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## (54) Title: USE OF ZIRCONIUM SALTS TO IMPROVE THE SURFACE SIZING EFFICIENCY IN PAPER MAKING

**(57) Abstract**

An aqueous surface sizing composition for sizing paper or paperboard having as essential components 50 to 70 parts of a water soluble or water dispersible hydroxylated polymer, an amount of a carboxylated polymer that is present relative to hydroxylated polymer in a ratio of 0.5:99.5 to 4:96 and not exceeding 7 parts carboxylated polymer, 0.3 to 3.0 parts of an alkali salt of a Group IV metal (e.g., zirconium, hafnium, and titanium), and sufficient water to obtain 1.5 to 2.0 percent total solids. The sizing compositions may further include polymeric additives, aqueous alkali, a pigment and a defoamer. Additionally, a new sizing composition containing: (a) a compound selected from the group consisting of alkenyl succinic anhydrides, alkyl ketene dimers and mixtures thereof and (b) a metal salt selected from the group of metals consisting of zirconium, hafnium, titanium and mixtures thereof are described.

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# *USE OF ZIRCONIUM SALTS TO IMPROVE THE SURFACE SIZING EFFICIENCY IN PAPER MAKING*

## Field of the Invention

This invention relates to an improved process of surface sizing of paper and paperboard that prevents the surface size polymer from penetrating into the paper and paperboard before it is dried and cured, thereby sealing the surface of the paper and paperboard and preventing dusting and linting of the paper and paperboard during further processing.

## Background of the Invention

Although many functional chemicals can be added to the wet end of the paper machine as internal sizes, some grades of paper require special properties that cannot be provided by the low levels of additives that are retained at the wet end of the paper machine. An example is a high quality printing and writing grade of paper or paperboard requiring high levels of surface size to provide good printing characteristics, as well as a high surface strength. To achieve the properties required for these grades of paper, it is necessary to apply the chemicals to a preformed paper web, also called surface sizing.

The most common method for the application of chemicals to the surface of a paper web is by a size applicator, such as a size press or a calendar water box. In the size press, dry paper is passed through a flooded nip and a solution or dispersion of the functional chemicals contact both sides of the paper. Excess liquid is squeezed out in the press and the paper is redried and cured.

The most commonly used materials for surface sizing of paper and paperboard are water soluble or water dispersible polymers, such as starches and modified starches, polyvinyl alcohols, styrene-maleic anhydride interpolymers and other carboxylated polymers, alkylketene-dimer emulsions, carboxymethyl cellulose, polyurethanes, epoxies and the like, either alone or in mixtures of two or more of these polymers. Other additives such as defoamers, pigments, alkali, and the like are also often added to the treatment solution.

Surface sizing is applied to paper or paperboard to improve various properties of the sheet to render it suitable for the end application. Typical properties imparted by surface size treatment to the paper sheet, after drying and curing, include improved resistance of the surface to moisture, enhanced strength, improved bonding of the cellulosic fibers to prevent subsequent linting, as well as preventing the loss by dusting of the mineral powders that are often added at the wet end of the paper machine to enhance optical properties and also lowering the cost of the final paper sheet. Other important properties of the paper sheet, such as reduced porosity, enhanced ink holdout when printed, and reduction of curl of the sheet can also be achieved by surface sizing.

Surface sizing of paper and paperboard also plays an even more important role when no internal size is used as is often the case, or when certain synthetic internal sizes are used, as is typical for papers made under neutral or alkaline pH conditions. On the other hand, certain synthetic internal sizes, if used at high dosage levels, can cause problems in the operation of the paper machine because of slipperiness and hydrolysis of the internal size, and in the reduced quality of the produced paper sheet. These problems can be eliminated by using to the maximum extent possible surface sizing as an alternative to internal sizing. As already mentioned above, surface sizing is applied to both sides of paper and paperboard.

