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3,102,064

## NOVEL PAPER SIZING PROCESS

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This invention relates to a process for the sizing of paper and to the improved paper thus prepared. More particularly, this invention relates to novel sizing agents for use in the sizing of paper and paperboard products.

It is the object of this invention to provide improved sizing agents whose use results in the preparation of paper which is characterized by its reduced water and ink absorption as well as its resistance to aqueous acid and alkaline solutions. A further object of this invention involves the use of sizing agents which may be employed with all types of paper pulp over the complete range of pH conditions which are normally encountered in paper manufacturing. An additional object involves the use of sizing agents which are fully compatible with alum and rosin as well as with the various fillers, pigments and other chemicals which may be added to paper.

As used herein, the terms "paper and paperboard" include sheet-like masses and molded products made from fibrous cellulosic materials which may be derived from both natural and synthetic sources. Also included are sheet-like masses and molded products prepared from combinations of cellulosic and non-cellulosic materials derived from synthetics such as polyamide, polyester and polyacrylic resin fibers as well as from mineral fibers such as asbestos and glass.

Paper and paperboard are often sized with various materials for the purpose of increasing their resistance to water as well as to other types of aqueous solutions. These materials are referred to as sizes or sizing and they may be introduced during the actual paper making operation wherein the process is known as internal or engine sizing. Or, on the other hand, they may be applied to the surface of the finished web or sheet in which case the process is known as external or surface sizing.

Various water-repellant materials have been utilized as sizing agents. These include rosin, mixtures of rosin with waxes, wax emulsions, ketene dimer emulsions, fluorocarbons, fatty acid complexes of chromium or aluminum chlorides, long chain thermoplastic copolymers, as well as some thermosetting condensation type resins. Although all of these materials are effective under certain conditions, their use is nonetheless subject to one or more limitations.

Thus, for example, in the case of rosin, although the latter is relatively low in cost and readily available, it has poor resistance to alkaline solutions and cannot be used for the sizing of neutral or alkaline pulps. It is inoperable with the latter since it must be ordinarily used in combination with alum, or an acidic aluminum ion donor, which is present for the purpose of precipitating and setting the sodium rosinate, i.e. the rosin soap, onto the fibers. The use of alum for this purpose is, however, precluded under neutral or alkaline conditions. This is a definite disadvantage since the paper produced from neutral and alkaline pulp has been found to have higher strength, greater stability and superior aging char-

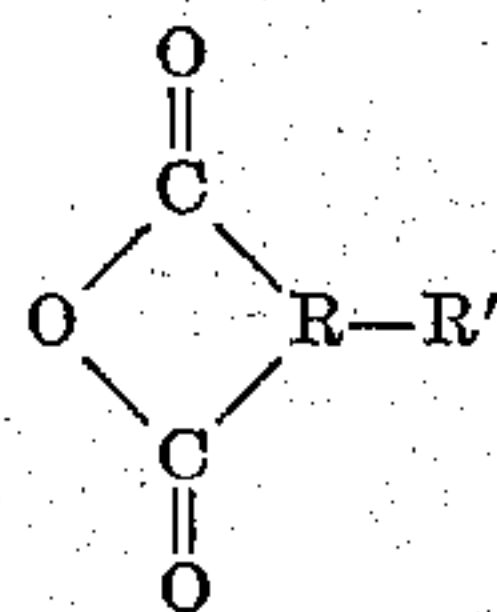
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acteristics in comparison with the paper prepared from acidic pulp. Also, the internal use of alkaline pigments such as calcium carbonate is precluded. This same limitation also applies to the use of most wax emulsions which cannot be used on the alkaline side since they are usually combined with small quantities of alum for the purpose of breaking the emulsions. On the other hand, certain sizing agents will not tolerate appreciable quantities of alum or high acidic conditions. In some cases, it may be desirable or necessary to use alum for filler retention purposes, for increasing sheet drainage, or to retain or set condensation resin additives, etc. Certain sizing agents cannot be adequately retained in the sheet during sheet formation and, consequently, are limited only to external or surface applications.

In addition to the above described pH limitations, the water resistance or water holdout which is attainable with many of the heretofore employed sizing agents is often inadequate for many applications which may require paper or paperboard displaying an exceptionally high degree of water resistance. Moreover, many of these sizing agents have been found to be incompatible with the pigments, fillers, or other ingredients which often are added to paper. A further disadvantage of some sizing agents is that a considerable degree of heat curing is required to develop full effectiveness. Thus, in using these materials, full effectiveness and full sizing value may not be obtained immediately after formation and drying of the paper web.

We have now discovered that the use of certain reagents as sizes for paper and paperboard has been found to result in the preparation of products which display an unusually high degree of water resistance along with resistance of acidic and alkaline solutions. Of prime importance is the fact that the successful use of these new sizing agents is not restricted to any particular pH range which thus allows for their utilization in the treatment of neutral and alkaline pulp as well as acidic pulp. Our sizing agents may also be used in combination with alum as well as with any of the pigments, fillers and other ingredients which may be added to paper. Still another advantage of these sizing agents is that they may be used in conjunction with other sizing agents so as to obtain additive sizing effects. A still further advantage of these sizing agents is that they do not detract from the strength of the paper and when used with certain adjuncts will in fact, increase the strength of the finished sheets. An additional advantage of our novel sizing agents is that only mild drying or curing conditions are required to develop full sizing value.

The novel sizing agents of our invention may be described as substituted cyclic dicarboxylic acid anhydrides corresponding to the following structural formula:



wherein R represents a dimethylene or trimethylene radical and wherein R' is a hydrophobic group containing more than 5 carbon atoms which may be selected from the class consisting of alkyl, alkenyl, aralkyl or aralkenyl groups. Substituted cyclic dicarboxylic acid anhydrides



falling within the above described formula are the substituted succinic and glutaric acid anhydrides.

