrolyzing step, as is to be seen from the following charts:



The cellulosic sheet material applicable for use in the present invention includes any highly absorbent hydrolyzable paper, such as unsized paper made from sulphite, sulphate (kraft), soda and cotton rag stock. Cotton rag and alpha cellulose paper are particularly advantageous in the process, due to their absorptive powers and the ease with which they are hydrolyzed.

The hydrolyzing or vulcanizing agent employed in the processes may be any compound or mixture of compounds capable of hydrolyzing cellulose, such as the usual acids or salt solutions in suitable concentrations now utilized in the manufacture of indurated fiber products; for example, zinc chloride, aluminum chloride, sulphuric acid, phosphoric acid or mixtures of sulphuric and phosphoric acid, or mixtures of sulphuric, phosphoric, and acetic acids.

The resins utilizable in conjunction with the present invention are that group of resins which result from the condensation of a primary aromatic amine and a formaldehyde yielding compound in the presence of an acid. The term "primary aromatic amine" as employed herein includes not only true primary aromatic amines, such as aniline and its homologues, but also such derivatives thereof which under the conditions of condensation react in the same manner as the primary aromatic amines to yield the same resins, for example, anhydroformaldehyde-aniline, formyl-aniline or the homologues of these compounds. The expression "formaldehyde-yielding compound" includes not only formaldehyde, but also its polymers and those analogous compounds which under the conditions of condensation split off formaldehyde and react in the same manner to yield the same resins. Preferably, the resin employed results from the condensation of aniline and formaldehyde in the presence of hydrochloric acid as the condensing agent. In place of hydrochloric acid, sulphuric acid, nitric acid, acetic acid and other strong mineral and organic acids capable of forming salts with the primary aromatic amine may be used. The amount of acid employed in the formation of the infusible but thermoplastic resins is usually approximately equivalent molecularly to the primary aromatic amine so that there is formed in the solution, the salt of the amine or the salt of the resin after the reaction of the amine with the formaldehyde. Acid in excess of this amount is not objectionable. In most cases, it will be desirable to add the acid to the amine prior to the addition of the formaldehyde-yielding compound. Instead of adding the acid separately as the condensing agent, the respective amine salts may be employed, adding if desired an excess of free acid.

After the condensation in the acid solution, the resin is precipitated from the solution by the elimination of the effect of the acid which may be accompiished by the addition of a suitable agent, such as inorganic or organic bases or salts or by extreme dilution which is applicable when an organic acid is used as a condensing agent. An inorganic basic substance, particularly caustic soda, has been found to be especially applicable, although alkaline earth bases, such as calcium hydroxide, may be used with equal facility. The term "primary aromatic amine-formaldehyde resin" is employed to designate the class of resins made by reacting a primary aromatic amine and a formaldehyde-yielding compound in an acid solution with the subsequent elimination of the effect of the acid.

As has previously been determined, the reaction products of primary aromatic amines and formaldehyde-yielding compounds obtained in acid solution may be either fusible or infusible, depending upon the ratio of the formaldehyde-yielding compound to the amine. If the ratio of formaldehyde-yielding compound to the amine is one to one or less than one to one, the resulting resin is fusible. On the other hand, if the ratio of formaldehyde-yielding compound to amine is even slightly greater than one to one, then a resin is obtained which is designated as an infusible, insoluble, thermoplastic resin. The fusible precipitated resins first obtained may be converted into infusible resins by reaction, at any stage, with further amounts of an aldehydic compound, or a compound having available aldehyde groups under the conditions of reaction, such as formaldehyde, paraformaldehyde, hexamethylenetetramine, or any of the potentially reactive aldehyde resins, such as the phenol-aldehyde, urea-aldehyde or thiourea-aldehyde resins. In the process of the present invention, either the fusible or the infusible resin may be employed, but for most purposes a final product is desired in which the resin is infusible. Accordingly, in the preferred instance, 1 mol. of aniline is reacted in the presence of an equimolecular proportion of acid in solution with more than 1 mol. of formaldehyde. The temperature at which the infusible resins become thermoplastic increases as the formaldehyde content of the resin increases, and, therefore, there is an upper limit as to the amount of the formaldehyde-yielding compound condensed with the amine which is usually not exceeded, since in the process of the present invention it is advisable to employ a resin which flows at the temperatures used in heating the partially hydrolyzed cellulosic sheets. This temperature obviously must be below that at which damage to the fibers occurs. It has been determined that if a resin is produced by combining 1.05 mols of formaldehyde with 1 mol. of aniline in the presence of an equimolecular proportion of hydrochloric acid with respect to the amine, the softening point of the infusible thermoplastic resin will be in the neighborhood of 200° F. With 1.15 mols of formaldehyde in the above reaction, the softening point is approximately 250° F.; while with 1.3 mols and 1.4 mols of formaldehyde the softening points are approximately 300° F. and 360° F. respectively. From these figures, it will be seen that the formaldehyde content is not usually carried beyond 1.4 to 1.5 mols of formaldehyde to 1 mol. of aniline. When fusible resins are used in the process of the present invention, it is usually desirable to employ the formaldehyde-yielding compound in a ratio of from .8 mol. to 1 mol. of the compound to 1 mol. of the primary aromatic amine. If the fusible resin is employed for impregnation purposes and the infusible but thermoplastic resin is desired in the final product the hydrolyzed cellulosic material containing the resins may be treated with the aldehydic compound, for example, by immersion in a suitable solution, before the final drying and pressing steps.

