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PAPER SIZING

Louis Leonard Larson, Wilmington, Del., assignor
to E. I. du Pont de Nemours & Company, Wil-
mington, Del., a corporation of Delaware

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This invention relates to the art of sizing and waterproofing, and more particularly to an improved process for sizing paper.

Various methods and materials have been used and suggested in the art of sizing paper for the purpose of increasing its water resistance, as in beater sizing, or in the case of surface sizing to improve the finish, writing qualities and printing properties of the paper. For beater sizing the sizing material now commonly used is an alkaline dispersion of rosin with alum as the precipitating agent. Rosin size, however, has the disadvantage of causing discoloration and degradation of paper with age. Also, the degree of water resistance that can be obtained with rosin is inadequate for many applications for paper. For surface sizing the commonly used materials are solutions of animal glue and starches. These solutions, however, do not materially increase the water resistance of the sheet. Solutions of starches containing emulsified wax have been used to a certain extent, especially in calender sizing, the wax ingredient improving the finish and water resistance. The use of wax in this connection has not been successful because the wax emulsion tends to break. The agglomerated particles of precipitated wax cause operating troubles on the calender and produce wax spots on the surface of the sheet.

It has also been proposed to use water soluble salts of polyhydric alcohol-polycarboxylic acid resins, including stearic acid modified resins of this kind, for impregnating paper. The resins heretofore proposed, however, are incapable of accomplishing the objects of the present invention.

An object of this invention is to provide improved processes for sizing absorbent material and particularly for sizing paper. Another object is the production of an improved paper product. Another object is the production of sized paper in which the size does not discolor or degrade the paper with age. A further object is to provide an economical process for improving the water resistance, finish, printing properties, and softness of "waterleaf" (unsized) or rosin-sized paper. A

still further object is to provide surface sizes that have improved working properties, especially when used in calender water-boxes. Other objects will appear hereinafter.

These objects are accomplished by the following invention which, in its preferred embodiment, consists in treating paper pulp before sheet formation, or in treating the surface of a sheet of paper with water emulsions of certain modified polyhydric alcohol-polycarboxylic acid resins.

I have discovered that the water resistance imparted to paper by sizing it with emulsified polyhydric alcohol-polycarboxylic acid resins is remarkably increased if the resin, from which the water emulsion is made, is prepared from certain percentages of a saturated monocarboxylic aliphatic acid and by processes hereinafter disclosed, as a modifying agent, and if the resin is prepared to yield a product with low acid number within stated limits. Any of the processes well known to the art may be used for preparation of the resin, although I prefer the fusion method whereby the ingredients are heated together at a sufficiently high temperature until the proper acid number has been reached. The emulsion of the resin is prepared by neutralizing a definite percentage of the resin acidity with an alkali in a suitable amount of water. In using these emulsions for sizing paper, I may use beater sizing by adding the water dispersion of the resin to the paper pulp in the beater prior to sheet formation, or I may apply the water dispersion of the resin to the surface of the paper sheet with a size press or with tub sizing equipment. In the present process, effective surface sizing is also obtained by the practical and economical method of applying the resin to the surface of a sheet during the calendering operation. In this process the water dispersion of the resin is placed in the calender water-boxes which are used for producing water-finished paper. The use of the water dispersion of the resin in place of water in the boxes gives a strongly sized as well as a highly finished sheet.

The saturated monocarboxylic aliphatic acids

used in partial replacement for the polybasic acid in the esterification of the polyhydric alcohol for the synthesis of the resin are defined as acyclic acids of the general formula $R-COOH$ where R is an alkyl radical containing not less than 15 carbon atoms. R is preferably a straight chain radical, such as that of a saturated fatty acid containing 16 or more carbon atoms. I prefer to use stearic acid because of economical reasons and because of the superior results obtained. The proportion of combined polyhydric alcohol ester of the saturated fatty acid is of primary importance in order to accomplish the objective of producing a very water resistant sheet of paper by the application of relatively small amounts of the resin. High water resistance cannot be developed if the saturated fatty acid ester content is too low, and above a certain content the effectiveness of the resin gradually decreases. The content of combined polyhydric alcohol ester of the fatty acid should be 65% or more and should be kept below 90%. Therefore, in order to realize the advantages of this invention, only a comparatively narrow range of resinous compositions can be used. To express this range I have used throughout the present specification and claims the terminology "combined polyhydric alcohol ester of a saturated fatty acid of the formula $R-COOH$ ".