Specific examples of the above described sizing agents include iso-octadecenyl succinic acid anhydride, n-hexadecenyl succinic acid anhydride, dodecenyl succinic acid anhydride, dodecyl succinic acid anhydride, decenyl succinic acid anhydride, octenyl succinic acid anhydride, nonenyl succinic acid anhydride, triisobutenyl succinic acid anhydride, capryloxy succinic acid anhydride, heptyl glutaric acid anhydride, and benzyloxy succinic acid anhydride. From among the reagents of this type, we have found that optimum results are obtained with acid anhydrides in which R' contains more than twelve carbon atoms. It should also be noted that it is possible to employ mixtures of any of these reagents in the process of our invention.

The actual use of our novel sizing agents in the manufacture of paper is subject to a number of variations in technique any of which may be further modified in light of the specific requirements of the practitioner. It is important to emphasize, however, that with all of these procedures, it is most essential to achieve a uniform dispersal of the sizing agent throughout the fiber slurry, thereby necessitating that its addition to the pulp be accompanied with prolonged and vigorous agitation. Uniform dispersal may also be obtained by adding the sizing agent in a fully dispersed form such as an emulsion; or, by the coaddition of chemical dispersing agents to the fiber slurry.

Another important factor in the effective utilization of the sizing agents of our invention involves their use in conjunction with a material which is either cationic in nature or is, on the other hand, capable of ionizing or dissociating in such a manner as to produce one or more cations or other positively charged moieties. These cationic agents, as they will be hereinafter referred to, have been found useful as a means for aiding in the retention of our sizing agents as well as for bringing the latter into close proximity to the pulp fibers. Among the materials which may be employed as cationic agents in the process of our invention, one may list alum, aluminum chloride, long chain fatty amines, sodium aluminate, polyacrylamide, chromic sulfate, animal glue, cationic thermosetting resins and polyamide polymers. Of particular interest for use as cationic agents are various cationic starch derivatives including primary, secondary, tertiary or quaternary amine starch derivatives and other cationic nitrogen substituted starch derivatives, as well as cationic sulfonium and phosphonium starch derivatives. Such derivatives may be prepared from all types of starches including corn, tapioca, potato, waxy maize, wheat and rice. Moreover, they may be in their original granule form or they may be converted to pregelatinized, cold water soluble products.

Any of the above noted cationic agents may be added to the stock, i.e. the pulp slurry, either prior to, along with or after the addition of the sizing agent. However, in order to achieve maximum distribution, it is preferable that the cationic agent be added either subsequent to or in direct combination with the sizing agent. The actual addition to the stock of either the cationic agent or the sizing agent may take place at any point in the paper making process prior to the ultimate conversion of the wet pulp into a dry web or sheet. Thus, for example, our sizing agents may be added to the pulp while the latter is in the headbox, beater, hydropulper or stock chest.

In order to obtain good sizing, it is desirable that our sizing agents be uniformly dispersed throughout the fiber slurry in as small a particle size as is possible to obtain. One method for accomplishing this is to emulsify the sizing agent prior to its addition to the stock utilizing either mechanical means, such as high speed agitators, mechanical homogenizers, or ultrasonic homogenizers, or by the addition of a suitable emulsifying agent. Where

possible, it is highly desirable to employ the cationic agent as the emulsifier and this procedure is particularly successful where cationic starch derivatives are utilized. Among the applicable non-cationic emulsifiers which may be used as emulsifying agents for our sizing agents, one may list such hydrocolloids as ordinary starches, non-cationic starch derivatives, dextrans, carboxymethyl cellulose, gum arabic, gelatin and polyvinyl alcohol as well as various surfactants. When such non-cationic emulsifiers are used, it is often desirable to separately add a cationic agent to the pulp slurry after the addition to the latter of the emulsified sizing agent. In preparing these emulsions with the use of an emulsifier, the latter is first dispersed in water and the sizing agent is then introduced along with vigorous agitation. If the sizing agent normally exists as a waxy solid, it must first be melted prior to its emulsification.

Further improvements in the water resistance of the paper prepared with our novel sizing agents may be obtained by curing the resulting webs, sheets or molded products. This curing process involves heating the paper at temperatures in the range of from 80° to 150° C. for periods of from 1 to 60 minutes. Such post curing is particularly recommended where use is made of those sizing agents of our invention having hydrophobic groups (i.e. R' in the above described formula) containing 12 or less carbon atoms. However, it should again be noted that post curing is not essential to the successful operation of our sizing process.

The sizing agents of our invention, may, of course, be successfully utilized for the sizing of paper prepared from all types of both cellulosic and combinations of cellulosic with non-cellulosic fibers. The cellulosic fibers which may be used include bleached and unbleached sulfate (kraft), bleached and unbleached sulfite, bleached and unbleached soda, neutral sulfite, semi-chemical, chemi-groundwood, ground wood, and any combination of these fibers. These designations refer to wood pulp fibers which have been prepared by means of a variety of processes which are used in the pulp and paper industry. In addition, synthetic fibers of the viscose rayon or regenerated cellulose type can also be used.

All types of pigments and fillers may be added to the paper which is to be sized with our novel sizing agents. Such materials include clay, talc, titanium dioxide, calcium carbonate, calcium sulfate, and diatomaceous earths. Other additives, including alum, as well as other sizing agents can also be used with our sizing agents.

