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METHOD OF WATERPROOFING CELLULOSIC MATERIALS AND PRODUCT THEREOF

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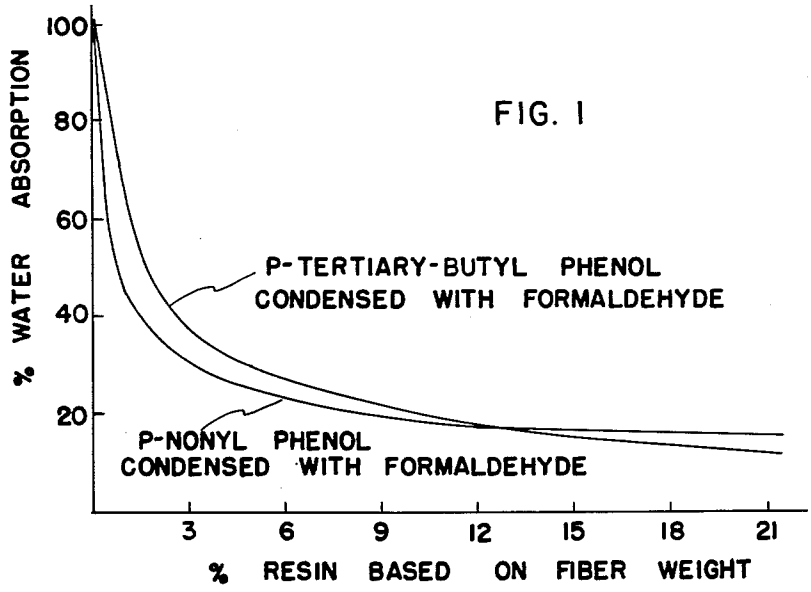


FIG. 1

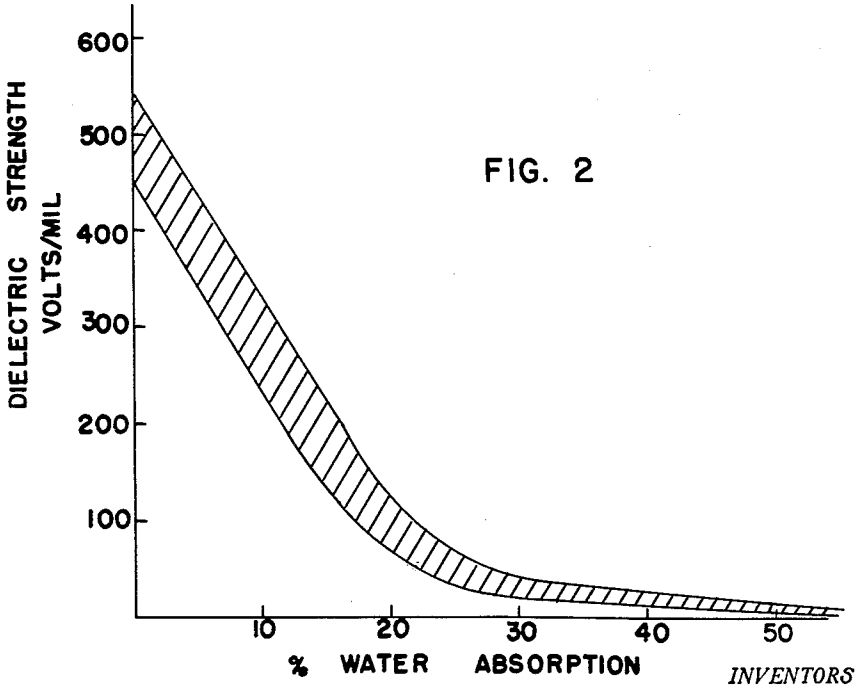


FIG. 2

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METHOD OF WATERPROOFING CELLULOSIC MATERIALS AND PRODUCT THEREOF

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13 Claims. (Cl. 162—165)

This invention relates to a process for waterproofing paper and the resulting waterproofed paper.

In many applications it is desirable to have available a waterproof paper which will absorb only a small amount of water even when completely immersed in it for extended periods. Among such applications may be cited the use of waterproof paper as insulating material in splashproof electric motors. Paper which is to be used in this application should exhibit a minimum water pick-up, at the same time have a maximum dielectric strength even after extended periods of exposure to water, and still be flexible enough to be folded through 180° without cracking. This means that a paper must be treated in such a way as to be capable of preventing the passage of an electric current therethrough even when wet. It is customary to use relatively dense paper as insulation in splashproof motors and hence the normal technique of saturating the paper by immersing it in a waterproofing composition is not satisfactory.