It will be understood that the total percentage of polyhydric alcohol ester of saturated fatty acid and polyhydric alcohol ester of polybasic acid will in each instance be 100% and that these two esters do not separately exist in the finished resin as such. This generalization is merely a convenient means of calculating the percentages of the various ingredients which go into the formation of the resin.

In the case of the preferred ingredients (stearic acid as the saturated fatty acid, glycerol as the polyhydric alcohol and phthalic anhydride as the polybasic acid) these percentages of combined polyhydric alcohol ester of the fatty acid correspond to a percentage of stearic acid in the ingredient formula (as distinguished from the ester formula) of preferably 58-70%, not less than 50%, the upper limit being not much above 75% and in any event under 80%. For a chosen amount of stearic acid, the proportion of glycerol and phthalic anhydride in the ingredient formula is fixed in accordance with recognized stoichiometrical calculations.

I have discovered, not only that the amount of the modifying acid must be kept within the limits defined above, but also that the acid number of the resin must be within a certain range to accomplish the objects of the invention. As will be understood by those skilled in the art, the acid number decreases as the esterification is carried toward completion. Acid number is defined as the milligrams of KOH required to neutralize one gram of resin. If the acid number is too high the resin does not develop water resistance. If the acid number is too low it is difficult to prepare very stable emulsions. The preferred acid number of the resin is 40-55, the maximum is about 64 and the minimum is about 25. An essential feature of this comparatively low acid number is that in using the resin as a surface size it is not necessary to treat with alum or some other precipitant to develop high water resistance. This is important in surface sizing because it eliminates an added operation and does not require the use of alum or acids which are known to degrade paper seriously.

A typical example of a suitable resin and its method of preparation follows:

Resin A

	Parts by weight
Glycerol.....	15.60
Phthalic anhydride.....	20.18
Stearic acid.....	64.22
	100.00

The ingredients are heated together with stirring in a suitable vessel, the temperature being carried to 200° C. over a period of one hour, then maintained at this point until an acid number of 47 has been reached. This requires approximately 2½ hours.

The preferred method of converting the resin into an aqueous emulsion, defined here as a dispersion of very fine particles of the resin in water, is as follows: 100 parts of Resin A at 100° C. and 61.0 parts of a 5% solution of sodium hydroxide at 60° C. are added simultaneously and in proportionate rates to 349 parts of water at 60° C., with rapid agitation during the mixing operation. The alkali solution should be added slightly in advance of the resin, and the emulsion should be stirred for a few minutes after the mixing operation has been completed. This gives a 20% emulsion of the resin. The amount of sodium hydroxide used in preparing the emulsion is insufficient to neutralize completely the titratable acid in the resin. The resin is therefore not present in the water in complete solution, but as an emulsion, i. e., it is largely in the form of a physical dispersion in the water. This is a very substantial difference from those cases in which the resin is completely neutralized, as in the prior art. The suitability of the present emulsions enables one to use resins which are carried to a lower acid number and, hence, a more complete resinification. Lower acid numbers and higher resinification are necessary to give the improved water resistance when applied for the purposes of this invention. High acid number resins require alum in addition to alkali to develop their maximum water resistance; the use of more completely esterified products obviates this disadvantage. The emulsion can be diluted with warm water to any desired concentration. This emulsion is referred to hereafter as Resin A size emulsion. An important feature of the emulsion is its excellent stability, which is a property required in size solutions and emulsions used in the paper industry. The emulsion may be prepared by any of the procedures well known to the art. I prefer to use the neutralization method, whereby the emulsion is formed by neutralizing not more than 95% nor less than 50% of the acidity of the resin with an alkali in the presence of a suitable amount of water. The amount of alkali is important because the emulsion must be nearly neutral to obtain the best results. Although either sodium hydroxide or ammonium hydroxide is preferred, other alkalies such as trisodium phosphate, sodium silicate, etc., can be used. Organic amines such as methyl amines, butyl amines, triethanolamine, etc. can be used.

Resins of the above type have been found to be particularly effective as sizes for paper. The amount of resin applied to the paper may vary from 0.24-10.0% by weight of the paper, depending on the application for which the paper is intended. In general, the most practical amount is 0.5-2%. On the other hand, amounts greater than 2% or less than 0.25% can be applied for

special purposes. The amount of emulsion applied to the sheet is governed accordingly by the concentration of the resin emulsion, by the process used for sizing the sheet, and the nature of the product. The process for sizing may be any one of the several that are used in the industry.