With respect to proportions, our sizing agents may be employed in amounts ranging from about 0.05 to about 5.0% of the dry weight of the pulp in the finished sheet or web. Within this range the precise amount which is to be used will, of course, depend for the most part upon the type of pulp which is being utilized, the specific operating conditions, as well as the particular end use for which the paper is destined. Thus, for example, paper which will require good water resistance or ink holdout will necessitate the use of a higher concentration of sizing agent than paper which will be used in applications where excessive sizing is not needed. These same factors also apply in relation to the amount of cationic agent which may be used in conjunction with our sizing agents. Thus, the practitioner will be able to use these materials in any concentration which is found to be applicable to his specific operating conditions. However, under ordinary circumstances a range of from 0.5 to 2.0 parts by weight of cationic agent per 1.0 part of sizing agent is usually adequate. Thus the cationic agent is in a quantity at least 0.025% of the dry weight of the pulp in the paper. In those cases where use is made of those sizing agents of our invention having hydrophobic groups containing 12 or less carbon atoms, it is advisable to employ these cationic agents in concentrations near the upper limit of this range.



In any event, the use of our reagents has been found to provide a degree of water resistance which is comparable, and in many cases superior, to the results obtained with other heretofore employed sizing agents. Moreover, our sizing agents impart a resistance to acid and alkali which is often unattainable with other sizing agents.

The following examples will further illustrate the embodiment of our invention. In these examples all parts given are by weight unless otherwise noted.

#### Example I

This example illustrates the use of our sizing agents in the form of aqueous emulsions wherein the emulsifier used is a tertiary amine cationic starch derivative. The use of our sizing agents in combination with alum is also illustrated. The water resistance of the resulting paper is compared with that of paper which had been sized with mixtures of fortified rosin and alum.

An aqueous emulsion of iso-octadecenyl succinic acid anhydride which for purposes of brevity will hereinafter be referred to as IODSA, was prepared by first cooking 7.5 parts of the beta-diethyl amino ethyl chloride hydrochloride ether of corn starch, whose preparation is described in Example I of U.S. Patent 2,813,093, in 85 parts of water which was heated in a boiling water bath. After being cooked for 20 minutes, the dispersion of the cationic starch derivative was cooled to room temperature and transferred to a high speed agitator whereupon 7.5 parts of IODSA were slowly added to the agitated dispersion. Agitation was continued for 5 minutes and the resulting emulsion was then diluted by the addition of another 900 parts of water. A final 10 fold dilution was then effected and this was added to an aqueous slurry of bleached sulfate pulp having a consistency of 1.5% and pH of about 8.5. Sheets were formed and dried in accordance with TAPPI standards and the latter contained 1%, as based on the weight of the dry pulp, of both the cationic agent and the IODSA. The basis weight of these sheets was 55 lbs./ream (24" x 36"—500 sheets). By means of the same procedure comparable sheets were made which contained varying amounts of IODSA as well as several which contained the IODSA in combination with varying amounts of alum. In all cases where alum was used, the pH of the aqueous pulp slurry was 5.0.

The water resistance of these sheets was compared with that of sheets prepared from comparable pulp which had been sized with a mixture of rosin and alum. In comparing the water resistance of these sheets, we used the uranine dye test and the ink dip test. The former test involves placing a small amount of uranine dye powder on the upper surface of a swatch of paper which is then set afloat in distilled water. As the water is absorbed into the paper, the dye is moistened and thus becomes sensitive to ultraviolet light. The time, in seconds, required for this UV sensitivity to occur is thus in direct relation to the water resistance of the paper since a more water resistant paper will, of course, retard the moistening of the dye which has been placed upon its upper surface.

The ink dip test is a qualitative comparison wherein a swatch of the paper being tested is dipped into a 1:1 mixture of water and blue ink. The swatch is then removed, washed with water and the remaining color evaluated with a colorimeter. Thus, a swatch with a greater degree of water resistance will have a lighter color than a swatch with poor water resistance. For this test an arbitrary color scale of 1-10 was used, with #1 indicating the least color or the best water resistance, and the #10 indicating the most color or the poorest water resistance. This test also provides a qualitative visual indication of the distribution of the sizing agent in the paper.

The following table presents data on the various sheets which were compared and gives the results obtained with both the uranine dye and the aquapal dip tests.

Sheet No.	Additives	Percent, by wt., of dry pulp	Uranine dye test (time in sec.)	Ink dip test (color value)
5				
1	None		Immediate	10
2	(Cationic corn starch	1	105	3
	IODSA	1		
3	(Cationic corn starch	1	118	2
	IODSA	1		
4	Alum	2	130	1
	(Cationic corn starch	3		
5	IODSA	3	132	1
	(Cationic corn starch	3		
6	IODSA	3	138	1
	Alum	2		
7	(Cationic corn starch	5	78	5
	IODSA	5		
	Rosin	1		
	Alum	2		

#### Example II

This example illustrates the use of varying concentrations of IODSA and thus points out the improved water resistance which is obtained when this reagent is used at various concentrations.

A series of aqueous emulsions of IODSA were prepared by means of the procedure described in Example I wherein the same tertiary amine cationic starch described therein was again used as the emulsifier. These emulsions contained varying amounts of both the IODSA and the cationic starch and, with agitation, they were added, at the headbox, to separate batches of bleached sulfate pulp having a freeness of 500 and a consistency of 0.5%. In all cases, the pH of the pulp slurry was 8.0 except where rosin was used in which case the resultant pH of the slurry after addition of the alum was 4.5-5.0. The basis weight of the resulting paper was 60 lbs./ream. Below are described the compositions of the various sheets which were prepared as well as the results obtained when the water resistance of these sheets was tested by means of the uranine dye test.