A number of methods have been developed in the past to render cellulosic materials and more particularly high-density papers waterproof. Such methods have included impregnating the paper with a resin such as phenol-formaldehyde or treating the paper with aluminum acetate and paraffin wax, the stearato-chrome complexes or with silicone treating agents. None of these treatments has produced entirely satisfactory waterproof paper. The introduction of resins in sufficient quantities to adequately waterproof the paper has resulted, in most cases, in the production of a very stiff and brittle material. Moreover papers thus waterproofed may assume the physical characteristics of the resins and lose most of their characteristics as paper. The other treatments mentioned have not resulted in the formation of waterproof papers which possess good wet dielectric strength throughout. Thus, for example, if the waterproof paper is somewhat spotty it means that certain sections of it will exhibit no dielectric strength and hence make the entire paper unsatisfactory as an insulation.

Many of the treatments for waterproofing paper in the prior art have tended to concentrate their waterproofing effects on the outside surface of the paper. This is not desirable for the production of a paper which should exhibit a high dielectric strength, for it is necessary that the paper possess good wet dielectric strength throughout. Moreover, limiting a treatment to the surface means that there exists a possibility of lateral leakage, especially if the paper is cut subsequent to treatment. In contrast, the treatment according to this invention provides the possibility of adding the treating material during paper formation, hence achieving a uniform treatment throughout the entire thickness of the paper.

It would therefore be desirable to have a waterproof paper (and a reliable method for making it) which does not absorb any substantial amount of water and which is capable of exhibiting high dielectric strength even after prolonged immersion in water.

It is therefore an object of this invention to provide a flexible waterproof paper which absorbs only a minor amount of water even when fully immersed, and which at the same time retains its other characteristics as a paper. It is another object to provide a waterproof paper which

exhibits a good dielectric strength even when immersed in water. Another object is to provide a method for waterproofing paper to impart to it high dielectric strength without materially decreasing its flexibility or depriving it of its other inherent paper or cellulosic characteristics.

It is yet another object of this invention to provide a paper which is uniformly treated throughout its entire thickness and which is not subject to lateral leakages. These and other objects will become apparent in the following description.

By the process of this invention paper is waterproofed and made to have good dielectric strength even after prolonged exposure to water characterized by the step of adding to the paper making stock a resin in the form of a water-alcohol or an alcohol solution. The material which is added to the paper making stock may be defined as a solution of a condensation resin formed by condensing substituted phenols with a formaldehyde source to form a resin which is soluble in acetone and the lower alcohols. More particularly, the waterproofing material may be defined as a solution of a condensation resin formed by reacting a formaldehyde source and a substituted phenol under refluxing conditions to form a condensation resin soluble in acetone. The substituted phenol must have substituent radicals so placed that not more than two methylol radicals can be added to the substituted phenol. The substituent radicals are selected from a group consisting of saturated and unsaturated aliphatic radicals having a total of between 4 and 12 carbon atoms and saturated and unsaturated cyclic hydrocarbon groups which when joined to the phenolic ring do not result in a compound having conjugated unsaturation throughout. The resin solution which is added to the paper stock contains from about 15 to about 35% resin solids dissolved in a mixture of a lower alcohol and water along with a strongly alkaline material present in a concentration equivalent from about 0.05 to about one mol of the alkaline material for each mol of the substituted phenol in the condensation resin.

By the process of this invention this solution of condensation resin is dispersed in the paper stock to form what may be essentially described as an emulsion whereby the resin solution forms the discontinuous phase and is present in droplets probably of colloidal dimensions.

In a co-pending application, Serial No. 788,369, filed January 22, 1959, there is disclosed the use of condensation resin products formed when certain substituted phenols are reacted with a formaldehyde source, put into solution and the solution applied to fibers and fabrics of natural or synthetic origin whether by immersion or surface coating.

This invention will be described in detail and with reference to the accompanying drawings in which:

FIG. 1 shows the relationship between the amount of condensation resin in the paper and the amount of water absorbed, the resin having been added in accordance with this invention; and

FIG. 2 shows the relationship between the amount of water absorbed and the wet dielectric strength of the resulting treated paper.

The condensation resin and its formation is first described and then the manner in which it is added to the paper stock is set forth.