As will be seen from the charts, the steps involving the precipitation of the resin from acid solution by the elimination of the effect of the acid may be an integral step in the process of the present invention, or in certain instances the precipitated resin will be used either in the form of a suspension or in solution. While the primary aromatic amine-formaldehyde resins when more than one mol. of formaldehyde is reacted with 1 mol. of the primary aromatic amine are termed insoluble and are in fact insoluble in all the usual organic solvents, they may be dissolved in certain unusual solvents of the chlorhydrin type, for example, ethylenechlorhydrin, glycolchlorhydrin and glyceroldichlorhydrin. When the solution of the precipitated resin is employed with a chlorhydrin solvent, the solvent is evaporated after treatment of the cellulosic treatment with the solution, leaving a resin-impregnated cellulosic material for use in subsequent steps in the process.

Method I

When the process of the present invention is carried out in accordance with Method I, the cellulosic sheet material is first subjected to the hydrolyzing bath to hydrolyze the cellulosic sheet material partially, and thereafter the sheets are superposed one above the other to obtain the thickness desired in either the form of flat stock or tubes, as is the usual practice in the manufacture of vulcanized fiber. Preferably the superposed sheets are then pured in order that the hydrolyzing agent may be recovered economically unaccompanied by impurities. The puring step is particularly advantageously carried out at this point if zinc chloride or equivalent salt is used as the hydrolyzing agent, due to the tendency of the resin to become insoluble therein. However, if desired, treatment with the resin in acid solution may immediately follow the step of superposing the partially hydrolyzed sheets, particularly if an acid hydrolyzing agent is employed. The superposed stock is immersed in the acid solution of the resin for a sufficient time to allow the solution to be absorbed by the sheets. This will depend upon the thickness of the superposed stock and the amount of resin which it is desired to have associated with the sheets. In general, the acid solution will not contain more than 18.5% resin figured as the precipitated resin, since above this percentage difficulties may be encountered in the preparation of the resin solution, or in impregnation. The amount of resin in the solution may vary from this figure downwards, as desired, but usually it will not go below 10%, since the use of more dilute solutions are uneconomical. In the preparation of the acid solution, the aniline is preferably suspended in water and hydrochloric acid is added until a solution which is neutral to Congo paper is obtained. Formaldehyde in solution is then added in the desired molecular amounts with respect to the aniline to give the resin desired. The solution at the time of the hydrochloric acid is preferably in the vicinity of room temperature, since during the reaction heat is generated, raising the temperature of the solution to some extent, for example, to 60° C. The temperature of the solution may rise higher than this without deleterious results, but sufficient water is employed so that the temperature does not approach the boiling point. The superposed sheets are immersed in the acid solution of the resin until the desired impregnation of the stock by the resin is obtained. This may be determined by the yellow coloration which is found where the solution has impregnated stock. In order to get complete penetration, the time of immersion depends upon the thickness of the stock, for example, in case of approximately $\frac{1}{16}$ to $\frac{3}{8}$ inch stock, whether the stock be in the form of tubes or flat stock, the time of immersion may be from forty-eight

hours to seventy-two hours. In a specific case, a tube whose wall thickness is approximately $\frac{5}{16}$ of an inch is completely impregnated when immersed in the resin solution for sixty-four hours. In the case of one inch stock, the time of immersion may be from one week to ten days.