Sheet No.	Additive	Percent, by wt., of dry pulp	Uranine dye test (time in sec.)
1	None		Immediate
2	(Cationic corn starch	0.25	92
	IODSA	0.25	
3	(Cationic corn starch	0.5	116
	IODSA	0.5	
4	(Cationic corn starch	1.0	134
	IODSA	1.0	
5	(Cationic corn starch	2.0	149
	IODSA	2.0	
6	Fortified rosin	1.0	94
	Alum	2.0	
7	Fortified rosin	2.0	124
	Alum	4.0	

#### Example III

This example illustrates the use of octenyl succinic acid anhydride. It also illustrates the importance of using the latter in combination with alum as well as the desirability for the post curing of the sheets sized with this short chain length derivative so as to obtain sizing results which are comparable to those obtained with longer chain derivatives.

An aqueous emulsion of octenyl succinic anhydride was prepared by means of the procedure described in Example I. The same cationic starch derivative was used as the emulsifier; however, in this case the derivative was pregelatinized, i.e. put into cold water soluble form, by passing an aqueous slurry of the derivative over heated metal drums. By employing the cationic starch in this pregelatinized form it was, of course, unnecessary to cook it up in order to disperse it. With agitation, the resulting emulsion of octenyl succinic acid anhydride was then added to a bleached sulfate stock having a freeness of 500 and a consistency of 1.5%. The slurry was then diluted to a 0.5% consistency and a quantity of alum was



introduced. After the addition of the alum, the pH of the slurry was 5.5. The basis weight of the resulting sheets was 60 lbs./ream. These sheets contained 1.0% of both octenyl succinic acid anhydride and the cationic starch, and 2.0% of alum as based upon the dry weight of the pulp. They were then cured for 1 hour at 105° C. For comparative purposes, additional sheets were prepared wherein an aqueous emulsion of IODSA, prepared with the cationic starch derivative described in Example I was used as the sizing agent; and, in another case, where a mixture of fortified rosin and alum were used. However with both of these latter procedures there was no post curing of the resulting sheets. The pH of the particular pulp slurry containing the IODSA was 8.0. Below are described the compositions of the various sheets which were prepared as well as the results obtained when the water resistance of these sheets was tested by means of the uranine dye test.

Sheet No.	Additives	Percent by wt. of dry pulp	Uranine dye test (time in sec.)
1	Cationic corn starch Octenyl succinic acid anhydride Alum	1.0 1.0 2.0	103 (cured 1 hour at 105° C.).
2	Cationic corn starch IODSA	1.0 1.0	152 (no curing).
3	Fortified rosin Alum	1.0 2.0	94 (no curing).

Example IV

This example illustrates the use of IODSA in its oily, unemulsified form and demonstrates the improvements obtained when, in one case, a cationic agent is added to the stock after the addition of the unemulsified IODSA; and, in another case, when ordinary corn starch is added to the stock before the addition of the IODSA and a cationic agent, the purpose of the corn starch being to aid in the dispersion of the sizing agent; and, in still another case, where corn starch is added to the stock prior to the addition of only the unemulsified IODSA.

With agitation, a quantity of IODSA was added to bleached sulfate pulp having a freeness of 500 and a 1.5% consistency. This quantity was sufficient to provide the finished sheets with a concentration of IODSA equivalent to 1.0%, by weight, of the dry pulp. Under comparable conditions sheets were then prepared wherein the following changes were made: (1) corn starch was added to the pulp prior to the addition of the unemulsified IODSA; (2) the cationic starch described in Example I was added to the pulp after the addition of the unemulsified IODSA; and (3) corn starch was added to the pulp prior to the addition of the unemulsified IODSA which was then followed by the addition of the cationic starch described in Example I. The basis weight of all of the above described sheets was 55 lbs./ream (24" x 36"—500 sheets). Below are described the compositions of the various sheets which were prepared as well as the results obtained when the water resistance of these sheets was tested by means of the uranine dye test.

Sheet No.	Additives	Percent, by wt., of dry pulp	Uranine dye test (time in seconds)
1	IODSA	1.0	0
2	Corn starch IODSA	0.5 1.0	0
3	Cationic corn starch IODSA	1.0 1.0	100
4	Corn starch Cationic corn starch IODSA	0.5 1.0 1.0	115

Example V

This example illustrates the use of ordinary corn starch as the emulsifying agent for IODSA.

An aqueous emulsion of IODSA was prepared using the procedure of Example I; however, in this case, ordinary corn starch rather than the cationic starch derivative was used as the emulsifier. With agitation, this emulsion was added to bleached sulfate pulp having a freeness of 500 and a 1.5% consistency. This was followed by the addition of alum to a pH of 5.5. The finished sheets contained 1.0% of IODSA and 1.0% of corn starch as based upon the dry weight of the pulp and had a basis weight of 60 lbs./ream. Below are described the compositions of the various sheets which were prepared as well as the results obtained when the water resistance of these sheets was tested by means of the uranine dye test. A comparison of sheets which had been sized with fortified rosin and alum is also offered.

Sheet No.	Additives	Percent, by wt., of dry pulp	Uranine dye test (time in sec.)
1	Corn starch IODSA	1.0 1.0	105
2	Alum (to adjust pH to 5.5) Fortified rosin Alum	1.0 1.0 2.0	94

Example VI

This example illustrates the use of IODSA for the sizing of paper containing an appreciable quantity of inert pigments.