The condensation resin product suitable for this invention is one which is formed by reacting a substituted phenol and a source of formaldehyde. The phenolic compound suitable for forming the condensation resin used in waterproofing according to the practice of this invention may be a mono- or di-substituted phenol, and the substituent groups may be in the ortho or para portions. The substituents may be saturated or unsaturated aliphatic groups having from 4 to 12 carbon atoms; or they may

be saturated or unsaturated cyclic groupings as long as such groupings do not result in the formation of a compound having conjugated unsaturation throughout its structure. If the phenol has two aliphatic substituents, the total number of carbon atoms in the two substituents should not be less than 4 nor greater than 12. Beyond the limit of a total of 12 carbon atoms the condensation reaction is extremely slow at the temperatures employed in forming the resin, while the methyl substituted phenols (mono- or di-) give a resin which when used in accordance with this invention is not adaptable to beater addition, and which results in undue embrittlement of the treated material. Monoethyl- and the propyl-substituted phenols are not known, at least they are not commercially available chemicals.

With regard to the cyclic substituents, it appears that if the resulting substituted phenol has conjugated unsaturation throughout (such as would result for example in the use of para-phenyl-phenol) there would occur active groups on the substituent which would interfere with the condensation reaction.

The substituted phenol may then generally be defined as a phenol having substituent radicals so placed that one or two $-CH_2OH$ groups supplied by the formaldehyde source may add to the phenol structure. The substituent radical groups on the phenol are selected from the group consisting of saturated and unsaturated aliphatic radicals having from 4 to 12 carbon atoms in any one aliphatic radical and from 4 to 12 total carbon atoms in two aliphatic radicals, and saturated and unsaturated cyclic hydrocarbon radicals which when joined to the phenolic ring do not result in the formation of a compound having conjugated unsaturation throughout.

This definition of the substituted phenols suitable for the practice of this invention eliminates the use of monomethyl substituted phenol (cresol) and of dimethyl phenol as well as monoethyl and the propyl substituted phenols. As pointed out above, the use of these results in excessive embrittlement of the material treated, and resins made with them are not suitable for beater addition. This definition therefore includes mono-substituted phenols having aliphatic substituents ranging from butyl to dodecyl and di-substituted phenols having aliphatic substituents ranging from diethyl to dihexyl. There appears to be a linear relationship between the chain length of the substituent group, in the case of aliphatics, and the final degree of waterproofing achieved. This linear relationship extends to propyl substituents but not to methyl, a fact which is in accordance with the usual differences in behavior existing between the first members of a homologous series and the higher members of the same group.

The source of formaldehyde may include formaldehyde, paraformaldehyde, trioxymethylene, hexamethylenetetramine or any other compound which will readily liberate formaldehyde at temperatures under about 200° F. It has been found that the higher aldehydes such as butyraldehyde and acetaldehyde are not practical reactants for this condensation reaction since the reaction does not proceed at any reasonable rate at the temperatures preferably employed.

In forming a condensation resin suitable for waterproofing paper in accordance with this invention it is necessary to form a resinous material which will, unlike normal phenol-formaldehyde resins, permit the paper to remain flexible. Therefore, the choice of the substituted phenol used in forming the condensation resin is important and to be distinguished from the phenol normally used in forming phenol-formaldehyde resins and from a mixture of substituted phenols and substantial amounts of unsubstituted phenols.

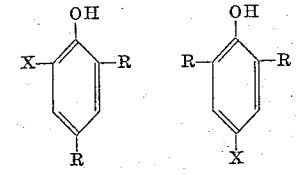
By substantial amounts of unsubstituted phenols is meant those quantities which will material effect the physical characteristics of the material, e.g., paper. Limiting the quantity of unsubstituted phenols does not, of course, preclude the incorporation of additives such as

resins, fillers, dyes, pigments, sizes and the like which are incorporated into the treated material for reasons other than waterproofing. The scope of this invention includes the incorporation of such additives.

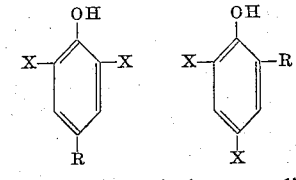
In condensing substituted phenols with formaldehyde a methylol phenol is formed by adding one or two

$$-CH_2OH$$

groups to the substituted phenol in ortho and/or para positions (the meta position will not react with formaldehyde). The possible mono-functional substituted phenols may be represented by



while di-functional substituted phenols may be represented by



where R represents the substituent radical as defined above and X represents the possible positions where the methylol group from the formaldehyde source may attach.

When di-functional phenols are used in the condensation reaction to form the paper-treating composition of this invention, the molar ratio of formaldehyde to substituted phenol may vary from about 2:1 to about 1:1. In reactions where mono-functional phenols are employed, this molar ratio may range from about 0.5:1 to about 1:1.

The condensation product which is used to waterproof the paper in accordance with the practice of this invention is prepared prior to its incorporation into the paper. The product is generally a viscous material and condensation is preferably carried out under moderate conditions of temperature and for periods which result in a resin which remains soluble in the lower alcohols and in acetone.

