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PLASTIC IMPREGNATED PAPER AND METHOD AND APPARATUS FOR MAKING SAME

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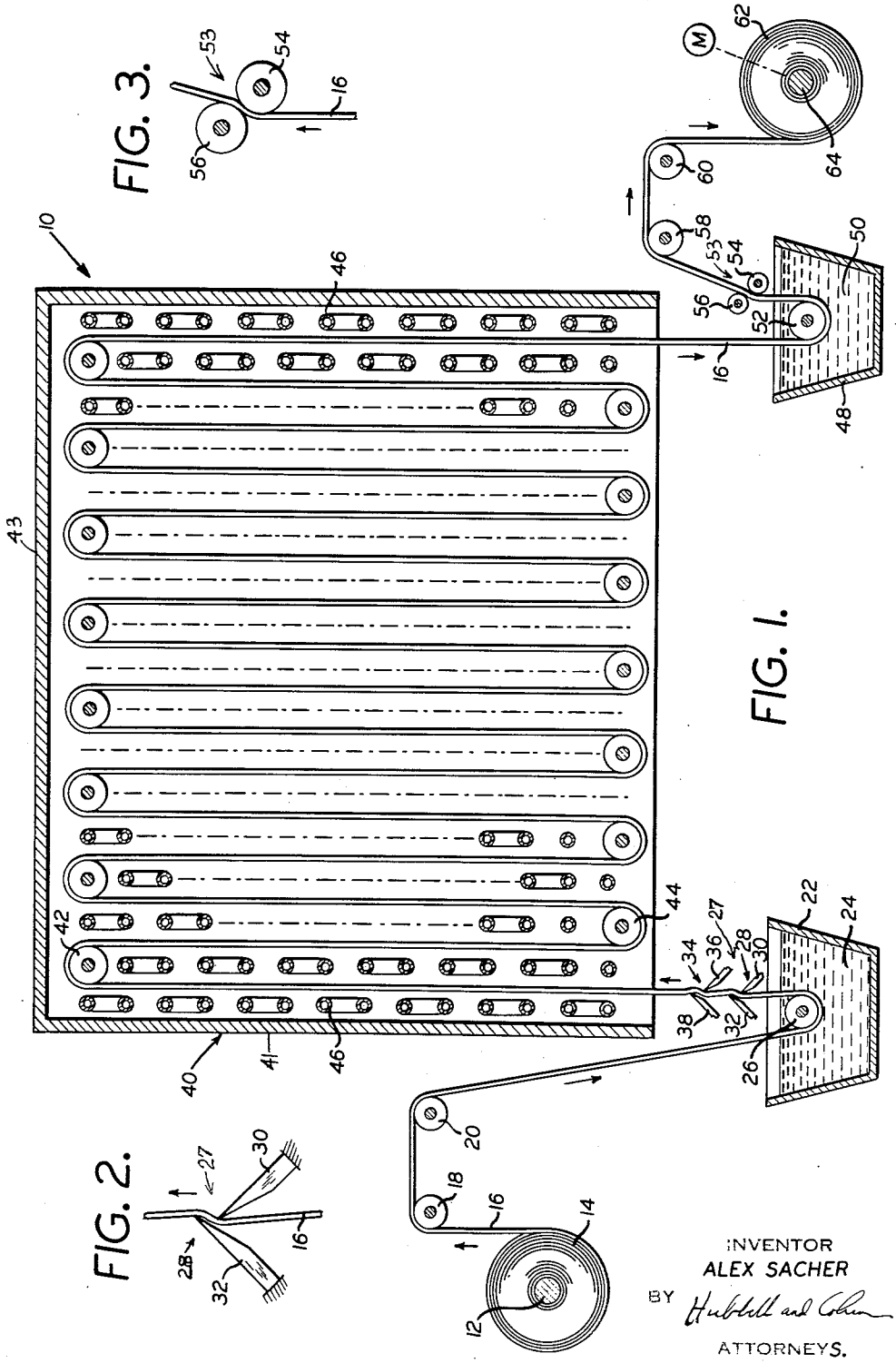


FIG. 1.