When sufficient penetration by the acid solution has been obtained, the stock is immersed in a resin precipitating solution, for example, a solution containing 3% of caustic soda, until the caustic soda has impregnated the stock to the depth previously penetrated by the resin in acid solution and has caused the resin to become precipitated. A visual examination of the stock will determine when the resin is precipitated, since the stock containing the precipitated resin is characterized by the whiteness of the precipitate in contradistinction to the yellow coloration of the resin in acid solution. The time of immersion in the resin precipitating solution varies with the thickness of the stock and the depth of penetration of the acid solution of the resin. Usually the immersion in caustic soda is longer than the immersion in the acid solution, due to the fact that the resin first precipitates near the surface of the stock and tends to block the spaces, so that the rate of absorption by the resin precipitating solution is increasingly reduced as it proceeds inwardly. In the case, for example, of a tube with a wall thickness of approximately $\frac{5}{16}$ of an inch which is immersed in the acid solution of the resin for sixty-four hours, it may be necessary to immerse the tube in the resin precipitating solution for approximately one hundred hours in order that the resin may be completely precipitated. At times it may be necessary to treat the stock in the resin precipitating solution for a period of time twice as long or even longer, than the time of immersion in the acid solution of the resin.

After the resin has been precipitated in the stock, it is washed free from electrolytes and is dried under normal drying conditions employed in the manufacture of vulcanized fiber of the same thickness, the greater the thickness the longer will be the drying time required. For example, in the case of $\frac{1}{16}$ inch stock, the drying usually requires about twenty-four hours at 120° F. to 140° F., while with $\frac{5}{16}$ inch stock forty-eight hours within this temperature range may be required. After the drying of the stock, it is subjected to such operations as calendering and pressing as may be desired, and thereafter it is preferably subjected to a heat and pressure treatment sufficient to cause the resin to be thermoplastic and to flow around the fibers of the cellulosic sheet material and cloak them.

In the case of sheet stock, after drying, the sheets may be pressed by subjecting them in a hot press, for example, to a temperature of about 340° F. and a pressure of about 100 pounds per square inch for about ten minutes. The stock may then be cooled and calendered which smooths the surfaces and presents them with a suitable finish. In the case of tubes, the dried tubes preferably containing about 3% of moisture may be rolled under pressure with or without heat to consolidate the tubes. This rolling under pressure in the case of tubes presents to them the desired finish. The final heat and pressure treatment may be brought about in an oven, in an oil bath, or in a press. In the case of tubes, for example, they may be heated from one-half to four hours, generally in the neighborhood of two hours, at temperatures of 270° F. to 300° F. in an oven or in an oil bath. In the case of sheets, the treatment under pressure is preferred in order to prevent warpage thereof. It will be understood that the factors of temperature, pressure and time may vary widely and are dependent one on the other and upon the thickness of the sheet stock or tube being treated, for example, the pressure used may even be as high as 2100 pounds per square inch. It will be obvious that if desired the pressing step may be combined with the final heat treatment step.

The resin content of the finally fabricated sheets depends in general upon the time of immersion of the sheets in the acid solution of the resin for any particular thickness of stock, and may vary from a relatively small percentage up to 20% resin content, or even higher. When the water-resistant indurated fiber is made in accordance with Method I, usually a larger resin content is found at the surface of the stock than is encountered in the interior thereof, due to the fact that the rate of absorption of the resin in acid solution is progressively slowed up as it proceeds inwardly. The resistivity of the product of this method toward water, therefore, depends on the relationship of the thickness to the resin content, that is to say, the thicker the product, the lower the resin content can be. With relatively heavy stock, a resin content of 5.0% will be found to be adequate; while with a very thin stock, it may be desirable to have a resin content of 20% or more.