A major disadvantage limiting the efficiency of a surface size is its tendency to penetrate excessively the paper or paperboard sheet when certain internal sizing agents with slow rates of internal sizing development are used. This reduces the effectiveness of the surface size, because less of the applied surface size is retained at the surface of the paper or board sheet, thereby requiring that higher pickup levels be used. It also places more reliance on the internal size to provide sizing levels required of the paper sheet. When salts of carboxylated polymers are used in the surface size in addition to water soluble hydroxylated polymers, i.e., polymers containing hydroxygroups, extra large addition levels are needed to compensate for this penetration. The reduced concentration of the surface sizing composition at the surface of the sheet can result in paper sheet problems. Other problems are caused by the large amount of carboxylated polymers necessary to overcome the effect of penetration into the sheet, a common problem being the generation of foam. Foam reduces pickup of the surface sizing composition, causes defects on the paper surface, and interferes with the efficient operation of the paper machine. Carboxylated polymers are also more expensive than hydroxylated polymers, such as starch, and their use should be minimized for that reason.

There has been found a way to improve the surface holdout of the surface size by adding a group IV (of the periodic system of elements) metal salt, for example ammonium zirconium carbonate (AZC) to the surface sizing composition to maximize its effect. Other group IV metal salts useful in the instant invention are those of hafnium and titanium. Zirconium salts have previously been suggested, for example, in U.S. Patent No. 4,400,440 issued to Shaw, as well as in Great Britain Patent No. 1,024,881 issued to the Inveresk Paper Company, to impart property improvements when used in conjunction with emulsion polymers for significantly improved block resistance of a pigmented coating composition that was heated and cured to crosslinking the coating binder. Zirconium salts have also been suggested as migration inhibitors for non-woven binders as taught in U.S. Patent No. 3,930,074 issued to Drelich.

Additionally, it is well known that alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD) are the 2 most popular internal sizes used to make paper in a neutral or alkaline papermaking condition. Both ASA and AKD cause problems on paper machines. These problems can be minimized if the amount of ASA or AKD used can be kept to a minimum.

Both ASA and AKD are prepared into an emulsion prior to adding them in the paper machine "wet end". During the emulsification step, starch or polymer is combined with the ASA or AKD to "activate" the ASA and AKD chemically in the papermaking system.

## Summary of the Invention

It has now been found that the addition of a zirconium salt to an aqueous surface sizing composition overcomes the difficulties presently associated with the surface sizing of paper and paperboard. The addition of a zirconium salt to the aqueous surface sizing composition not only results in crosslinking the water soluble or water dispersible polymer on drying and curing, i.e., by the elimination of water from the surface of the paper or paperboard, but the zirconium salt also immobilizes the surface sizing composition in the wet state by complex formation with the polymer in the surface sizing composition, and thereby prevents its penetration into the paper or paperboard sheet in the wet state before the sheet enters the drying section of the paper machine. This results in a more efficient use of the surface sizing composition resulting in improved properties as later described in more detail. The instant invention consists of a multi-step process to make and apply the surface sizing composition as follows:

a) Preparing an aqueous surface sizing composition by combining and mixing an aqueous solution of at least one water soluble or dispersible polymer or interpolymer, a solution or dispersion of auxiliary materials, and an aqueous solution of a metal salt, selected from the group of metals consisting of zirconium, hafnium and titanium, to the polymer solution;

b) Adjusting the pH of the aqueous sizing composition from about 5 to about 10.5 by the addition of alkali, thereby increasing the molecular weight of the polymer or interpolymer by chemically or physically reacting the polymer or interpolymer with the salt of zirconium, hafnium or titanium, resulting in an increase in viscosity of the aqueous sizing composition;

c) Applying the aqueous surface sizing composition to the surface of the paper or paperboard by means of a coating device, where the aqueous surface sizing composition is immobilized in the wet state, thereby preventing penetration of the aqueous surface sizing composition into the paper or paperboard;

d) Drying and curing the aqueous surface sizing composition by applying heat to the treated paper or paperboard thereby crosslinking the polymer or interpolymer contained in the surface sizing composition, and also forming bonds with the pigment particles and fiber present at the surface of the paper or paperboard, and thereby anchoring the polymer or interpolymer to the surface of the paper or paperboard.