An aqueous emulsion of IODSA was prepared using the procedure of Example I. With agitation, portions of this emulsion were added to a series of bleached sulfite pulps having a freeness of 440 and a consistency of 1.5% and which also contained, respectively, 10% of titanium dioxide, 10% of calcium carbonate, and 10% of clay as based upon the dry weight of the pulp. The resulting sheets each contained 0.5% of IODSA and 0.5% by weight of the cationic starch derivative as based upon the dry weight of the pulp and had a basis weight of 60 lbs./ream. Below are described the compositions of the various sheets which were prepared as well as the results obtained when the water resistance of these sheets was tested by means of the uranine dye test. A comparison of pigment containing sheets which had been sized with fortified rosin and alum is also offered.

Sheet No.	Additives	Percent, by wt., of dry pulp	Uranine dye test (time in sec.)
1	Cationic corn starch IODSA	0.5 0.5	130
2	Titanium dioxide Cationic corn starch IODSA	10.0 0.5 0.5	153
3	Clay Cationic corn starch IODSA	10.0 0.5 0.5	200
4	Calcium carbonate Fortified rosin Alum Titanium dioxide	10.0 1.0 2.0 10.0	96

Example VII

This example illustrates the use of IODSA in its oily, unemulsified form which was, however, added to the pulp in combination with a cationic starch.

With agitation, separate portions of IODSA and the cationic corn starch derivative described in Example I were added, simultaneously, to a mixture of 73% ground-wood and 27% bleached sulfite pulps having a freeness of 350 and a consistency of 1.5%. The resulting sheets contained 1.0% of IODSA and 1.0% of the cationic corn starch as based upon the dry weight of the pulp. The



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basis weight of these sheets was 33 lbs./ream (24" x 36"—500 sheets). Below is described the composition of the sheets which were prepared as well as the results obtained when the water resistance of these sheets was tested by means of the uranine dye test. A comparison of sheets which had been sized with fortified rosin and alum is also offered.

Sheet No.	Additives	Percent, by wt., of dry pulp	Uranine dye test (time in sec.)
1-----	{Cationic corn starch-----	1.0	104
	{IODSA-----	1.0	
2-----	{Fortified rosin-----	1.0	
	{Alum-----	2.0	80

### Example VIII

This example illustrates the use of IODSA in the form of an emulsion prepared with a non-cationic, starch derivative emulsifier. The resulting emulsion was then used in combination with a cationic starch.

An aqueous emulsion of IODSA was prepared by means of the procedure described in Example I. However, in this case, the emulsifier which was used was a corn starch acid ester of octenyl succinic acid as prepared by means of the procedure described in Example II of U.S. Patent 2,661,349. With agitation, this emulsion along with a quantity of the cationic corn starch derivative described in Example I of this disclosure, were added, at the headbox, to a bleached sulfate pulp having a freeness of 500 and a consistency of 0.5. The resulting sheets, in this case, contained 1.0% of IODSA, 1.0% of the corn starch acid ester emulsifier, and 1.0% of the cationic starch as based upon the dry weight of the pulp. Below is described the composition of the sheets prepared as well as the results obtained when the water resistance of these sheets was tested by means of the uranine dye test. A comparison of sheets which had been sized with fortified rosin and alum is also offered.

Sheet No.	Additives	Percent, by wt., of dry pulp	Uranine dye test (time in sec.)
1-----	{Corn starch acid ester-----	1.0	139
	{IODSA-----	1.0	
	{Cationic corn starch-----	1.0	
2-----	{Fortified rosin-----	1.0	115
	{Alum-----	2.0	

### Example IX

This example illustrates the use of IODSA in the form of an emulsion wherein a number of different cationic corn starch derivatives were each used, respectively, as the emulsifying agent.

Listed below are the various cationic amine corn starch derivatives used as emulsifiers along with a brief description of the method used for their preparation.

(A) *Primary amine corn starch*.—Prepared by reacting 100 parts of corn starch, 20 parts of ethylene imine and 50 parts of toluene in a pressure vessel for 20 hours at a temperature of 60° C. The product was recovered by the addition of 200 parts of methanol and 35.7 parts of concentrated hydrochloric acid and was then filtered, washed with methanol and air dried.

(B) *Secondary starch amine*.—Prepared by reacting 100 parts of corn starch, 15 parts of n-butyl ethylene imine and 25 parts of toluene under the same conditions as described above for the preparation of the primary amine corn starch derivative.

(C) *Quaternary starch amine*.—Prepared by reaction of corn starch with the reaction product of triethylamine and epichlorohydrin as described in Example I of U.S. Patent 2,876,217.

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Each of the above described starch amines was then used as the emulsifier for the preparation of aqueous emulsions of IODSA. These emulsions were each, in turn, added to bleached sulfate pulp having a freeness of 500 and a consistency of 1.5%. The resulting sheets, in each case, contained 1.0% of IODSA and 1.0%, respectively, of the primary, secondary and quaternary starch amine derivatives as based upon the dry weight of the pulp. Below is described the composition of the sheets prepared as well as the results obtained when the water resistance of these sheets was tested by means of the uranine dye test. A comparison of sheets which had been sized with fortified rosin and alum is also offered.

Sheet No.	Additives	Percent, by wt., of dry pulp	Uranine dye test (time in sec.)
1-----	{Primary amine corn starch-----	1.0	123
	{IODSA-----	1.0	
2-----	{Secondary amine corn starch-----	1.0	
	{IODSA-----	1.0	120
3-----	{Quaternary amine corn starch-----	1.0	128
	{IODSA-----	1.0	
4-----	{Fortified rosin-----	1.0	98
	{Alum-----	2.0	

### Example X

This example illustrates the use of IODSA in the form of an emulsion wherein a number of cationic amine derivatives of various starch bases were each, respectively, used as the emulsifying agent. The improvements in water resistance obtained by post curing are also demonstrated.