Tubes

Dimensions	Type of resin	Water-absorption in 24 hours	Water absorption of corresponding untreated stock
		Percent	*Percent*
5/16" inside diameter by 1/2" outside diameter.	1 mol. of aniline to 1.3 mols of formaldehyde.	4.5	40
1/4" inside diameter by 3/8" outside diameter	1 mol. of aniline to 1.05 mols of formaldehyde	10.8	41
2 1/32" inside diameter by 1" outside diameter	1 mol. of aniline to 1.3 mols of formaldehyde	6.5	40
5/16" inside diameter by 1/2" outside diameter	1 mol. of aniline to 1.05 mols of formaldehyde	8.3	40
1/4" inside diameter by 3/8" outside diameter	1 mol. of aniline to 1.05 mols of formaldehyde	9.8	41
5/16" inside diameter by 1/2" outside diameter	1 mol. of aniline to 1.05 mols of formaldehyde	7.7	40

Sheet stocks

Thickness	Water absorption of product of present invention in 24 hrs.	Water absorption of corresponding untreated stock in 24 hrs.
	Percent	*Percent*
1/16"	17	59
1/8"	15	46
3/16"	12	36
1/4"	8	24
5/8"	5	15

It will thus be seen that the product is resistant to water and that by the process of the present invention a product is provided in which the water absorption is very materially lower than the water absorption of the untreated product. In fact, the water absorption encountered in the untreated product renders it unavailable for electrical uses under high humidity. In the product

of the present invention, however, the water absorption is sufficiently low so that no difficulties whatever are encountered in such use of the product. The product furthermore is mechanically and electrically comparable to vulcanized fiber and may, therefore, be used in all applications in the industry where that product is now employed.

Example 1

An acid solution of the resin is prepared by suspending aniline in water and adding hydrochloric acid thereto in amounts sufficient to render the solution neutral to Congo paper. Formaldehyde in solution is then added in sufficient amounts so that the formaldehyde content is equivalent to 1.3 mols of formaldehyde to 1 mol. of aniline. For example, 652 litres of a solution containing aniline hydrochloride in an amount which figured as aniline contains 28.56% thereof is made up to 1,000 litres. Formaldehyde of 38.6% strength is added to the solution in an amount equal to 202 litres. The temperature of the aniline hydrochloride solution made up to 1,000 litres is 25° C., but at the end of the reaction with the formaldehyde, the temperature is increased to 61° C. After the reaction, the solution contains 16.7% resin by weight figured as precipitated resin. Wet pured vulcanized fiber ⅛ inch in thickness is immersed in the resin solution for seventy-two hours. The fiber is then immersed in a caustic soda solution, preferably of 3% strength, until the caustic soda has precipitated the resin in the pores of the fiber, for example, the time of immersion may be from seventy-two to ninety-six hours. The stock is then washed free from electrolytes and is dried for about twenty-four hours at 120° F. to 140° F. After drying, the sheets are pressed flat in a hot press for about two minutes at 340° F. and 100 pounds per square inch. The sheets are then cooled and calendered, which smooths the surface giving them the desired finish. The sheets are then subjected to a heat and pressure treatment sufficient to cause the resin to become thermoplastic, for example, ten minutes with a line pressure of 100 pounds per square inch and a temperature of 325° F. to 340° F.

Example 2

An aqueous acid solution of the resin is prepared by reacting 1 mol. of aniline with 1.05 mols of formaldehyde in the presence of sufficient hydrochloric acid to form aniline hydrochloride. The dilution is adjusted so that it contains approximately 13.5% of resin by weight. The wet pured gray fiber tubing with an inside diameter of ⅜ inch and an outside diameter of $\frac{13}{32}$ inch is immersed in the solution for sixty-four hours. The tubes are then removed and placed in a 3% caustic soda solution for one hundred hours. The tubes are then washed free from soluble salts and dried for forty-eight hours at approximately 120° F. and are then rolled with a moisture content of 3%. The tubes after this process have an inside diameter of $\frac{5}{16}$ inch and an outside diameter of ½ inch. The tubes are then placed in an oven at 290° F. for two hours. After this treatment, a water absorption test in which the tubes are immersed for twenty-four hours in water at room temperature shows that the water absorption is only 7.7%. With tubes similarly treated whose final dimensions are ¼ inch inside diameter and ⅜ inch outside diameter, the water absorption in twenty-four hours is 9.8%.