An additional finding of the present invention is the surprising discovery that when a metal salt selected from the group of metals consisting of zirconium, hafnium and titanium is mixed with a water soluble hydroxylated polymer and an alkylketene dimer (AKD) and/or an alkenyl succinic anhydride (ASA), a cellulosic sizing composition is obtained which improves significantly the properties of the resulting paper when in contact with liquid foods such as milk, juices, etc. That is the resulting paper products have improved resistance to liquid penetration.

Applicant has also discovered that:

If ammonium zirconium carbonate ("AZC") is added to the starch prior to emulsification of the starch with AKD and/or ASA, the results are:

1) with AKD a 20-40% improvement results in hydrogen peroxide size test.

2) with AKD and ASA in combination, a 30-40% improvement results in hydrogen peroxide size test.

If AZC is used in AKD and/or ASA after emulsification, sizing imparted by the AKD and/or the ASA significantly improves.

The hydrogen peroxide size test is explained herein in detail under the Examples section of this application.

The present invention further relates to sizing compositions useful in the manufacture of cellulosic products comprising (a) a composition selected from the group consisting of alkenyl succinic anhydrides, alkyl ketene dimers and mixtures thereof, and (b) a metal salt selected from the group of metals consisting of zirconium, hafnium, titanium and mixtures thereof.

The instant invention is also directed to aqueous emulsions suitable for sizing cellulosic materials comprising: (a) water; (b) at least one emulsifier agent selected from the group consisting of anionic, nonionic and cationic emulsifiers; (c) a composition selected from the group consisting of alkenyl succinic anhydrides, alkyl ketene dimers and mixtures thereof; (d) a metal salt selected from the group of metals consisting of zirconium, hafnium, titanium and mixtures thereof; and (e) a polymer selected from the group consisting of water soluble hydroxylated polymers, water soluble carboxylated polymers and mixtures thereof.

In another aspect of the invention, a process is described for sizing cellulosic materials which comprises the step of intimately dispersing within the wet pulp, prior to the ultimate conversion of said pulp into a dry web, a composition containing: (a) a composition selected from the group consisting of alkenyl succinic anhydrides, alkyl ketene dimers and mixtures thereof, and (b) a metal salt selected from the group of metal consisting of zirconium, hafnium, titanium and mixtures thereof.

The invention is further directed to a cellulosic article of manufacture having incorporated therein a sizing composition comprising: (a) a composition selected from the group consisting of alkenyl succinic anhydrides, alkyl ketene dimers and mixtures thereof and (b) a metal salt selected from the group of metals consisting of zirconium, hafnium, titanium and mixtures thereof.

## Detailed Description of the Invention

The above and related objects of this invention are achieved through the addition of a zirconium, hafnium or titanium salt to the surface sizing composition. The zirconium salts that may be employed are water soluble. Examples of these salts include: ammonium zirconium carbonate (AZC); ammonium zirconium sulfate; ammonium zirconium lactate; ammonium zirconium glycolate; zirconium oxynitrate; zirconium nitrate; zirconium hydroxychloride; zirconium orthosulfate; zirconium acetate; potassium zirconium carbonate (KZC); zirconium mandelate; tripotassium zirconium sulfate; trisodium zirconium carbonate; zirconium glycolate; monosodium zirconium glycolate; zirconium sulfate; zirconium carbonate, and the like. The equivalent hafnium or titanium salts may also be used. Generally, 0.15 percent to 1.5 percent of zirconium dioxide, based on the dry weight of the water soluble or dispersible polymers, are being added as its salt, preferably 0.2 to 1 percent of zirconium dioxide as its salt. If, for example, ammonium zirconium carbonate (AZC) is used as the zirconium composition, the amounts added on the dry weight of the water soluble or dispersible polymers would be 0.85 percent to 8.5 percent, preferably 1.1 percent to 5.6 percent. Hafnium typically is found in conjunction with zirconium, and as a result, AZC and other zirconium salts typically contain a small percentage of hafnium compounds. Hafnium has chemical properties similar to zirconium. Accordingly, any comments applicable to zirconium based products described in the instant invention apply to hafnium as well. Titanium salts may be used in equivalent amounts.