Moderate temperature conditions in the process of this invention may be further defined as ranging from about 150° F. to about 200° F. Condensation reactions carried out at room temperature do not give as satisfactory condensation products (with respect to waterproofing in this invention) as those carried out within the range specified. It is important that the final condensation resin to be used be soluble in acetone, for if it is carried out to the point where it is no longer soluble in acetone the resulting resin is not suitable for the treatment of paper to obtain the results desired.

In general the condensation product is formed by mixing the substituted phenol, the source of formaldehyde, a suitable catalyst and one of the lower alcohols, along with some water if desired. This mixture is then refluxed for a period ranging from about one-half to ten hours and at a temperature preferably below about 200° F., but above about 150° F. The temperature and time may be varied within these limits as long as the resulting condensation product remains soluble in acetone.

In the formation of the condensation product either an acidic or basic catalyst may be used. For example, it has been found equally acceptable to use strong bases such as sodium hydroxide, a milder base such as calcium hydroxide, or an acid such as hydrochloric. This wide choice of catalyst is apparently due to the nature of the linkages formed in the condensation reaction, i.e., few, if any cross-linkages are formed. Although it would

probably be possible to achieve the required condensation reaction without a catalyst, the catalyst is preferable if the reaction is to take place in a reasonable length of time in the required temperature range.

The condensation product resulting from the reaction of this invention may be handled in one of two ways. After the product has been formed it may be washed with water and then redissolved in a suitable solvent (acetone or the lower alcohols with or without some water) prior to its introduction into the paper stock. It is preferable, however, to use the reaction product as it is formed since it is not necessary to wash it and redissolve it. In this case, as will be seen in the following description, it is preferable to employ a strongly alkaline material for the reaction catalyst.

In any case the final resin which is added to the paper stock before it is laid must be a true solution of the condensation product made up in one of the lower alcohols or in acetone (usually along with some water) as a solvent. Moreover, the solution must contain from about 0.05 to about one mol of a strongly alkaline material (preferably sodium hydroxide) for each mol of substituted phenol present in the resin. If the concentration of the strongly alkaline material is less than the minimum specified, the resin will not be effective as a waterproofing agent; while if quantities which are substantially greater than that specified are used, the excess may impair some of the characteristics (e.g., dielectric strength) of the finally treated paper.

The solution which is added to the paper stock may also contain a small amount of water as long as none of the resin is precipitated out. The water may be added to reduce the cost of the resin solution. It is possible that water also causes a somewhat more rapid dispersion of the resin into the fiber stock. In determining the amount of water which can be added to the resin solution it is preferable to allow a margin of safety to compensate for alcohol evaporation and the like. The margin of safety may easily be determined by titrating a sample of resin dissolved in alcohol with water. Water tolerance of the resin is indicated when a milkiness is developed.

The requirement for the addition of the strongly alkaline material in the resin solution which is added to the paper stock makes it preferable to use a strongly alkaline material as the catalyst in the formation of the condensation resin, but as pointed out above, other catalysts are suitable in the actual formation of the resin.

The resin solution which is to be added to the paper stock may be further characterized as an alcohol, water-alcohol, acetone, or water-acetone solution of the resin condensation product in which the resin is present in concentrations equivalent to from about 15 to about 35% by weight resin solids with a preferable range from about 20 to about 25%. If the resin is present in concentrations over about 35%, it is difficult to get it properly dispersed on the paper fibers. If, on the other hand, solutions are used in which the resin is present in less than about 15%, there results a waste of solvent. The resin solution may further be characterized by the fact that it must contain from about 0.05 to about one mol of a strongly alkaline material for each mol of substituted phenol. Water may also be present in the solution in a quantity below that at which any of the resin will precipitate.

In order to make a dense paper with a good dielectric strength it is necessary to have the waterproofing material thoroughly and equally distributed throughout the entire thickness of the paper. The waterproofing material must also be deposited on the individual fibers in a way to effect maximum protection against the water. Good distribution and maximum protection are achieved by the resins of this invention and by the process by which these resins are applied.

The mechanism by which the process of this invention actually functions may not be fully understood. It is, however, known that it is necessary to disperse the resin solution in the paper stock in the form of very fine droplets, many of which are apparently of colloidal dimensions. In order to do this it appears necessary to introduce the resin in the form of a solution and to form an emulsion of the resin in the paper stock so that the resin solution is in effect the discontinuous phase and the water in the stock is the continuous phase. To form this type of emulsion it appears necessary to make up the resin solution with sufficient alcohol and a strongly alkaline material to furnish hydrophillic groups at the interface between the resin droplets and the water of the paper stock. When an exhausting agent is subsequently added the interface is broken and the resin in the solution is immediately attracted to the cellulosic fibers. It is believed that the role of the alcohol and the strongly alkaline material in the resin solution is one of furnishing these required hydrophillic groups.