Method II

When the process of the present invention is carried out in accordance with Method I, the cellulosic sheet material to be hydrolyzed partially is immersed in the acid hydrolyzing solution containing the precipitated primary aromatic amine-formaldehyde resin in solution. After the sheets have been partially hydrolyzed in the presence of the resin, the sheets are superposed to obtain the desired thickness and the superposed material either in the form of flat sheet stock or tubes is then pured and thereafter dried. Subsequent to the drying, the superposed sheets are subjected to rolling, calendering or pressing operations such as were described in conjunction with Method I. Preferably, also as in Method I, the material is subjected to a heat treatment with or without pressure which causes the resin to become thermoplastic and to flow around the fibers.

While any of the acid hydrolyzing agents may be employed, in this method a hydrolyzing solution containing sulphuric acid, phosphoric acid, and acetic acid such as described in Patent No. 1,894,907, dated January 17, 1933, is preferred. It has been found that this solution is particularly applicable in hydrolyzing cellulosic sheet material and that the primary aromatic amine-formaldehyde resin is completely soluble therein. The amount of resin dissolved in the hydrolyzing solution may vary widely, for example, from 2% to 10%, although higher percentages may be utilized if desired. It may be added to the acid hydrolyzing agent as a wet precipitated resin or as a dry pure resin. The dry pure resin is preferred since the water introduced with the wet resins tends to dilute the acid mixture to a point where the hydrolyzing action is not as efficiently effective. The strength of the hydrolyzing solution and the other factors employed in treating the sheets may be within the ranges described in Patent No. 1,894,907, and, therefore, need not be repeated here.

Example 3

Dried precipitated aniline-formaldehyde resin made by reacting 1 mol. of aniline in acid solution with 1.05 mols of formaldehyde is pulverized so that it passes through a thirty-mesh sieve. 13 grams of this pulverized resin is then mixed with 10 cubic centimeters of glacial acetic acid until a thick paste is formed. 100 cubic centimeters of 85% phosphoric acid is added to the paste, followed by the addition of 20 cubic centimeters of 93% sulphuric acid. The resin completely dissolves in a few minutes and the resin content is 5.2% by weight of dry precipitated resin in the solution. Alpha cellulose paper is then immersed in the solution for a few seconds. The partially hydrolyzed sheets are then superposed one above the other until the desired thickness is obtained and are thereafter pured and dried in the usual manner employed in the manufacture of vulcanized fiber and are subsequently subjected to the heat treatment as disclosed in Method I. The product upon test shows that it absorbs only 19.5% water in twenty-four hours. With higher resin contents and proper manipulation, still greater resistance to water can be obtained.

Method III

Method III, as has previously been discussed, contemplates an association of the precipitated resin with the cellulosic material, making up the sheets prior to the hydrolyzing step. The resin

may be associated with the pulp prior to the manufacture of the paper, or it may be associated with the finished paper sheets. When the resin is associated with the pulp, it may be added to the pulp in acid solution, for example, in the beater containing partially beaten pulp and may, thereafter be precipitated in and around the fibers by the elimination of the effect of the acid preferably by the addition of a basic solution, or a wet suspension of the precipitated resin may be brought in contact with the pulp, for example, in the beater. Regardless of the particular method of association the resin with the pulp, it is thereafter manufactured into paper, for example, by the usual paper-making processes involving the use of Fourdrinier or cylinder machines of the plain or vacuum type. Preferably, the pulp either immediately before or during the paper-making process is washed free from electrolytes.

When it is desired, the cellulosic sheet material after fabrication may be associated with the resin, for example, by passing the paper through the resin in acid solution followed by treatment thereof in a precipitating solution; or the cellulosic sheet material may be passed through a solution of the precipitated resin in a solvent of the chlorhydrin type with the subsequent evaporation of the solvent.

The amount of resin associated with the cellulose by either of the two described methods may vary widely and may be relatively low, for example, 5% or may be high, for example, 40%, or more. In general, a resin content of from 5% to 15% will be found satisfactory. If a high resin content is desired, the treatment of the pulp with the resin is recommended due to ease of manipulation. The cellulosic sheet material with the resin in association therewith, regardless of its method of manufacture, is thereafter subjected to immersion in the hydrolyzing bath according to the well known methods of making vulcanized fiber which causes the partial hydrolysis of the cellulosic fibers. The partially hydrolyzed sheets are then superposed one above the other to obtain the desired thickness and the superposed material in the form of tubes or flat sheet stock is subjected to the puring and drying operations as is the case in the manufacture of vulcanized fiber. Subsequently, the superposed material may be subjected to heat treatment with or without pressure to allow the resin to become thermoplastic as is described in connection with Method I.