Starch is primarily used as the water soluble hydroxylated polymer in the surface sizing composition. Examples of starches are: corn starch, potato starch, rice starch, tapioca starch, converted starches, either by means of enzymes, acid or persulfate treatments, dextrin, modified starches including ethylated starch, propylated starch or butylated starch, cyanoethylated starch, cationic starch, acetylated starch, oxidized starch and the like. Other water soluble hydroxylated polymers that may be used are carbohydrates such as alginates; carrageenan; guar gum; gum arabic; gum ghatti; gum karaya; gum tragacanth; locust bean gum; pectins; xanthan gum; tamarind gum; and the like. Modified cellulosic gums such as carboxylated cellulose, such as carboxymethyl cellulose (CMC), and hydroxyalkyl cellulose, such as hydroxyethyl cellulose, may be employed as the water soluble polymer. Water soluble polymers containing amide, lactone, pyrrolidinone or imidazolinone groups may also be used in the surface sizing composition. Synthetic water soluble hydroxylated polymers such as fully and partially hydrolyzed polyvinyl alcohols can also be used.

Salts of carboxylated polymers such as salts of low molecular weight polyacrylic acid or polymethacrylic acid, the ammonium and sodium salts of styrene-maleic anhydride interpolymers (NH4 SMA and Na SMA respectively), salts of styrene-acrylic acid interpolymers, of ethylene-acrylic or methacrylic acid interpolymers, salts of vinyl acetate-crotonic acid interpolymers; polymeric additives, such as water soluble or dispersible urethane-, polyester-, polyamides-, and epoxy polymers, and the like, can be used alone or in conjunction with starches and other hydroxylated polymers, such as polyvinyl alcohols. In case they are used as additives to starch or polyvinyl alcohol, these compounds are generally employed in a ratio of 0.5 to 99.5, preferably in a ratio of 4 to 96, to starch or polyvinyl alcohol.

If starch or modified starch alone is used as the water soluble hydroxylated polymer in the surface sizing composition, a zirconium salt such as ammonium zirconium carbonate (AZC) or potassium zirconium carbonate (KZC) is added in the appropriate amount after the starch is dissolved. If polyvinyl alcohol is used instead of starch, the appropriate amount of zirconium salt is added to the surface sizing composition based upon the dry content of the polyvinyl alcohol, after dissolution of the polyvinyl alcohol.

If a synthetic water soluble polymer such as a salt of a styrene maleic anhydride interpolymer (SMA) is used in combination with starch or polyvinyl alcohol or other hydroxylated polymers, the appropriate amount of the zirconium salt is added based on the total dry content of the starch, the carboxylated polymer and the other components of the surface sizing composition other than the zirconium salt. The zirconium salt should always be added as an aqueous solution after make-up of the surface sizing composition. The exact amount of the zirconium salt, that is desirable, can vary depending upon the concentration of the zirconium salt solution, and the speed of immobilization and crosslinking required for the respective application.