The resin solution, as defined above, may be added to the paper stock at any point in the paper-making process before the actual formation of the paper, i.e., before the stock enters the paper machine. That is, it may be added in the beater, in the stock chest, or to the stock stream as proceeds to the paper machine. It is, however, preferable to add the resin in the beater inasmuch as it has been found that some agitation of the stock after resin addition achieves better mixing and better distribution of the resin on the fibers in the exhausting process.

Once the resin has been added to the paper stock and after the solution has been thoroughly dispersed to form the necessary emulsion, it is necessary to exhaust out the resin on the fibers. This is done by adding an acid to the stock before it gets on the paper machine. The acid acts to break the emulsion and deposit the resin on the fibers. The acid is preferably introduced in the form of so-called paper maker's alum (aluminum sulfate). This acid material is particularly well suited to the process of this invention because of the tendency of the trivalent aluminum ion to precipitate the resin and deposit it on the fibers. This is due to the electrostatic attraction which cellulose has for the aluminum ion. However, other acids such as acetic acid or a small amount of a strong mineral acid may be used.

The amount of resin or condensation product which is taken up by the paper to waterproof it in accordance with this invention may be varied from about 2 to about 40% by weight of the fiber in the paper. The preferred amount of resin pickup is from about 3 to 12% by fiber weight. Generally from about 75 to about 95% of the resin present in the stock is taken up by the fibers. The amount of resin which must be added to the stock may then be calculated to give the desired fiber pickup, knowing the concentration of the resin in the solution which is added to the stock.

After the condensation resin has been introduced into the stock and the paper laid, the paper is dried at normal paper-drying temperatures and then it may be compacted by calendering or glazing to obtain maximum densities. The paper may then be cured, conveniently from about one-quarter to about three hours at about 275 to about 400° F. Curing apparently achieves chemical bonding between the resin and the cellulose molecules as well as cross-linking of the resin. Thus the resin introduced into the paper becomes an integral part of it and imparts permanent waterproof characteristics to it.

The curing step may be postponed, for the compacted paper may be stored indefinitely and cured at any convenient time or step in later processing or use. Compacting by calendering or glazing may be carried out after the curing step, although this is not the preferred process order.

The resulting treated paper after curing is flexible, exhibits especially low water absorption and has a very high dielectric strength even when exposed to or im-

mersed in water for an extended period of time. This invention may be further described in the following examples which are meant to be illustrative and not limiting.

EXAMPLE I

Eighty-two grams of para-tertiary-butyl phenol (100%), 3.0 grams NaOH (96%), 90.4 grams of formalin (37% formaldehyde), 200 grams of water and 200 grams of isopropyl alcohol were mixed and refluxed for 6 hours at 186° F. The amount of NaOH present was equivalent to 0.13 mol NaOH for one mol para-tertiary-butyl phenol. The resulting solution of the condensation resin product was cooled and used with no further modification or treatment.

This solution was added with rapid stirring to the water slurry of the beater containing 2% by weight refined rag fiber stock. Concentrations were adjusted so that there were present 33 parts by weight of resin solids added to 100 parts by weight of pulp solids. After the resin solution and paper stock had been thoroughly emulsified, the resin was exhausted out onto the fibers by adding paper maker's alum (aluminum sulfate). The stock containing the treated fibers was then introduced into a paper machine and a hand sheet of paper made. It was dried on a drum drier maintained at about 220° F. and then cured for one hour at 300° F. When samples of this treated paper were immersed in water at 70° F. for four hours, there resulted 13% water pickup by the treated paper. This compared with 100 to 110% water pickup by an untreated control sample.

Dielectric strengths were measured in accordance with the specifications and method of ASTM test D–149–55T (Section 15A Short Time Test). The treated sample of this example had a dry dielectric strength of 450 volts/mil and a wet dielectric strength of 200 volts/mil compared to 550 volts/mil and zero, respectively, for the untreated control. Wet dielectric strength measurements were made immediately after the samples were removed from the four-hour water immersion.

EXAMPLE II

A condensation resin was made up as in Example I to the point where the solution after refluxing was cooled. The product was then washed with water, and redissolved in a mixture of 250 grams of isopropyl alcohol and 150 grams of water along with 5 grams of NaOH. This solution was added to a water slurry of refined rag fiber stock as in Example I. The paper made from this stock after drying, calendering and curing exhibited dry and wet dielectric strengths similar to the papers of Example I.