Paper is surface-sized with the resin on what is known in the paper industry as a size press. The paper is passed under a roll to submerge it in a size solution, then between press rolls to remove excess size emulsion and to produce an evenly sized surface and then it is passed into a loft or over a nest of driers to dry the sheet. This operation is frequently carried out during the manufacturing of the paper by locating the size press on the drier. The paper is formed on a Fourdrinier or a cylinder paper machine and it is then passed onto the drying cans. The size press is located at a point where the paper is approximately 60% bone dry. After the size emulsion is applied on the size press, the sheet passes over several additional drying cans, then through the calenders and onto the wind-up reel. The concentration of the size emulsion is regulated to give 0.25-2% of resin based on the dry weight of the paper, depending upon the degree of size required in the sheet. For best results the bath of the resin emulsion should be maintained at 50-60° C., although the process is not limited to this temperature range.

The sheet coming to the size press may be either unsized or rosin-sized paper. The latter means paper that has been sized by treating pulp with rosin before sheet formation by procedures well known to the art. A feature of my process of surface sizing with Resin A described above is that it enables the production of more highly waterproofed paper than can be obtained by sizing with rosin alone. It is well known in the art that the water resistance of rosin-sized paper reaches a maximum at approximately 3-4% of rosin based on the weight of the paper. This maximum can be doubled at least by surface sizing the sheet with the resins disclosed herein. It is also known in the industry that the use of high amounts of rosin, say greater than 2%, causes operating troubles on the paper machine. Also, it is known that the alum used to precipitate the rosin size accelerates corrosion in the Jordan engine and pipe lines and that it degrades the paper to a serious extent on aging. Consequently, another feature of surface sizing with the resins described herein is that their emulsions have good working properties in contrast to very poor working properties of rosin size.

I have discovered that the size emulsions can be used in water-boxes on a stack of calenders without any operating troubles. Consequently, a very practical and economical method of surface sizing paper with the resin is its application during the calendering operation. The common procedure for calendering is to pass the sheet as it comes from the drier through one or two stacks of calenders. The size emulsion can be applied to either one or both surfaces on the first stack of calenders, as follows: On a seven-roll stack of calenders, for example, the emulsion is fed from a water-box onto the fifth roll down from the top of the stack. This roll carries the emulsion to the surface of the paper as the sheet passes through the fourth nip. Another water-box may be located on the next lower roll for applying the emulsion to the other side of the sheet. Following this first stack of calenders, the sheet is generally passed through another

stack of calenders in order to obtain a higher finish and to dry the sheet. The concentration of the size emulsion in the water-boxes may vary from 0.5-4.0%, or higher. The temperature of the emulsion should be between 50° C. and 80° C. to obtain the best results. It is possible by this process to apply as much as 2% of resin based on the weight of the paper.

The procedure for beater sizing paper with the resin is different from the surface sizing processes, and is as follows: The pulp is beaten in a paper-beater until it is nearly ready to form into a sheet on any standard type of paper machine. The size emulsion is then added to the beater and the beating is continued for a sufficient length of time to disperse the size intimately in the pulp. Any of the common size precipitants known in the art, such as alum for example, is then added with the result that the size is uniformly deposited in a finely divided state onto the surface of the fibers. I prefer to use alum as the precipitant, which is added until the pulp has an acidity of pH 4.8. The preferred amount of size is 2% by weight based on the fiber, although satisfactory results can be obtained with as little as 0.25% and as much as 10% or more can be used. The sized pulp is formed into a sheet and dried on any standard paper making machine.

The following examples are given to illustrate the process of sizing paper with the emulsions and the properties of the sized sheets.

Example I

This example illustrates the sizing of paper pulp before sheet formation with Resin A.

A beater was charged with high alpha cellulose chemical wood pulp at 3% consistency; i. e., three parts of fiber to 97 parts of water. The pulp was beaten until sufficiently hydrated for sheet formation. For every 100 parts of fiber there was added 66.6 parts of a 3% Resin A size emulsion prepared as described above. After the size emulsion was intimately mixed with the pulp, aluminum sulfate was added until the pulp had an acidity of pH 4.8. Sheets were formed by means of a hand mold, pressed between wool felts, and dried at 100°-110° C. Sheets weighing 7.5 g./10" x 10" area were used for test purposes.