FIG. 3.

FIG. 2.

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PLASTIC IMPREGNATED PAPER AND METHOD AND APPARATUS FOR MAKING SAME

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This invention relates to impregnated paper and particularly to paper impregnated with epoxy resins and to a method and apparatus for impregnating paper.

The use of paper with business machines, such as data processing machines and time clocks, has grown markedly in recent years. In these two applications which are illustrative of other applications of paper with business machines, the paper is usually in the form of a relatively stiff card. In data processing machines the card is usually provided with a plurality of apertures which represent bits of information. The punched cards are passed through the machine and the apertures actuate certain sensing devices to supply data to the machine for action thereon. The tolerances for the passageway for the cards through such data processing machines must be relatively fine and, therefore, the cards themselves must be cut to precise dimensions and must have substantial dimensional stability so as to maintain said dimensions.

In automatic time clocks and the like, the cards are often subjected to rough wear and for this reason they must be tough and not brittle. Furthermore, dimensional stability is also important for these cards as tolerances in such apparatus are also quite fine. One of the most common ways for paper to vary its dimension is by way of swelling or shrinking in response to variations in relative humidity. Particular difficulty has been encountered in using cards of the type described in areas of extremely high relative humidity. In such places the cards lose their stiffness due to high moisture content and further swell to such an extent that they cannot be used in connection with their intended application.

The main object of the present invention is to provide a new and improved card or paper which has extremely fine dimensional stability regardless of humidity conditions, which is tough enough to withstand relatively hard handling, and which may be written and printed on with ease.

Another object of the present invention is the provision of a new improved epoxy resin impregnated paper.

Still another object of the present invention is the provision of a new and improved epoxy resin to serve as an impregnating agent for paper and the like.

Still another object of the present invention is the provision of a new and improved method of impregnating paper and the like with resin.

Yet a further object of the present invention is the provision of a new and improved method for impregnating paper and the like with epoxy resin which method results in a controlled moisture content for the finished product.

Still another object of the present invention is the provision of new and improved apparatus for impregnating paper and the like with resin.

The above and other objects, characteristics and features of the present invention will be more fully understood from the following description taken in connection with the accompanying illustrative drawing.

In the drawing:

FIG. 1 is a diagrammatic vertical sectional view of apparatus for impregnating paper with resin;

FIG. 2 is an enlarged detailed view illustrating means

for controlling the amount of resin in the paper being impregnated; and

FIG. 3 is an enlarged sectional view showing means for controlling the amount of water contained in impregnated paper.

Referring now to the drawing in detail the apparatus for impregnating paper and the like is generally designated in FIG. 1 by the reference numeral **10**. This apparatus includes a shaft **12** on which is rotatively mounted a roll of paper **14** which supplies paper **16** to the remainder of the apparatus. Paper **16** is passed over two guide rollers **18** and **20** and into a container or pot **22** holding a resinous impregnating agent **24**. The nature of impregnating agent **24** will be described in detail as this description proceeds. The paper passes around a roller **26** disposed within container **22** and thence directly upwardly past a scraping means **27** here shown as being made up as a first set of knives **28** including two offset knives **36** and **38**. From the scraping means **27**, paper **16** passes into a curing tower **40** wherein the impregnating agent is subjected to suitable heat to cure the resin therein. After the resin in the paper **16** has been cured, the paper is passed out of curing tower **40** directly vertically downward into a container or pot **48** for water **50**. Disposed within the container **48** is a roller **52** around which the paper **16** passes to then pass upwardly out of the water **50** through a squeezing means **53** made up of two offset cylindrical bars **54** and **56**. From the squeezing means **53** paper **16** passes over two guide rollers **58** and **60** and thence onto a roll of paper mounted on a shaft **64** driven by any suitable motor means M.