The product of the invention when made in accordance with Methods II and III has the resin homogeneously distributed throughout the sheets in contradistinction to the product made by Method I where usually greater amounts of resin are found at the surface of the product than in the interior thereof. Furthermore, Method III permits the association of larger amounts of resin with the cellulosic material than in either Methods I or II, since the resin is associated with the cellulosic material prior to the hydrolyzing step. Method III also requires less time than Method I and is easier to control than Method II and is, therefore, advantageous for use where the saving of time is an important factor.

Example 4

470 grams of cotton rag pulp (air dried) are put into a small beater to which is added 443 cubic centimeters of an acid solution of a resin made by reacting 1 mol. of aniline with 1.05 mols of formaldehyde in the presence of hydrochloric acid. The resin solution used contains 79 grams of resin figured as the precipitated resin or 15% resin based on the bone dry weight of the pulp. When the resin solution is entirely mixed with the pulp by circulation in the beater, 32 grams of caustic soda dissolved in 1 litre of water are added and mixed thoroughly until the resin is completely precipitated. The stock containing the precipitated resin is removed from the beater, placed on a filter, and washed free of the electrolytes. The washed stock may then be returned to the beater and diluted with water prior to making paper. If desired, the stock may be beaten prior to the addition of the acid solution of the resin and may also be beaten either before or after the addition of the caustic precipitating solution. Paper sheets are made in any suitable way from the electrolyte-free pulp-resin magma, and in commercial production the use of a vacuum type cylinder machine has proved to be particularly applicable. The dried sheets, for example, sheets .009 inch in thickness, are then cut to the desired size and passed through the hydrolyzing solution in accordance with the usual practice in the manufacture of vulcanized fiber, for example, a solution of zinc chloride 71.1° Baumé at 140° F. may be used, the time of immersion being a few minutes. If desired room temperature may be employed, in which case a longer time of immersion is required. The sheets are then superposed in the form of sheet stock or tubes and are pured and dried in the well known manner. In the case of tube stock, for example, tubes $\frac{7}{16}$ inch by ½ inch are heated in oil for two hours at 145° C. to 150° C. and then ground to $\frac{11}{32}$ inch outside diameter. The tubes absorb only 17½% moisture in twenty-four hours in contradistinction to ordinary vulcanized fiber tubes of the same size which absorb 42% moisture in twenty-four hours. In the case of sheet stock, the laminated superposed partially hydrolyzed sheets may be treated as described in Method I.

Example 5

Dry precipitated resin, made by reacting 1 mol. of aniline with 1.3 mols of formaldehyde in the presence of hydrochloric acid with the subsequent precipitation of the resin by the elimination of the effect of the acid, is formed into a wet suspension by adding 105 grams of the resin to a ball mill with 700 cubic centimeters of water, the ball mill being rotated for approximately forty-eight hours. This suspension of precipitated resin is then added to a beater containing 470 grams of pulp (air dried) suspended in water in accordance with the usual paper-making practice. After a thorough mixing is obtained by circulation in the beater, paper sheets are made from the pulp-resin magma which are thereafter dried, treated with a hydrolyzing agent, superposed, pured, and dried in accordance with well known methods employed in making vulcanized fiber as hereinbefore described in connection with other examples. If desired, the sheet or tube stock thus formed may be subjected to the heat treatment step hereinbefore described. The product is comparable in properties and water resistivity to the products made by the other methods herein set forth.

Example 6

An absorbent paper sheet, for example, unsized cotton paper, is passed slowly through an acid

solution of a resin, which solutions contains, for example, 8% of any desired aniline-formaldehyde resin, the paper becoming saturated with the resin solution. The excess solution may be removed from the paper sheets by passing them through squeeze rolls or otherwise and the sheets are subsequently passed slowly through a 3% solution of caustic soda in order to precipitate the resin, the time of immersion in the caustic solution being about two minutes. After this treatment, the electrolytes are removed by washing in water and the sheets dried. The dried paper sheets of any desired size are then treated with a hydrolyzing solution, superposed, pured, and dried by the usual methods of manufacturing vulcanized fiber. Thereafter, if desired, the product may be heat treated as described herein. The product, like the products of other processes, is characterized by high water-resistivity.