The paper thus sized has the unusual and valuable properties of high water resistance, permanence of strength and color, and improved resistance to size destruction by alkali. To illustrate, the water resistance, measured by the well known dry indicator method, was 40% greater than paper sized with an equal amount of rosin. The permanence of color and strength of the paper was not affected by the size, whereas paper sized with rosin was discolored and weakened by accelerated aging for three days at 100° C. in an atmosphere of air, and also by exposing to ultraviolet light from a carbon arc for 24 hours.

If it is desired to increase the strength of the sheet this may be done by the addition of starch or casein to the pulp without impairing the important properties of high water resistance and permanence of color and strength. The process for using starch follows: In the above example, 100 parts of a 2% solution of cornstarch (prepared by mixing 2 parts of starch with 2 parts of cold water and adding this paste to 96 grams of water at 180° F.) was added to the pulp before addition of the size emulsion. The size emulsion and alum were then added as above. An example for the use of casein follows: 2 parts of casein

was dissolved by first wetting it with 6 parts of water, then adding 2 parts of a 5% solution of sodium hydroxide, and then diluting with water to a total of 100 parts. This solution was added to the pulp in the beater and then the size emulsion and alum were added as above. The amount of starch or casein can be varied in accordance with the properties desired in the sheet.

Comparable results are obtained by surface sizing paper formed from high alpha cellulose chemical wood pulp or cotton rag pulp with the resin. In this case, the pulp is formed into the sheet without the addition of any size in the beater, then the sheet is dried and sized with a 2% Resin A size emulsion by means of a size press as previously described.

Example II

This example illustrates the sizing of paper with Resin A by the procedure known as tub sizing.

A sheet of kraft liner paper (0.009" thick) was passed through a bath of the resin size emulsion, then through squeeze rolls to express the excess size emulsion from the surface of the sheet, and then dried on a drying can at 100–110° C. The concentration of the size emulsion was 0.5%. The temperature of the bath was 50° C. The sheet, 10" x 10" in area, weighed 8.00 grams before sizing, 17.50 grams after sizing and passing through the squeeze rolls, and 8.05 grams after sizing and drying. The resin content of the sized sheet was 0.6% based on the dry weight of the paper.

The water resistance of the sheet, measured by the dry indicator method, was increased from 2 seconds to 194 seconds by application of the resin.

Example III

Resin B:	Parts by weight
Glycerol.....	14.19
Phthalic anhydride.....	15.17
Stearic acid.....	70.64
	100.00

These ingredients were heated together in a vessel with stirring. The temperature was raised to 200° C. in one hour, and the reaction mixture was held at this temperature until an acid number of 47 had been reached (approximately 2½ hours). The resin was converted into an aqueous emulsion by adding 100 parts of the resin at 100° C. and 63.7 parts of 5% sodium hydroxide solution at 60° C. to 344 parts of water at 60° C., in accordance with the procedure given for preparation of Resin A size emulsion. The emulsion was diluted to the desired concentrations by adding warm water (60° C.). This emulsion is referred to below as Resin B size emulsion.

The sizing operation was carried out on a 196"

Fourdrinier paper machine equipped with two stacks of calenders. The machine was operated at 346 feet per minute and was producing 7,000 pounds of 70 pound basis weight kraft paper per hour. The basis weight is the weight of 480 sheets, 24" x 36" in area. The kraft pulp, made by the kraft process from southern pine, was treated in the beater with rosin size, starch, and dyes by procedures well known to the art. Alum was added to the headbox. The pulp water after treatment with alum had an acidity of pH 6.0.

The Resin B size emulsion was applied to the surface of the sheet on the calenders as follows: A 4% Resin B size emulsion at 70° C. was fed from a 250-gallon tank to the water-boxes, which were located on the fifth and sixth rolls of the first stack of calenders (7-roll stack). The water-boxes fed the size emulsion to the calender rolls, which in turn fed the size emulsion to the surface of the sheet as it passed between the fourth and fifth nips. This sized both sides of the sheet. Following the first stack of calenders, the sheet passed through the second stack of calenders and then onto the wind-up reel. 410 pounds of the 4% emulsion of the resin was applied per ton of paper. The finished sheet contained, therefore, 0.82% size based on the weight of the paper.