While many types of papers are suitable for this application, I generally prefer bleached or unbleached sulphite or sulphate papers made of northern or southern pine having a thickness of about 7 mils. I presently prefer to use bleached sulphite paper made of northern pine. Such papers are available in relatively large rolls, such as the roll **14** rotatably mounted on shaft **12**. As already stated, paper **16** is fed off the roll **14** and over two spaced guide rollers **18** and **20** and thence into a container **22** for impregnating agent **24**. Roller **26** which is disposed in container **22** is preferably totally immersed in the resin **24**, here shown as being about an inch below the surface of the resin. With a resin of the type to be described hereinafter having a given viscosity and other properties, the immersion time of the paper in the resin is critical. I have found that a suitable impregnation is achieved without undue waste of resin if the paper is immersed in the resin **24** for between about 1½ and 3 seconds. For a relatively high linear speed of the paper of the order of about 500 yards per hour, the duration of the immersion time can best be controlled by the diameter of roller **26** and the depth of its immersion in resin **24**. However, the diameter of the roller is critical as if it is too small, the paper will crack or the pores will be opened too wide and thus cause the paper to take up too much resin, and if the diameter of roller **26** is too large, the pores will not be opened sufficiently wide. I have found that the diameter of roller **26** should be between 2½ and 3½ inches, with 2½ inches presently being preferred. With the roller **26** immersed to a depth of 1 inch below the surface of resin **24** such a roller will yield an immersion time of about 1.66 seconds for a linear speed of about 500 yards per hour. Paper **16** passes into the resin **24** around the roller **26** and thence substantially vertically upward out of the container **22** past scraping means **27**.

The knives making up scraping means **27** are supported in the position shown in any suitable manner. The positioning of the knives is such as to scrape the surfaces of

paper **16** so as to remove the excess of resin picked up during the immersion of the paper in the resin **24**. It is vital to the present invention that the paper not contain an excess of resin as that would render the product difficult to print or write on. The two sets of knives **28** and **34** overcome this problem by forcing relatively sharp knife edges against the surfaces of paper **16** to scrape off an excess of resin.

This scraping action is controlled by the positioning of the knives relative to one another and to the roller **26**. preferably, the edge of knife **30** is disposed one-half inch to the left of the rightmost element of roller **26** and about one-half inch above the surface of resin **24**. The edge of knife **32** is approximately 1½ inches above and 1½ inches to the right of the edge of knife **30** whereby with the paper **16** being pulled substantially vertically upward, both surfaces of the paper **16** will be thoroughly scraped by the knife edges of knives **30** and **32**. Knife set **34** is about three inches above knife set **30** and the edges of knives **36** and **38** are disposed relative to one another in substantially the exact positions as knives **30** and **32**, respectively. Such a positioning of the knives will result in the desired amount of resin **24** being left in the paper **16** when the knives are about 5/16 of an inch thick and have a throat of about ⅛ of an inch and are disposed at an angle to the horizontal somewhere between about 0° and 30°. The resin scraped off by the knives will flow down the knives away from the paper and ultimately drip back into container **22**.

After the impregnated paper has passed over the knives to effect a scraping and hence a removal of excess resin to bring the resin content in the paper down to the desired amount of about 8% to 11% by weight, the paper is passed into the curing tower **40** to set the resin.