A number of other substituted phenols and formaldehyde sources were reacted in varying ratios to give condensation resins suitable for treating paper to render it waterproof in accordance with the practice of this invention. Rag paper samples containing from about 5 to about 14% of these resins were then tested for water absorption and dielectric strengths as described in Example I.

Methyl alcohol, ethyl alcohol and isopropyl alcohol were used as reaction media and solvents, the isopropyl being preferred for health, safety and economic reasons. The amount of resin solids in the solutions which were emulsified in the aqueous paper-making stock varied from 15 to 30% by weight. In the example in which HCl was used as a catalyst in the condensation reaction, NaOH was added to provide the required amount of strongly alkaline material in the resin solution before it was added to the paper stock.

The amount of water absorption, based on fiber weight, and the wet dielectric strengths of the paper samples are given in Table 1.

TABLE 1

Water Absorption and Wet Dielectric Strength Measurements for Paper Samples Treated With Condensation Resins Formed by Reacting a Substituted Phenol and a Formaldehyde Source

Substituted Phenol	Formaldehyde Source	Molar Ratio, HCHO/C_6H_5OH	Catalyst	Reflux Temp., ° F.	Reflux Time, Hrs.	Percent Resin Based on Fiber	Percent Water Absorption	Wet Dielectric Strength,[1] volts/mil
p-octyl phenol	formalin	2:1	NaOH	188	6	8.1	13.3	230
p-dodecyl phenol	do	2:1	NaOH	186	6	9.1	17.5	115
dinonyl phenol	do	1:1	NaOH	186	6	unworkable		
p-phenyl phenol [2]	do	2:1	NaOH	182	4	8.5	11.2	250
α-phenyl-p-cresol	do	2:1	NaOH	182	6	5.3	13.5	230
p-cyclohexyl phenol	do	2:1	NaOH	180	6	5.6	19.0	100
p-nonyl phenol	do	1:1	NaOH	188	6	5.5	19.8	100
p-tertiary-amyl phenol	m-butyraldehyde.	2:1	NaOH	185	6	unworkable		
Do	paraldehyde	2:1	NaOH	184	6	do		
Do	formalin	2:1	HCl	186	6	5.8	13.5	230
p-tertiary-butyl phenol	do	2:1	NaOH	186	5	5.0	15.1	250
Do	trioxane	2:1	NaOH	181	5	8.1	8.4	300
o-secondary-amyl phenol	formalin	2:1	NaOH	185	4	11.7	16.2	130
di-secondary-butyl phenol	do	1:1	NaOH	184	5	13.7	24	60
Control						0	100	0

[1] After 4-hour immersion in water at 70° F.
[2] Gave a very brittle sheet because of cross-linking due to conjugated unsaturation.

A wide variation in substituted phenols falling within the definition given is illustrated in the above tabulation. Likewise the use of formaldehyde sources other than formalin are illustrated in the employment of trioxane, and the use of an acid catalyst is also shown.

The above table also indicates that dinonyl-phenol, wherein the total number of carbon atoms in the substituent groups is greater than 12, and p-phenyl phenol, which results in the formation of a condensation reaction product having conjugated unsaturation throughout, are unsuitable. Finally, the unsatisfactory behavior of n-butyraldehyde and paraldehyde is illustrated, due to the fact that they are unable to react under the operating conditions specified.

The performance of paper treated in accordance with the practice of this invention is further illustrated in FIG. 1 in which percent water absorption by the paper is plotted against percent condensation resin based upon fiber weight. The substituted phenols were p-tertiary-butyl phenol and nonyl-phenol.

The effect of such treatment on preventing water absorption by the paper is shown to increase with increasing amounts of condensation resin until it is present in the paper from about 4 to 8 percent by fiber weight. Over this amount the increase in hydrophobic properties of the paper begins to level off. This is particularly im-

portant since it shows that a relatively small amount of the condensation resin achieves a marked decrease in water absorption by the paper containing it. This means that the paper retains its flexibility and its other inherent paper characteristics.

FIG. 2 shows the direct relationship between the amount of water absorbed by a paper and its wet dielectric strength. The data in FIG. 2 are expressed as ranges since it can be appreciated that these parameters will vary within a range for different materials treated.