Example 7

88.5 grams of wet pure resin, containing 89.6% water, made by reacting 1 mol. of aniline with 1.3 mols of formaldehyde in the presence of hydrochloric acid with the subsequent precipitation of the resin by the elimination of the effect of the acid, is added to 219 grams of ethylenechlorhydrin. The resin for the most part dissolves in the ethylenechlorhydrin, but the very small fraction which remains insoluble is removed by filtration. The filtered solution contains 2.7% resin by weight. Sheets of unsized absorbent cotton paper are passed through the clear solution until the sheets have become impregnated therewith. If necessary or desirable, the sheets may be dried and subsequently immersed again in the solution of the resin. The resin impregnated strips after the final drying are treated with a hydrolyzing agent, superposed, pured and dried by the well known methods of making vulcanized fiber. The sheet or tube stock thus made may then be treated by the heat and pressure steps herein described, for example, they may be heated for one hour under dry heat at 105° C. followed by treatment for one and one-half hours under dry heat at 152° C. The product obtained differs markedly from vulcanized fiber, since it has a very low water-absorptive capacity.

From the above description, it is to be noted that the present invention contemplates a process in which the sheets are placed in superposed relation while still moist. This results in a binding of the sheets together by the hydrolyzed cellulose although when the superposed material is subjected to the final heat treatment the resin may also aid in the binding of the individual sheets together. In the product of the present invention, however, the hydrolyzed cellulose is relied upon at least in part to bind the superposed sheets. No claim is laid herein to the invention of drying the partially hydrolyzed sheets associated with the resin prior to the step of superposing, the same being the subject matter of a co-pending application filed by Gustave Widmer on May 12, 1933, Serial No. 670,795.

While in the foregoing examples resins made by combining given percentages of the primary aromatic amine and the formaldehyde have been recited, it will be clear from the specification that any desired primary aromatic amine-formaldehyde resin, whether fusible or infusible, may be employed. Also the times, temperatures, pressure and other conditions mentioned may vary widely within the skill of the operator, the specific figures being merely illustrative.

Considerable modification is possible in the choice of the cellulosic material, the hydrolyzing agent, and the primary aromatic amine-formaldehyde resin employed, as well as in the steps of the process and the physical factors employed in carrying out the process without departing from the present invention.

I claim:

1. An indurated fiber product characterized by low water absorption, comprising a plurality of superposed sheets of partially hydrolyzed cellulose joined together and containing a primary aromatic amine-formaldehyde resin within its pores and upon its surfaces associated with said partially hydrolyzed cellulose.

2. The product of claim 1 wherein the resin is an aniline-formaldehyde resin.

3. The product of claim 1 wherein the resin is an insoluble, infusible, thermoplastic aniline-formaldehyde resin.

4. An indurated fiber product characterized by low water absorption, comprising a plurality of superposed sheets of partially hydrolyzed cellulose joined together and containing a primary aromatic amine-formaldehyde resin within its pores and upon its surfaces associated with said partially hydrolyzed cellulose, the resin being present in greater amounts at the surfaces of the product than at the interior thereof.

5. The product of claim 4 wherein the resin is an aniline-formaldehyde resin.

6. The product of claim 4 wherein the resin is an infusible, insoluble, thermoplastic aniline-formaldehyde resin.

7. An indurated fiber product characterized by low water absorption, comprising a plurality of superposed sheets of partially hydrolyzed cellulose joined together and containing a primary aromatic amine-formaldehyde resin associated with said partially hydrolyzed cellulose and homogeneously distributed through the said product.

8. The product of claim 7 wherein the resin is an aniline-formaldehyde resin.

9. The product of claim 7 wherein the resin is an insoluble, infusible, thermoplastic aniline-formaldehyde resin.

10. In the process of making an indurated fiber product of low water absorption by subjecting hydrolyzable cellulosic sheets to the action of a cellulose hydrolyzing agent to hydrolyze the sheets partially, superposing a plurality of said sheets one upon the other to cause adherence of said sheets by the partially hydrolyzed cellulose, washing and drying said superposed material, the step which comprises associating a primary aromatic amine-formaldehyde resin which has been precipitated from the acid salt of said resin by the elimination of the acid therefrom, within the pores and upon the surfaces of the cellulose material of said sheets in a stage in said process prior to the drying of said superposed material.