Resin B size emulsion operated very well in the water-boxes and on the calender rolls. The sheet was very evenly sized and free from wax spots and mottled appearance. The size emulsion did not foam excessively or cause sticking of the sheet on the calender rolls.

The water resistance of the sheet was increased 150% by this treatment. The resin-sized sheet had a softer and more leather-like feel, brighter color, improved scuff-resistance, and lower porosity than the untreated sheet. The tearing strength was not changed; the Mullen bursting strength and the tensile strength were lowered approximately 10%.

A 4% Resin B size emulsion applied on only one side of the sheet, by using one instead of two water-boxes, gave an improvement of 80% in the water resistance of the sheet. The application of a 2% emulsion of the resin on one side of a 50-pound kraft paper increased its water resistance 75%. In this case the amount of resin applied was 0.31% based on the weight of the paper.

The addition of starch or casein to the size emulsion of the resin improves the finish and grease-resistance of the paper. The size emulsion may contain as high as 3% of starch or casein. Low-viscosity starches should be used for calender sizing.

The following table gives the properties of rosin-sized kraft paper surface-sized on the calenders with Resin B size emulsion:

60				Properties of sized sheet					60
	Size emulsion	Sides treated	Pounds of size solids per ton of paper	Basis weight	Water resistance ¹	Mullen tearing strength			Porosity ²
						Percent ³	Percent ³ M. D.	Percent ³ C. D.	
65	4% Resin B.....	2	16.3	74	110	89.2	282	298	37
	4% Resin B.....	1	9.0	74	84	92.0	275	298	30
	Control (untreated paper)			72	44	104.0	268	292	17
70	2.2% Resin B.....	1	6.2	51	36	95.0	241	273	114
	2.2% Resin B—2.8% Starch.....	1	13.9	50	31	90.0	260	289	81
	Control (untreated paper)			51	19	100.0	251	295	21

¹ Water resistance is given in seconds as determined by the standard dry indicator method.

² Percent Mullen or percent tearing strength is actual Mullen or tearing strength divided by basis weight times 100.

³ Porosity is given in seconds for 100 cc. displacement of air using the Gurley densometer.

As indicated above, the invention may be carried out with acids other than stearic acid which conform to the formulæ given above for the saturated monocarboxylic aliphatic acids. Thus, an emulsion of a resin of acid number 45 prepared from 16.66% glycerol, 21.55% phthalic anhydride and 61.79% palmitic acid (which corresponds to an "ester formula" of 70% palmitic glyceride and 30% glyceryl phthalate), when used for sizing paper in accordance with the process of Example I, produces a paper having a water resistance 25% greater than paper sized with an equal amount of rosin. Other suitable acids of this type are margaric, nondecylic, arachidic, behenic, lignoceric, cerotic, melissic, or mixtures thereof. Suitable mixtures are obtainable by saponification of completely hydrogenated fatty oils, or other saturated glycerides and esters generally whose acid radical or radicals consist of fatty acids of more than 15 carbon atoms. Any acid, or mixture of acids, of the formula $R-COOH$, regardless of source, is suitable if R is an alkyl radical of more than 15 carbon atoms. It will be understood by those skilled in the art that when stearic acid is replaced by palmitic or the other monocarboxylic acids mentioned, the replacement is upon the basis of recognized stoichiometrical calculations. As the polyhydric alcohol, instead of or in addition to glycerol, I may use ethylene glycol and higher homologs; diethylene glycol and other polyglycols; polyglycerols; triethanolamine; pentaerythritol; partial ethers and esters of glycerol such as monobenzylin, monoethylin, etc.; polyvinyl alcohol; or mixtures thereof. Instead of or in addition to phthalic anhydride, I may use succinic, adipic, sebacic, azelaic, fumaric, itaconic, suberic, tartaric, citric, dilactylic, thiodilactylic, salicylacetic, chlorophthalic, diphenic, naphthalic, pyromellitic, trimesic, tricarballic acids, or mixtures thereof. Polycarboxylic acids which tend to decompose on resinification, such as oxalic and malonic, are not generally suitable. Regardless of which particular polyhydric alcohol, polybasic acid, or saturated fatty acid is chosen for the synthesis of the resin, the critical percentage of combined polyhydric alcohol ester of the fatty acid remains the same, viz., 65-90%.