From the above examples, tabulation and figures, it will be seen that it is desirable to reduce water absorption particularly in paper to below about 30% and preferably to below about 22% if good wet dielectric strengths are desired. These figures correspond to about 40 and 100 volts/mil, respectively, wet dielectric strengths. In order to formulate papers in accordance with this invention, which will exhibit these wet dielectric strengths it is desirable to introduce sufficient of one of the suitable condensation resins so that the resin is present in the paper in a range from about 2% to 40% by weight of fibers and preferably from about 3% to 12% by weight of fibers.

Paper treated in accordance with the practice of this invention remains flexible and can be easily handled, folded, cuffed for insulation without fracturing and can generally be treated as any other normal type heavy paper. This treated paper is particularly well suited for splashproof motor insulation and for any other applications where a minimum amount of water should be absorbed by the paper even when completely immersed in water.

We claim:

1. An aqueous stock of paper-making fibers, characterized by containing dispersed therein in the form of a discontinuous phase a condensation resin introduced as a solution, said resin being formed by the step of reacting a formaldehyde source and a substituted phenol under refluxing conditions at a temperature below about 200° F. to form a condensation resin soluble in acetone, said substituted phenol having substituent radicals so placed that not more than two methylol radicals of said formaldehyde source can add to said substituted phenol, said substituent radicals being selected from the group consisting of saturated and unsaturated aliphatic radicals having a total of between 4 and 12 carbon atoms and saturated and unsaturated cyclic hydrocarbon groups which when joined to the phenolic ring do not result in the formation of a compound having conjugated unsaturation throughout, said solution of said resin comprising from about 0.05 to one mol of a strongly alkaline material for each mol of said substituted phenol present, from about 15 to about 35% resin solids by weight of said solution and a mixture of a lower monohydric alcohol and water as a solvent, the quantity of said water in said mixture being less than that which will precipitate out said resin.

2. An aqueous stock of paper-making fibers, characterized by containing dispersed therein in the form of a discontinuous phase a condensation resin introduced as a solution, said resin being formed by the step of reacting a formaldehyde source and a substituted phenol under refluxing conditions at a temperature below about 200° F. to form a condensation resin soluble in acetone, said substituted phenol having substituent radicals so placed that not more than two methylol radicals of said formaldehyde source can add to said substituted phenol, said substituent radicals being selected from the group consisting of saturated and unsaturated aliphatic radicals having a total of between 4 and 12 carbon atoms and saturated and unsaturated cyclic hydrocarbon groups which when joined to the phenolic ring do not result in the formation of a compound having conjugated unsaturation throughout, said solution of said resin comprising from about 0.05 to one mol of a strongly alkaline material for each mol of said substituted phenol present, from about 20 to about 25% resin solids by weight of said solution and a mixture of a lower monohydric alcohol and water as a solvent, the quantity of said water in said mixture being less than that which will precipitate out said resin.

3. An aqueous stock in accordance with claim 2 wherein said substituted phenol is nonyl-phenol.

4. An aqueous stock in accordance with claim 2 wherein said strongly alkaline material is sodium hydroxide.

5. Method of forming a paper stock from which waterproofed paper may be formed, comprising the steps of thoroughly dispersing a solution of a condensation resin in an aqueous paper-making stock containing fibers thereby forming an emulsion of said resin in said stock, said solution being the discontinuous phase of said emulsion, said condensation resin being formed by the step of reacting a formaldehyde source and a substituted phenol under refluxing conditions at a temperature below about 200° F. to form a condensation resin soluble in acetone, said substituted phenol having substituent radicals so placed that not more that two methylol radicals of said formaldehyde source can add to said substituted phenol, said substituent radicals being selected from the group consisting of saturated and unsaturated aliphatic radicals having a total of between 4 and 12 carbon atoms and saturated and unsaturated cyclic hydrocarbon groups which when joined to the phenolic ring do not result in the formation of a compound having conjugated unsaturation throughout, said solution of said resin comprising from about 0.05 to one mol of a strongly alkaline material for each mol of said substituted phenol present, from about 15 to about 35% resin solids and a mixture of a lower monohydric alcohol and water as a solvent, the quantity of said water in said mixture being less than that which will precipitate out said resin.