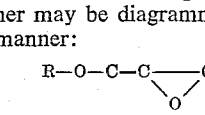
Curing tower **40** comprises a peripheral side wall **41** here shown as rectangular in configuration and a rectangular top or roof **43** which effectively closes the tower on all surfaces but the bottom. Disposed within tower **40** are a plurality of serpentine tubes **46** each tube winding in a vertical plane and being horizontally spaced from each other tube. The spaces in between the tubes **46** comprise passageways for the paper **16** to pass upwardly and downwardly through the tower. In order to provide for the reversal of the direction of movement of paper **16**, a plurality of rollers **42** are provided adjacent the top of the tower **40** and another plurality of rollers **44** which are horizontally offset from the rollers **42** are provided adjacent the bottom of tower **40**. The tubes **46** are adapted to have super-heated steam passed therethrough in order to heat the tower to a curing temperature for the resin **24**. For the resin now preferred in the present invention, the temperature in the heating tower is controlled to between about 300° F. and 315° F. With this temperature it has been found that a complete curing of the resin **24** can be effected in about 14 minutes. Accordingly, if the paper is advanced through apparatus **10** at a rate of about 500 yards per hour, it will be seen that a path length of 120 yards through the tower will provide a curing time of 14.4 minutes which is presently preferred. This governs the dimensions of the curing tower and the only other factor which must be considered is that the tower must be tall enough to provide sufficient curing of the resin **24** during the initial upward passage of the paper through the tower to prevent adhesion of the paper with the left-most roller **42**. With the resin which is preferred in the present invention it has been found that sufficient curing to prevent adhesion with the left-most roller **42** can be effected in about 50 seconds. Accordingly, the height of the tower should be about 7½ yards which will give the resin about 54 seconds of heating prior to its initial engagement with a roller **42** and thus prevent adhesion with said roller. Accordingly, as shown herein the tower is about 7½ yards high and is arranged to provide 8 upward and 8 downward passes through the tower in order to effect the proper curing of the resin **24** in a path length through tower **40** of 120 yards. It will be understood that in lieu of using pipes **46** for carrying super-heated steam to supply the necessary heat in tower **40** for curing resin **24** in paper **16**, other suitable heating means may be employed such as, for instance, electric heating elements and the like.

After the paper **16** passes vertically downwardly out of the tower it passes into the container **48** for water **50**. As set forth above, the horizontal roller **52** is disposed within container **48** and is preferably immersed in the water, here shown to a depth of about 2 inches.

While the diameter of the roller **52** is not as critical as the diameter of the roller **26** discussed above, it too must not be of so small a diameter that the paper will be cracked when passing around it. I have found that immersion time of the cured impregnated paper **16** in water **50** is preferably between about 3½ and 4½ seconds and this can be achieved by employing a 6 inch diameter roller which is immersed to a depth of 2 inches below the surface of water. Such an arrangement will yield an immersion time in water **50** of about 3.8 seconds at a speed of 500 yards per hour. The immersion of the impregnated paper in the water permits the paper to take up a substantial amount of water **50** and thus, after further treatment, as will be described hereinafter, to provide the finished paper with a suitable water content to reduce its sensitivity to variations in relative humidity. After paper **16** passes around the roller **52**, it is subjected to a squeezing action by the two horizontally extending horizontally and vertically offset cylindrical bars **54** and **56** to remove the excess of water in the paper. I have found that a proper squeezing can be effected by using bars with a ¾ inch diameter which are offset at an angle of 45°. The bars are biased towards each other for squeezing action by any suitable means such as, for instance, springs, elastic bands or the like. After passing between the squeezing bars **54** and **56** the paper passes over the two additional guide rollers **58** and **60** and is then wound onto the rotating roll **62**.

In accordance with one of the features of the present invention, after the roll **62** has been wound to desired size, it is removed from the shaft **64** and placed in a substantially water impervious container and held in said container for sufficient time to permit the water in the paper to equally distribute itself throughout the roll. One extremely satisfactory type of container is a plastic film such as, for instance, Saran which may be wrapped around the roll and which will act as an excellent moisture barrier with a roll **62** having a diameter of about 24 inches, a width between about 24 and 37 inches and a weight between about 200 and 300 pounds; excellent moisture distribution is achieved within about 7 days of storage. The desired percentage of water is between 4½ and 5½ percent by weight of the finished product and this percentage is readily achieved by the described method. After the water distribution has been achieved, the paper may be unrolled from roll **62** and cut into desired shape.