The size emulsion can be modified with most aqueous dispersions or solutions. In some cases it is desirable to add a strengthening agent. Starch and casein have been cited for this purpose. Other useful strengthening agents are animal glue, gelatin, water-soluble gums, viscose, etc. These can be incorporated in any desired amounts by first preparing their water solution or dispersion and then adding this to the size emulsion. Polyhydric alcohols, such as glycerin, or carbohydrates, such as dextrin, sucrose, etc., can be incorporated into the size emulsion. Dyes or pigments may be used with the size emulsion either in surface sizing or in beater sizing in order to color the sheet or to increase its opacity and finish. Examples of pigments that can be

used are clays, china clay, satin white, titanium dioxide, lithopone, barium sulfate, p-toner red, ultramarine blue, chrome green, etc.

It is possible to improve the effectiveness of the resin by the incorporation of limited amounts of waxes. It is very important, however, that the amount of wax should not be increased to the point where the stability of the emulsion is impaired. The best method of incorporating the waxes is to melt the resin and wax together, and then emulsify in accordance with the procedure described herein. It is desirable in this case to add to the water some emulsifying agent, such as a sulfonated oil, sulfonated petroleum residue, triethanolamine stearate, or sodium stearate, etc. For purposes of illustration, examples of waxes that can be used are petrolatum, paraffin, Asiatic, ceresin, Carnauba, Japan, etc. The best results are obtained with the higher melting-point hydrocarbon waxes, or with Carnauba wax.

It is possible also to modify the resin with other synthetic resins such as phenol-formaldehyde, urea-formaldehyde, vinyl resins, etc., or natural resins such as rosin, ester gum, copal, kauri, etc. The natural or synthetic resin is melted with the stearic acid modified glycerol phthalate resin and the emulsion is formed in accordance with the process described herein. Again it is important that the amount of resin should not be great enough to impair the excellent stability of the emulsion and an emulsifying agent should also be used to improve the stability of the emulsion. It is also desirable when modifying the stearic acid modified glycerol phthalate resin with a wax and/or resin to add a small amount of a protective colloid, such as casein, glue, or egg albumen, to the water, thereby improving the stability of the emulsion. A colloid mill may be used in preparing the size emulsions. Another modifying agent that can be incorporated into the size emulsions is rubber latex.

The resin emulsion described herein is useful in the manufacture of paper which has permanence of color and strength. These properties are of particular importance in high grade bond, ledger, lithographic, writing, wall, poster, and label papers. The resin is useful for improving the water resistance of rosin-sized kraft paper in applications where high water resistance is of extreme importance, such as fuel sack, gumming, and butcher papers. The resin is useful for improving the alkali- and scuff-resistance of kraft liner and kraft board used in the manufacture of corrugated paper boxes, etc. The invention is not limited to the sizing of paper. The size emulsion may be used for water-proofing woven cotton, wool, felts, and textiles in general, leather and other fabrics, and mineral fibers such as asbestos, etc. It is also useful for waterproofing wall board as well as other bibulous and absorbent materials.

The advantages incident to the practice of this invention, as well as the importance of the stearic acid content of the resin and the acid number

of the resin will be apparent from the following table:

scribed limits of stearic acid glyceride content, it is possible to produce a strongly sized (i. e.,

5	Stearic acid modified glycerol phthalate resin			Percent combined stearic glyceride	Acid number	Kraft paper sized with resin—0.6 percent resin based on weight of paper		5
	Ingredient composition (percent by weight)					Water resist- ance (dry indicator method)	Mullen bursting strength	
	Stearic acid	Glycerol	Phthalic anhydride					
10	00.00	29.73	70.27	0.00	165	Seconds	58	10
	6.15	28.11	65.74	7.05	134	2.0	57	
	17.52	25.88	56.60	20.00	115	2.0	57	15
	35.27	21.98	42.75	40.00	75	3.0	56	
	48.76	19.01	32.23	55.00	64	6.0	56	
	57.84	17.01	25.15	65.00	78	11.0	50	
	57.84	17.01	25.15	65.00	64	50.0	55	
	57.84	17.01	25.15	65.00	55	83.0	57	
	64.22	15.60	20.18	72.00	78	22.0	55	
	64.22	15.60	20.18	72.00	68	40.0	53	20
	64.22	15.60	20.18	72.00	57	140.0	53	
	64.22	15.60	20.18	72.00	45	194.0	53	
	70.64	14.19	15.17	79.00	45	160.0	53	
	78.02	12.56	9.42	87.00	49	130.0	53	
	90.10	9.90	-----	100.00	47	122.0	55	

¹ This is glyceryl stearate made from glycerine and stearic acid which is different from the natural product but which does not have characteristics similar to the resins claimed herein and which therefore is not included in this invention. Stearic acid causes intense foaming which renders commercial operation impracticable. Both stearic acid and glyceryl stearate are inferior as regards water resistance imparted to paper.