6. Method of making a waterproofed paper, comprising the steps of thoroughly dispersing a solution of a condensation resin in an aqueous paper-making stock containing fibers thereby forming an emulsion of said resin in said stock, said solution being the discontinuous phase of said emulsion, said condensation resin being formed by the step of reacting a formaldehyde source and a substituted phenol under refluxing conditions at a temperature below about 200° F. to form a condensation resin soluble in acetone, said substituted phenol having substituent radicals so placed that not more than two methylol radicals of said formaldehyde source can add to said substituted phenol, said substituent radicals being selected from the group consisting of saturated and unsaturated aliphatic radicals having a total of between 4 and 12 carbon atoms and saturated and unsaturated cyclic hydrocarbon groups which when joined to the phenolic ring do not result in the formation of a compound having conjugated unsaturation throughout, said solution of said resin comprising from about 0.05 to one mol of a strongly alkaline material for each mol of said substituted phenol present, from about 15 to about 35% resin solids and a mixture of a lower monohydric alcohol and water as a solvent, the quantity of said water in said mixture being less than that which will precipitate out said resin, acidifying said emulsion whereby said resin is exhausted out onto said fibers, introducing the resulting stock to a paper machine to form paper, and drying said paper.

7. Method of making a waterproofed paper, comprising the steps of thoroughly dispersing a solution of a condensation resin in an aqueous paper-making stock containing fibers thereby forming an emulsion of said resin in said stock, said solution being the discontinuous phase of said emulsion, said condensation resin being formed by the step of reacting a formaldehyde source and a substituted phenol under refluxing conditions at a temperature below about 200° F. to form a condensation resin soluble in acetone, said substituted phenol having substituent radicals so placed that not more than two methylol radicals of said formaldehyde source can add to said

substituted phenol, said substituent radicals being selected from the group consisting of saturated and unsaturated aliphatic radicals having a total of between 4 and 12 carbon atoms and saturated and unsaturated cyclic hydrocarbon groups which when joined to the phenolic ring do not result in the formation of a compound having conjugated unsaturation throughout, said solution of said resin comprising from about 0.05 to one mol of a strongly alkaline material for each mol of said substituted phenol present, from about 15 to about 35% resin solids and a mixture of a lower monohydric alcohol and water as a solvent, the quantity of said water in said mixture being less than that which will precipitate out said resin, acidifying said emulsion whereby said resin is exhausted out onto said fibers, introducing the resulting stock to a paper machine to form paper, drying said paper, and curing it at temperatures ranging between 275 and 400° F.

8. Method in accordance with claim 7 including the step of compacting said paper subsequent to said drying to maximize its density.

9. A condensation resin product suitable for adding to papermaking stock to render the resulting paper made therefrom waterproof, said resin being formed by the steps of reacting a formaldehyde source and a substituted phenol for from about one-half to about ten hours in a lower alcohol in the presence of a catalyst at temperatures between about 150 and 200° F. under refluxing conditions to form a condensation resin soluble in acetone, said formaldehyde source and said substituted phenols being present in molar ratios ranging from about one-half mol of formaldehyde to one mol of said substituted phenol to about two mols of formaldehyde to one mol of said substituted phenol, said substituted phenol having substituent radicals so placed that not more than two methylol radicals of said formaldehyde source can add to said substituted phenol, said substituent radicals being selected from the group consisting of saturated and unsaturated aliphatic radicals having a total of between 4 and 12 carbon atoms and saturated and unsaturated cyclic hydrocarbon groups which when joined to the phenolic ring do not result in the formation of a compound having conjugated unsaturation throughout.

10. Condensation resin in accordance with claim 9 wherein said substituted phenol is nonyl-phenol.

11. Condensation resin product in accordance with claim 9 wherein said formaldehyde source is formalin.

12. A waterproof paper characterized by having chemically bonded to substantially all of the fibers thereof a condensation resin present in an amount ranging from about 2 to about 40% by fiber weight, said resin being formed by reacting a formaldehyde source and a substituted phenol under refluxing conditions at a temperature below about 200° F. to form a condensation resin soluble in acetone, said substituted phenol having substituent radicals so placed that not more than two methylol radicals of said formaldehyde source can add to said substituted phenol, said substituent radicals being selected from the group consisting of saturated and unsaturated aliphatic radicals having a total of between 4 and 12 carbon atoms and saturated and unsaturated cyclic hydrocarbon groups which when joined to the phenolic ring do not result in the formation of a compound having conjugated unsaturation throughout, said resin being introduced in said paper by the steps of thoroughly dispersing a solution of said resin in an aqueous paper making stock containing fibers thereby forming an emulsion of said resin in said stock, said solution of said resin comprising from about 0.05 to one mol of a strongly alkaline material for each mol of said substituted phenol present, from about 15 to 35% resins solids and a mixture of a lower monohydric alcohol and water as a solvent, the quantity of said water in said mixture being less than that which will precipitate out said resin; acidifying said emulsion whereby said resin is exhausted onto said fibers, introducing the resulting stock into a paper machine to form said paper, and drying said paper.

13. Paper formed in accordance with claim 12 wherein said fibers are refined rag fibers formed into a dense sheet.

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