The various emulsifiers used were the tertiary amine, beta-diethyl amino ethyl chloride hydrochloride starch ethers prepared as described in Example I, of U.S. Patent 2,813,093. However, in place of the corn starch base, we substituted a variety of starch bases including waxy maize, tapioca, potato, a waxy maize starch which was acid converted to a degree known in the trade as 85 fluidity, and a corn starch which was acid converted to a degree known in the trade as 75 fluidity.

Each of the above described tertiary starch amines was then used as the emulsifier for the preparation of aqueous emulsions of IODSA. These emulsions were each, in turn, added at the headbox to bleached sulfate pulp having a freeness of 500 and a consistency of 0.5%. The resulting sheets in each case, contained a 1.0% of IODSA and 1.0% respectively, of the various tertiary amine starches as based upon the dry weight of the pulp. The water resistance of these sheets was then evaluated by means of the uranine dye test, as described in Example I. Additional samples of these sheets were then cured by being heated for 1 hour at a temperature of 105° C. The water resistance of these cured sheets was similarly determined by means of the uranine dye test. The results of these tests are presented in the following table.

Sheet No.	Additives	Percent, by wt., of dry pulp	Uranine dye test (time in sec.)	
			Immediate	Cured
1-----	{Waxy maize tertiary amine-----	1.0	102	102
	{IODSA-----	1.0		
2-----	{Tapioca tertiary amine-----	1.0		
	{IODSA-----	1.0	110	118
3-----	{Potato tertiary amine-----	1.0	112	118
	{IODSA-----	1.0		
4-----	{Acid conv. waxy maize tert. amine.-----	1.0	83	93
	{IODSA-----	1.0		
5-----	{Acid conv. corn starch tert. amine.-----	1.0	95	109
	{IODSA-----	1.0		



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Example XI

This example illustrates the use of several of the sizing agents of our invention including n-hexadecenyl succinic acid anhydride, dodecenyl succinic acid anhydride, dodecyl succinic acid anhydride, and a mixture of iso-alkenyl succinic acid anhydrides wherein the alkenyl groups of the mixed anhydrides contained from 18 to 22 carbon atoms.

An aqueous emulsion of each of the above described sizing agents was prepared by means of the procedure described in Example I using, as an emulsifier, the same cationic starch derivative described therein. With agitation, the emulsions of the mixed iso-alkenyl succinic acid anhydrides and the n-hexadecenyl succinic acid anhydride were added, respectively, at the hydropulper to bleached sulfate pulps having a consistency of 1.5% and a freeness of 510. The emulsions of dodecenyl succinic acid anhydride and dodecyl succinic acid anhydride were added, at the headbox, to a bleached sulfite pulp having a consistency of 0.5% and a freeness of 500. The resulting sheets, in each case, contained 1.0% of the various sizing agents and 1.0% of the cationic starch as based upon the dry weight of the pulp. Below is described the composition of the sheets prepared as well as the results obtained when the water resistance of these sheets was tested by means of the uranine dye test. A comparison of bleached sulfate sheets which had been sized with fortified rosin and alum is also offered.

Sheet No.	Additives	Percent, by wt., of dry pulp	Uranine dye test (time in sec.)
1	{Mixture of iso-alkenyl succinic acid anhydrides.	1.0	120
	{Cationic corn starch.	1.0	
	{N-hexadecenyl succinic acid anhydride.	1.0	
2	{Cationic corn starch.	1.0	118
	{Dodecenyl succinic acid anhydride.	1.0	
3	{Cationic corn starch.	1.0	110
	{Dodecyl succinic acid anhydride.	1.0	
4	{Cationic corn starch.	1.0	105
	{Fortified rosin.	1.0	
5	{Alum.	2.0	98

Example XII

This example illustrates the use of our sizing agents in combination with a variety of cationic agents. It also demonstrates their use in the treatment of paper pulp under a broad range of pH conditions.

An aqueous emulsion of IODSA was prepared by means of the procedure described in Example I using, as the emulsifier, the corn starch acid ester of octenyl succinic acid prepared by means of the procedure described in Example II of U.S. Patent 2,661,349. With agitation, portions of this emulsion along with a quantity of one or more cationic agents were added to separate bleached sulfate stocks each having a freeness of 510 and a consistency of 0.5% but which were, however, at a variety of pH conditions. The resulting sheets, in each case, contained 1.0% of IODSA and 1.0%, respectively, of the corn starch acid ester emulsifier and had a basis weight of 55 lbs./ream. The water resistance of these sheets was then evaluated by means of the uranine dye test, as described in Example I. The results of these tests as well as the nature of the cationic agents utilized and the pH of each pulp are presented in the following table.

Sheet No.	Additives	Percent, by wt., of dry pulp	pH of pulp	Uranine dye test (time in sec.)
5				
1	{Corn starch acid ester.	1.0	5.0	101
	{IODSA.	1.0		
	{Alum.	2.0		
2	{Corn starch acid ester.	1.0	5.0	101
	{IODSA.	1.0		
	{Polyacrylamide.	0.1		
10				
3	{Corn starch acid ester.	1.0	8.0	55
	{IODSA.	1.0		
	{Sodium aluminate.	1.0		
4	{Corn starch acid ester.	1.0	5.0	96
	{IODSA.	1.0		
	{Sodium aluminate.	1.0		
15				
5	{Corn starch acid ester.	1.0	6.0	82
	{IODSA.	1.0		
	{Animal glue.	1.0		
6	{Corn starch acid ester.	1.0	4.8	105
	{IODSA.	1.0		
	{Aluminum chloride.	2.0		
7	{Corn starch acid ester.	1.0	7.0	102
	{IODSA.	1.0		
	{A polyamide.	1.0		
20				
8	{Corn starch acid ester.	1.0	8.0	90
	{IODSA.	1.0		
	{A long chain amine.	1.0		

Example XIII

This example illustrates the improved strength which is obtained with the use of our sizing agents as compared with the strength of unsized sheets as well as with sheets sized with mixtures of fortified rosin and alum.