While polyhydric alcohol-polybasic acid resins other than those disclosed herein may be useful in the impregnation of paper for certain purposes, this is not true in the practice of the present invention since an increase of 40 seconds or more in the water resistance of the paper is necessary before the resin has any practical value as a paper size. It will be seen from the table that the stearic acid glyceride content of the resin must be at least 65%. Furthermore, it will be seen that the proper stearic acid glyceride content must be coupled with an acid number within the range previously given. Thus, in the case of the three resins in the table containing 65% stearic acid glyceride, the water resistance for the resin of acid number 78 is only 11 seconds as compared to 50 seconds and 83 seconds for the resins of the same composition having acid numbers of 64 and 55, respectively. Likewise, in the case of the four resins of 72% stearic acid glyceride content, the water resistance rises from 22 seconds to 194 seconds with an acid number decrease of from 78 to 45. Resins of low stearic acid glyceride content and high acid number, such as the resin containing 7.05% stearic acid glyceride, are wholly unsuitable for paper sizing because of the low water resistance; these resins cannot be carried to a sufficiently low acid number because of gel formation. It must be observed, also that the objects of my invention can be accomplished only with the use of the saturated fatty acid resins described above. An unsaturated oil fatty acid modified polyhydric alcohol-polybasic acid resin, such as linseed oil modified resin, produces at best a resin emulsion comparable in waterproofing action to a stearic acid modified resin of about 40% stearic acid glyceride content. An inspection of the above table will show that this represents a water resistance of only 3 seconds and is wholly inadequate since the commercial requirement is at least about a 50 second increase in water resistance.

A particular and highly important advantage of this invention is that the resin emulsion does not cause discoloration or degradation of the paper with age. By working within the pre-

water resistant) sheet of paper with very small amounts of the resin. This is an essential property of a size for use in the paper industry, because the application of large amounts of the resin would render the process prohibitive in cost, and would change the characteristics of the paper so greatly that the paper could not be used for the purposes for which it had been manufactured. Another advantage of the invention, particularly when it is applied to surface sizing, is that it provides a practical process for producing highly sized paper without the use of alum which is known to be harmful to the life of paper. The process of this invention does not, as in the case of the prior practice of impregnating paper with water solutions of salts of stearic acid modified resins, require treatment of the resin after its application to the paper with an acid or a heavy metal salt to render the resin water-insoluble, and therefore to render the sized paper water resistant. The invention provides a practical process for producing highly sized paper that is free from the objections encountered in the use of fairly large amounts of rosin size; i. e., lower production, gumming of the machine felts, and corrosion accelerated by the use of alum. A practical process is provided for producing highly sized paper by surface sizing paper that has been slack-sized in the beater with rosin. Another feature is that it provides a process for sizing paper on one side only, which is important in certain applications such as kraft liner and kraft board for paper boxes and containers where it is desirable to have the inner surface slack-sized in order to obtain good penetration of adhesives during construction of the box or container, and the outer surface heavily sized in order to waterproof the box or container. The invention provides unusually stable emulsions of waterproofing resins. This excellent stability is an important feature because it insures good working properties in a size press or calender water-boxes. Still another feature is that a size is provided which improves the feel, softness, scuff-resistance, and alkali-resistance of paper.

As many apparently widely different embodiments of this invention may be made without de-

parting from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

5 I claim:

1. A process of increasing the water repellency of absorbent material which comprises adding to said material an aqueous emulsion of polyhydric alcohol-polybasic acid resin, said resin having an acid number of 25 to 64 and containing in combined form from 65% to about 90% by weight of a polyhydric alcohol ester of an aliphatic monocarboxylic acid of the formula $R-COOH$ in which R is an alkyl radical containing not less than 15 carbon atoms.

2. The process set forth in claim 1 in which the monocarboxylic acid is stearic acid.

3. In a process of imparting to paper a water resistance of at least 40 seconds for a paper of 0.009 inch thickness, the steps which comprise treating paper pulp with an aqueous emulsion of polyhydric alcohol-polybasic acid resin, and precipitating the resin on the fibers of the pulp, said resin having an acid number of 25 to 64 and containing in combined form from 65% to about 90% by weight of a polyhydric alcohol ester of an aliphatic monocarboxylic acid of the formula $R-COOH$ in which R is an alkyl radical containing not less than 15 carbon atoms.