While many resins may be employed as impregnating agents for paper, I have found that a superior product is obtained by impregnating the paper with an epoxy resin. Preferably the impregnating agent **24** comprises four components. The first component is an epoxy resin which has been polymerized to a molecular weight between about 350 and 475, a viscosity of from about 4,000 to about 90,000 centipoises at about 73° F. and has an epoxy equivalent of from about .44 to about .48 mol per 100 grams. To the epoxy resin is added a flexibilizing agent in the form of a monomer having reactive epoxy groups. Such a monomer may be diagrammatically illustrated in the following manner:



where "R" is preferably an aliphatic radical. A cross linking agent in the form of an anhydride constitutes the third component of the impregnating agent **24**. Anhydrides suitable for use in the present application are those

having a side group taken from the class consisting of aromatics and aliphatics containing 4 to 18 carbon atoms. The fourth component of impregnating agent **24** is a temperature latent amine catalyst. By temperature latent is meant a catalyst which will be effective as a catalyst only at elevated temperatures and will not be effective at room temperatures. This insures a good pot life for impregnating agent **24**.

More specifically, impregnating agent 24 is composed of the condensation product of bis-phenol-A and epichlorhydrin which has been polymerized to a molecular weight of between 350 and 475, a viscosity of 4,000 to 90,000 centipoises at about 73° F. and has an epoxy equivalent of about .44 to .48 mol per 100 grams. Most preferably the condensation product of bis-phenol-A and epichlorhydrin has an epoxy equivalent of .44 to .48 mol per 100 grams, a molecular weight between about 420 and 460 and a viscosity between about 42,000 and 44,000 centipoises at 80° F. Such a resin may be purchased from the Ciba Company under the designation Araldite 6030. The preferred monomer for inclusion as a flexibilizing agent is butyl glycidyl ether which may be purchased from the Ciba Company under the trade designation RD1. Considering that the condensation product and the monomer together form the resin in the impregnating agent 24, in order to achieve a final product having the proper flexibility, not too brittle and not tacky, the resin should consist of about 50 to 90% of the condensation product and about 10% to 50% of the monomer such as, for instance, butyl glycidyl ether. A cross linking agent which I have found excellent for the present application is dodecynyl succinic anhydride and the anhydride should be present in sufficient quantity to provide a ratio of epoxy groups in the resin to anhydride groups of about 1 to 1. The temperature latent amine catalyst is preferably a tertiary or quaternary amine as such amines provide longer pot life than would a primary or secondary amine. One amine which I have found to be extremely well suited for the present application is tri-dimethyl amino-methyl phenol which may be purchased from Rohm and Haas under the designation DMP–30. Again taking the condensation product and the monomer together as the resin in the impregnating agent, there should be about 1 to 2 parts of the amine catalyst for about every 100 parts of the resin.

One excellent composition for impregnating agent 24 is composed as follows:

	Percent
Condensation product of bis-phenol-A and epichlorhydrin having an epoxy equivalent of about .44 to .48 per 100 grams, a molecular weight between 420 and 460 and a viscosity of 42,000 to 44,000 centipoises at 80° F. (Araldite 6030)	34
Butyl glycidyl ether (RD1)	21.5
Dodecynyl succinic anhydride	43.5
Tri-dimethyl amino-methyl phenol (DMP–30)	1

The viscosity of the above defined impregnating agents immediately after mixing same will generally be too low for immediate use as the viscosity of the impregnating agent is relatively critical. If the viscosity is too low, there will be too much impregnation which will render the final product difficult to write on and have other deleterious effects. If the viscosity of the impregnating agent is too high, it will be difficult to attain the desired degree of impregnation which is between 8% and 11% of plastic in the final product. It has been found that satisfactory results can be obtained if the viscosity of the impregnating agent falls between 60 and 90 centipoises at 80° F., 80° F. being the temperature of the room in which the impregnating agent **24** contained by container 22 is disposed. As the viscosity of the initial mixture is relatively low, and is generally well below the lower limit of both the broad and narrow ranges of viscosity, it is necessary after mixing the impregnating agent to let it stand for some time of the order of about one and a half hours in order for the viscosity to be raised into the desired range preferably to 68 centipoises. As the process is worked, the viscosity of the impregnating agent in the pot **22** will continue to rise and it therefore becomes necessary to periodically add fresh (unaged) resin to maintain the viscosity in the desired range. This addition may be accomplished by adding to the pot **22** fresh impregnating agent that has been just mixed in a separate container or by having an automatic metering device which separately adds at desired time intervals or continuously, the proper amounts of the condensation product and monomer on the one hand and the anhydride and amine catalyst on the other. By either expedient the viscosity of the impregnating agent **24** can be closely controlled to yield an impregnating agent with the desired characteristics.