An aqueous emulsion of IODSA was prepared by means of the procedure described in Example I wherein the same teritiary amine cationic starch described therein was again used as the emulsifier. With agitation, this emulsion was added, at the headbox, to an unbleached sulfate pulp having a freeness of 550 and a consistency of 0.5%. The resulting sheets contained 1.0% of both IODSA and the cationic starch as based upon the dry weight of the pulp and had a basis weight of 57 lbs./ream (24" x 36" —500 sheets). The water resistance of these sheets was then evaluated by means of the uranine dye test.

The strength of these sheets was also determined using the Mullen tester. In this apparatus a sheet of the paper is clamped between two ring shaped platens, thus leaving an exposed circular surface of paper under which there is an inflatable rubber diaphragm. As air is pumped into this diaphragm it expands and comes into contact with the exposed surface of the paper. Note is made of the pressure, in p.s.i., at which the diaphragm caused the paper to burst. The Mullen factor is then calculated by dividing the latter figure by the basis weight of the paper, a higher Mullen factor thus indicating a stronger paper.

Using the same paper making procedure as described above, comparable sheets were prepared which in this case were, however, sized with a mixture of fortified rosin and alum. Still other sheets were prepared which did not contain any sizing agents. These sheets served as a blank. The Mullen factor as well as the water resistance of these sheets was also determined and the following table presents the results of these tests.

Sheet No.	Additives	Percent, by wt., of dry pulp	Mullen factor	Uranine dye test (time in sec.)
65				
1	{Cationic corn starch.	1.0	1.36	200
	{IODSA.	1.0		
2	{Blank.		1.27	0
3	{Fortified rosin.	1.0	1.23	160
	{Alum.	2.0		

The above data not only shows the improved strength and water resistance of the sheets treated with our sizing agents, but also indicates that the use of rosin-alum mixtures actually decreases the strength of the sheets which contain these materials.



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## Example XIV

This example illustrates the excellent resistance to acidic and alkaline solutions which is displayed by the paper which has been treated with our novel sizing agents as compared with that displayed by sheets which have been sized with mixtures of fortified rosin and alum.

An aqueous emulsion of IODSA was prepared by means of the procedure described in Example I wherein the same tertiary amine cationic starch described therein was again used as the emulsifier. With agitation, this emulsion was added to a bleached sulfate stock having a freeness of 500 and a consistency of 0.5%. The resulting sheets contained 0.5% of both IODSA and the cationic starch and had a basis weight of 55 lbs./ream.

In testing the water resistance of these sheets by means of the uranine dye test, the procedure described in Example I was modified so that in one case the paper swatch containing the dye on its upper surface was set afloat in a 10%, by wt., aqueous solution of lactic acid rather than the distilled water which is normally employed. In still another modification of the uranine dye test procedure, additional swatches of the above described sheets were set afloat in a 10%, by wt., aqueous sodium hydroxide solution. The same tests were also applied to comparable sheets which, in this case, had been sized with a mixture of fortified rosin and alum. Below are listed the compositions of the various sheets which were prepared as well as the results obtained when the water resistance of these sheets was tested by means of the above described modifications of the uranine dye test.

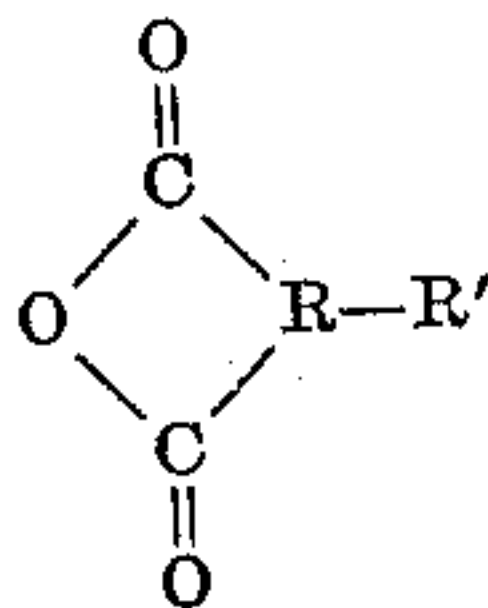
Sheet No.	Additives	Percent, by wt., of dry pulp	Uranine dye test (time in sec.)	
			Lactic acid	Sodium hydroxide
1	Cationic corn starch	0.5	106	>200
	IODSA	0.5		
2	Fortified rosin	1.0	80	25
	Alum	2.0		

It was noted at an earlier point in this disclosure that various surfactants may also be utilized as emulsifiers for the sizing agents of our invention. Thus, among the different examples of surfactants which may be utilized, one may list polyoxyethylene sorbitan trioleate, polyoxyethylene sorbitol hexaoleate, polyoxyethylene sorbitol laurate, and polyoxyethylene sorbitol oleate-laurate.

Summarizing, our invention is thus seen to provide the practitioner with novel sizing agents which are operable under a wide variety of conditions and are capable of providing paper products which are characterized by their exceptionally high degree of water resistance. Variations may be made in proportions, procedures and materials without departing from the scope of this invention which is limited only by the following claims.