4. The process set forth in claim 3 in which the monocarboxylic acid is stearic acid.

5. A process of increasing the water-repellency of absorbent material which comprises adding to said material 0.5% to 2% resin in the form of an aqueous emulsion of polyhydric alcohol-polybasic acid resin, said resin having an acid number of 25 to 64 and containing in combined form from 65% to about 90% by weight of a polyhydric alcohol ester of an aliphatic monocarboxylic acid of the formula $R-COOH$ in which R is an alkyl radical containing not less than 15 carbon atoms.

6. A process which comprises adding at least 0.6% of resin to paper and imparting to the paper a water resistance of at least 40 seconds for a paper 0.009 inches thick by treating paper pulp with an aqueous emulsion of polyhydric alcohol-polybasic acid resin, and precipitating the resin on the fibers of the pulp, said resin having an acid number of 25 to 64 and containing in combined form from 65% to about 90% by weight of a polyhydric alcohol ester of an aliphatic monocarboxylic acid of the formula $R-COOH$ in which R is an alkyl radical containing not less than 15 carbon atoms.

7. A process of imparting to paper a water resistance of at least 40 seconds for a paper of 0.009 inch thickness which comprises applying to the surface of the paper an aqueous emulsion of polyhydric alcohol-polybasic acid resin, and drying the paper, said resin having an acid number of 25 to 64 and containing in combined form from 65% to about 90% by weight of a polyhydric alcohol ester of an aliphatic monocarboxylic acid of

the formula $R-COOH$ in which R is an alkyl radical containing not less than 15 carbon atoms.

8. A process which comprises adding at least 0.6% of resin to paper and imparting to the paper a water resistance of at least 40 seconds for a paper 0.009 inch thick by applying to the surface of the paper an aqueous emulsion of polyhydric alcohol-polybasic acid resin, and drying the paper, said resin having an acid number of 25 to 64 and containing in combined form from 65% to about 90% by weight of a polyhydric alcohol ester of an aliphatic monocarboxylic acid of the formula $R-COOH$ in which R is an alkyl radical containing not less than 15 carbon atoms.

9. In a process for making paper of improved water repellency the steps which comprise treating paper pulp with an aqueous emulsion of polyhydric alcohol-polybasic acid resin, precipitating the resin on the fibers of the pulp, and forming the pulp into paper, said resin having an acid number of 25 to 64 and containing in combined form from 65% to about 90% by weight of a polyhydric alcohol ester of an aliphatic monocarboxylic acid of the formula $R-COOH$ in which R is an alkyl radical containing not less than 15 carbon atoms.

10. As a new article of manufacture, paper of improved water repellency, said paper carrying as the water repellent material polyhydric alcohol-polybasic acid resin having an acid number of 25 to 64 and containing in combined form from 65% to about 90% by weight of a polyhydric alcohol ester of an aliphatic monocarboxylic acid of the formula $R-COOH$ in which R is an alkyl radical containing not less than 15 carbon atoms.

11. As a new article of manufacture, paper of improved water repellency, said paper carrying as the water repellent material glycerol-phthalic anhydride-stearic acid resin having an acid number of 25 to 64 and containing in combined form from about 65% to about 90% stearic acid glyceride.

12. The article set forth in claim 10 in which the polyhydric alcohol-polybasic acid resin is present in an amount of from 0.5% to 2%.

13. The article set forth in claim 11 in which the polyhydric alcohol-polybasic acid resin is present in an amount of from 0.5% to 2%.

14. As a new article of manufacture, paper of improved water repellency, said paper having a water resistance of at least 40 seconds for a paper of 0.009 inch thickness and carrying as the water repellent material polyhydric alcohol-polybasic acid resin having an acid number of 25 to 64 and containing in combined form from 65% to about 90% by weight of a polyhydric alcohol ester of an aliphatic monocarboxylic acid of the formula $R-COOH$ in which R is an alkyl radical containing not less than 15 carbon atoms.

15. The article set forth in claim 14 in which the polyhydric alcohol-polybasic acid resin is present in an amount of not less than 0.6%.

LOUIS L. LARSON.