The final product will be composed of paper having a substantially uniform distribution of cured impregnating agent and moisture. The impregnating agent will make up 8% to 11% of the finished product by weight and preferably about 9% and the moisture in the final product will make up between about 4½% and 5½% of the final product and preferably about 5%. If there is too little moisture in the final product, it will be too brittle and it also will display a tendency to shred. If there is too much moisture, it will be difficult to punch and will show a tendency to swell thus eliminating the desired dimensional stability.

The final product of the type described hereinbefore is required to have a folding endurance of 300 and actually has an average folding endurance of about 619. No fuzz is present on the surface. The expansion of a card 3¼ inches by 7⅜ inches made from paper which has been processed in the above described manner will be only about .19% in the longitudinal direction and only about .7% in the transverse direction during a change in relative humidity from 20% to 75%. The contraction of such a card during a decrease in relative humidity of from 75% to 20% is only .22% in the longitudinal direction and .67% in the transverse direction. Moreover, such a card shows absolutely no warp. The coefficient of static friction of a card made from paper processed as described above may be between .35 and .45 and actually is about .39 and the coefficient of kinetic friction is the same. The stiffness of such a card as measured on a Tabor V–5 machine must be more than 18 in the longitudinal direction and more than 8.5 in the transverse direction. Actual measurements show that a card made in accordance with the present invention has a stiffness of 24 in the longitudinal direction and 11 in the transverse direction. The bursting strength of the finished product is about 72 p.s.i. and the thickness thereof is about 7.3 mils. The average weight of 500 sheets 24 inches by 36 inches is about 101.1 pounds.

With paper having the properties described above, excellent cards for use in association with business machines can be made. Such cards may be readily written and printed upon, roughly handled, subjected to wide variations in humidity without failing to cooperate properly with the associated machine. This highly desirable result stems from toughnes, dimensional stability, absence of warp and high folding strength of the described product. Hence, highly reliable paper stock for use with business machines is afforded by the present invention.

While I have herein shown and described the preferred embodiment of my invention and have suggested various changes and modifications therein, other changes and modifications may be made therein within the scope of the appended claims without departing from the spirit and scope of this invention.

What is claimed is:

1. A plastic impregnated paper, said paper being taken from the group consisting of bleached and unbleached sulfite and sulfate papers of northern and southern pine, said plastic being a fully polymerized impregnating agent,

said impregnating agent comprising a resin consisting essentially of about 50% to 90% of the condensation product of bis-phenol-A and epichlorhydrin having an epoxy equivalent of from about .44 to about .48 mol per 100 grams and a viscosity of from about 4,000 to about 90,000 centipoises at about 73° F., and about 10% to 50% of a monomer having reactive epoxy groups; said agent further comprising an anhydride having a side group taken from the class consisting of aromatics and aliphatics containing 4 to 18 carbon atoms, said anhydride being present in such quantity as to provide an anhydride group to epoxy group ratio of about 1:1; and about 1 to 2 parts of a temperature latent amine for about every 100 parts of said resin said plastic being substantially uniformly distributed throughout said paper and constituting from about 8% to 11% by weight of said impregnated paper, said plastic impregnated paper containing from about 4½ to 5½% water, this water being uniformly distributed throughout said paper.