We claim:

1. The method of sizing paper which comprises the step of intimately dispersing within the wet pulp, prior to the ultimate conversion of said pulp into a dry web, a sizing agent which comprises a cyclic dicarboxylic acid anhydride corresponding to the structural formula



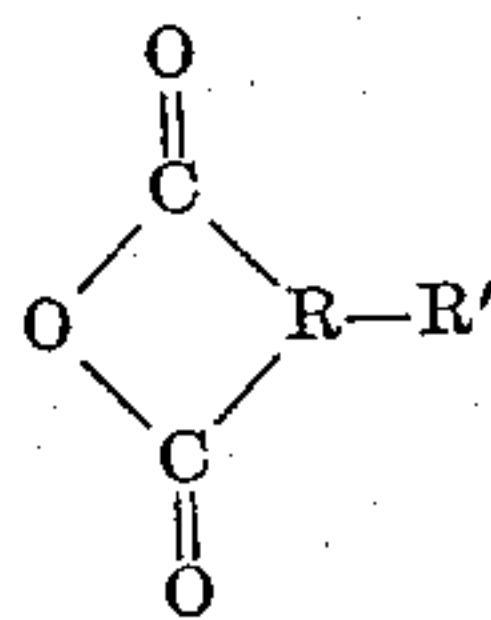
wherein R is selected from the class consisting of di-

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methylene and trimethylene radicals and wherein R' is a hydrophobic group containing more than five carbon atoms and is selected from the class consisting of alkyl, alkenyl, aralkyl, and aralkenyl groups.

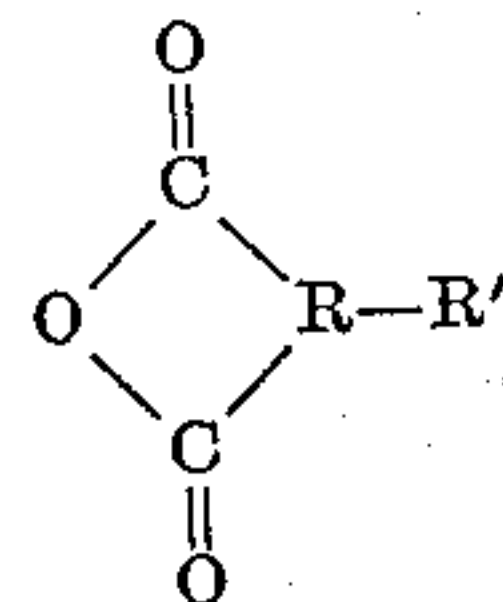
2. The method of claim 1 in which the sizing agent is in the form of an aqueous emulsion.

3. A paper product having intimately dispersed within the wet pulp thereof, prior to its conversion into a dry web, a sizing agent which comprises a cyclic dicarboxylic acid anhydride corresponding to the structural formula



wherein R is selected from the class consisting of dimethylene and trimethylene radicals and wherein R' is a hydrophobic group containing more than five carbon atoms and is selected from the class consisting of alkyl, alkenyl, aralkyl and aralkenyl groups.

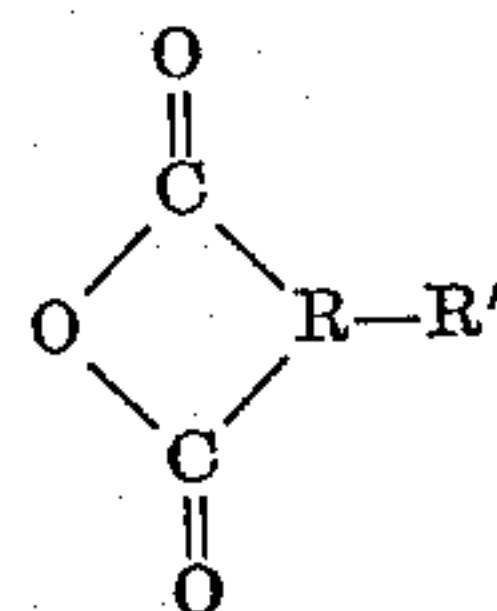
4. A paper product having intimately dispersed within the wet pulp thereof, prior to its conversion into a dry web, (a) a sizing agent which comprises a cyclic dicarboxylic acid anhydride corresponding to the structural formula



wherein R is selected from the class consisting of dimethylene and trimethylene radicals and where R' is a hydrophobic group containing more than five carbon atoms and is selected from the class consisting of alkyl, alkenyl, aralkyl and aralkenyl groups, and (b) at least 0.025%, based on the dry weight of the pulp, of a cationic agent.

5. The paper product of claim 4, in which said cationic agent is selected from the group consisting of alum, aluminum chloride, long chain fatty amines, sodium aluminates, polyacrylamide, animal glue, polyamide polymers, primary amine starch derivatives, secondary amine starch derivatives, tertiary amine starch derivatives and quaternary amine starch derivatives.

6. The method of sizing paper which comprises the steps of intimately dispersing within the wet pulp, prior to the ultimate conversion of said pulp into a dry web, (a) a sizing agent which comprises a cyclic dicarboxylic acid anhydride corresponding to the structural formula



wherein R is selected from the class consisting of dimethylene and trimethylene radicals and wherein R' is a hydrophobic group containing more than five carbon atoms and is selected from the class consisting of alkyl,

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alkenyl, aralkyl and aralkenyl groups, and (b) at least 0.025%, based on the dry weight of the pulp, of a cationic agent.

7. The method of claim 6, in which said cationic agent is selected from the group consisting of alum, aluminum chloride, long chain fatty amines, sodium aluminate, polyacrylamide, animal glue, polyamide polymers, primary amine starch derivatives, secondary amine starch derivatives, tertiary amine starch derivatives and quaternary amine starch derivatives.

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