11. The process of claim 10 in which the resin is an aniline formaldehyde resin.

12. The process of claim 10 in which the resin employed is an infusible, insoluble, thermoplastic aniline-formaldehyde resin.

13. The process of making an indurated fiber product of low water absorption which comprises immersing hydrolyzable cellulosic sheet material in a hydrolyzing solution to hydrolyze said sheets partially, superposing said sheets one above the other, to obtain the thickness desired and to cause adherence of said sheets by the partially hydrolyzed cellulose, immersing said superposed prod-

uct in an acid solution of a primary aromatic amine-formaldehyde resin until the solution has penetrated said product, immersing said product in a resin precipitating solution until the resin has precipitated within the pores of the product, washing the product, and thereafter drying it.

14. The process of claim 13 in which the resin employed is an aniline-formaldehyde resin.

15. The process of claim 13 in which the resin employed is an infusible, insoluble, thermoplastic aniline-formaldehyde resin.

16. The process of making an indurated fiber product of low water absorption which comprises immersing hydrolyzable cellulosic sheet material in a hydrolyzing solution to hydrolyze said sheets partially, superposing said sheets one above the other, to obtain the thickness desired and to cause adherence of said sheets by the partially hydrolyzed cellulose, puring said product, immersing said superposed product in an acid solution of a primary aromatic amine-formaldehyde resin until the solution has penetrated said product, immersing said product in a resin precipitating solution until said resin has precipitated within the pores of the product, washing and drying the product, and thereafter subjecting it to heat treatment to cause the resin to flow around the fibers.

17. The process of claim 16 in which the resin is an aniline-formaldehyde resin.

18. The process of claim 16 in which the resin employed is an infusible, insoluble, thermoplastic aniline-formaldehyde resin.

19. The process of making an indurated fiber product of low water absorption which comprises immersing cellulosic sheet material in an acid hydrolyzing solution containing in solution a primary aromatic amine-formaldehyde resin, said resin having been precipitated from acid solution, superposing said resin-impregnated partially hydrolyzed sheets one above the other, puring and drying said superposed material.

20. The process of claim 19 in which the resin is an aniline-formaldehyde resin.

21. The process of claim 19 in which the resin employed is an infusible, insoluble, thermoplastic aniline-formaldehyde resin.

22. The process of making an indurated fiber product of low water absorption which comprises immersing cellulosic sheet material containing a primary aromatic amine-formaldehyde resin, said resin having been precipitated from acid solution by the elimination of the acid therefrom, in a hydrolyzing solution to partially hydrolyze said cellulose, superposing said sheets one above the other, puring and drying said product.

23. The process of claim 22 in which the resin is an aniline-formaldehyde resin.

24. The process of claim 22 in which the resin employed is an infusible, insoluble, thermoplastic aniline-formaldehyde resin.

25. The process of making an indurated fiber product of low water absorption which comprises immersing cellulosic sheet material in an acid solution of a primary aromatic amine-formaldehyde resin until said sheets have become impregnated by said resin, immersing said resin-containing sheet material in a resin precipitating solution to cause precipitation of the resin, immersing said resin-containing paper in a hydrolyzing solution, superposing said sheets one above the other, puring and drying said product.

26. The process of claim 25 in which the resin is an aniline-formaldehyde resin.

27. The process of claim 25 in which the resin employed is an infusible, insoluble, thermoplastic aniline-formaldehyde resin.

28. The process of making waterproof indurated fiber of low water absorption which comprises immersing cellulosic sheet material in a chlorhydrin solution of a primary aromatic amine-formaldehyde resin, said resin having been precipitated from acid solution by the elimination of the acid therefrom, causing said sheet material to become impregnated by said resin, immersing said resin-containing paper in a hydrolyzing solution, superposing said sheets one above the other, puring and drying said product.

29. The process of claim 28 in which the resin is an aniline-formaldehyde resin.

30. The process of claim 28 in which the resin employed is an infusible, insoluble, thermoplastic aniline-formaldehyde resin.

DUNCALF W. HOLLINGWORTH.