2. A plastic impregnated paper, said paper being taken from the group consisting of bleached and unbleached sulfite and sulfate papers of northern and southern pine, said plastic being a fully polymerized impregnating agent, said agent comprising a resin consisting essentially of about 50% to 90% of the condensation product of bis-phenol-A and epichlorhydrin having an epoxy equivalent of from about .44 to about .48 mol per 100 grams and a viscosity of from about 4,000 to about 90,000 centipoises at about 73° F., and butyl glycidyl ether; said impregnating agent further comprising dodecinal succinic anhydride in such quantity as to provide an anhydride group to epoxy group ratio of about 1:1; and about 1 to 2 parts of tri-dimethyl amino-methyl phenol for about every 100 parts of said resin said plastic being substantially uniformly distributed throughout said paper and constituting from about 8% to 11% by weight of said impregnated paper, said plastic impregnated paper containing from about 4½ to 5½% water, this water being uniformly distributed throughout said paper.

3. A plastic impregnated paper, said paper coming from the group consisting of bleached and unbleached sulfite and sulfate papers of northern and southern pine, said plastic being a fully polymerized impregnating agent, said impregnating agent consisting essentially by weight of about 34% of the condensation product of bis-phenol-A and epichlorhydrin having an epoxy equivalent of about .44 to .48 mol per 100 grams and a viscosity of 42,000 to 44,000 centipoises at 80° F., about 21.5% butyl glycidyl ether, about 43.5% dodecinal succinic anhydride, and about 1% tri-dimethyl amino-methyl phenol said plastic being substantially uniformly distributed throughout said paper and constituting from about 8% to 11% by weight of said impregnated paper, said plastic impregnated paper containing from about 4½ to 5½% water, this water being uniformly distributed throughout said paper.

4. A plastic impregnated paper, said paper coming from the group consisting of bleached and unbleached sulfite and sulfate papers of northern and southern pine, said plastic being a fully polymerized impregnating agent, said impregnating agent consisting essentially by weight of about 34% of the condensation product of bis-phenol-A and epichlorhydrin having an epoxy equivalent of about .44 to .48 mol per 100 grams and a viscosity of 42,000 to 44,000 centipoises at 80° F., about 21.5% butyl glycidyl ether, about 43.5% dodecinal succinic anhydride, and about 1% tri-dimethyl amino-methyl phenol, said plastic being substantially uniformly distributed throughout said paper and constituting from about 8% to 11% by weight of said impregnated paper, said plastic impregnated paper containing from about 4½ to 5½ percent water, this water being uniformly distributed throughout said paper.

5. The method of making plastic impregnated paper comprising immersing a paper selected from the group consisting of bleached and unbleached sulfite and sulfate papers of northern and southern pine in a liquid impregnating agent, said agent comprising (1) a resinous mixture consisting essentially of about 50 to 90% of the condensation product of bis-phenol-A and epichlorhydrin having an epoxy equivalent of from about .44 to .48 mol per 100 grams and a viscosity of from about 4000 to 90,000 centipoises at about 73° F., (2) about 10% to 50% of a monomer having reactive epoxy groups, (3) an anhydride having side groups taken from the group consisting of aromatics and aliphatics containing from 4 to 18 carbon atoms, said anhydride being present in such quantity as to provide an anhydride group to epoxy group ratio of about 1:1 and (4) about 1 to 2 parts of a temperature latent amine for about 100 parts of said resinous mixture, removing said paper from said impregnating agent, scraping both surfaces of said paper to remove excess impregnating agent until said impregnating agent constitutes from about 8 to 11% by weight of said impregnated paper, heating said scraped impregnated paper to cure the impregnatng agent therein, dipping said cured impregnated paper in water, and containing said wetted paper in a moisture impervious container until the water therein is substantially uniformly distributed and present in an amount equal to from 4½ to 5½% by weight of said plastic impregnated paper.

6. The method of claim 5 wherein after said impregnated paper is dipped into water the paper is subjected to squeezing to remove excess water therefrom, this squeezing carried out prior to said step of containing said wetted paper in a moisture impervious container.

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