Auxiliary materials may be added to the surface sizing composition such as defoamers, bactericides, pigments, alkali, and the like as required. Often pigments such as number 1 filler clay are added to the surface sizing composition to obtain additional smoothness and opacity, as well as cost savings of the treated paper or paperboard sheet. Other pigments which are suitable are, for example, calcium carbonate, titanium dioxide, silica, and talc. When pigments are used in such a way, the amount can vary from 0 to 70 percent, preferably, from 20 to 50 percent based on the weight of the water soluble or dispersible polymer in the surface sizing composition. The surface sizing composition is adjusted to a pH of 5 to 10.5. Preferably, when 100 percent starch or polyvinyl alcohol is used as the water soluble polymer, the pH should be adjusted from 5 to 8. When an ammonium salt of a carboxylated polymer is present in the surface sizing composition, the pH should be adjusted from 7.5 to 9, for the potassium or sodium salt from 6 to 9. The pH adjustment should be made with alkali such as ammonia, sodium hydroxide, sodium carbonate, potassium hydroxide and the like.

The aqueous surface sizing composition of the instant invention for sizing paper or paperboard consists essentially of:

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|---|---|
| 50-70 parts | water soluble hydroxylated polymer |
| 0-7 parts | water soluble carboxylated polymer |
| 0.3-3 parts | alkali salt of zirconium carbonate (calculated as $ZrO_2$) |
| 0-7 parts | polymeric additive |
| 0-2 parts | aqueous alkali |
| 0-80 parts | pigment |

and enough water to obtain from 1.5 to 20 percent total solids, and, optionally, a small amount of defoamer.

The preparation of the surface sizing composition is done in a conventional kettle equipped with heating and cooling means, and an agitator. The water to dissolve the dry polymer or mixture of polymers is added first, the polymer powder is sifted in and the water is heated to the appropriate temperature to effect dissolution of the polymer. Where a concentrated solution or dispersion of the polymer is available, that can be added at this point also. The batch is then cooled, the pH adjusted with alkali to about 7 to 8, and the other ingredients, such as defoamers, pigments and the like, are then added as needed. A solution of the zirconium salt is added last under good agitation.

The surface sizing composition thus prepared is applied to the sheet in the normal manner by a size applicator, such as the size press of the paper machine or a calendar water box as mentioned above and well known in the art.

When the surface sizing composition has been applied to the paper or paperboard sheet, surface sizing composition is immobilized on the surface of the sheet by the zirconium salt through complex formation with the hydroxylated and carboxylated polymer, as the case may be. It is believed that the zirconium salt also forms a complex with the cellulose of the paper at the surface of the sheet, thereby preventing the surface sizing composition to penetrate into the sheet. The zirconium complexes also contain considerable amounts of bound water that prevent crosslinking of the polymer as well as of the cellulose of the paper at the surface of the sheet in the wet state. After the paper or paperboard sheet enters the drying and curing section of the paper machine, the hydrated zirconium complexes are changed by the elimination of water to effect crosslinking of the polymer in the surface sizing composition. The hydrated zirconium complexes also react with the cellulose at the surface of the paper sheet, thereby anchoring the solid polymer of the surface sizing composition to the surface of the paper sheet. The temperature of the drying and curing section of the paper machine is from about 250° to 350° F. The surface temperature of the paper sheet is about 190° to 212° F during the drying and curing cycle. After drying and curing, the paper sheet should still contain about 4-6 percent moisture to prevent embrittlement of the sheet.

The surface sizing composition of the instant invention is advantageously applied to paper or paperboard that has been filled with calcium carbonate pigment at the wet end of the paper machine. The use of calcium carbonate as a filler pigment is dictated by the desire to produce alkaline paper, rather than acidic paper. The longevity of the paper is very much enhanced by using alkaline ingredients, thus keeping the paper pH above 7. The zirconium salt is especially well suited to form complexes and then crosslink both the polymer of the surface sizing composition and the cellulose of the paper surface because it reacts well with these materials under mildly acidic and alkaline conditions. The zirconium salt also forms complex bonds with ions at the surface of pigments which have been added to the paper or paperboard at the wet end, thereby further strengthening the surface of paper and paperboard. This is not true of previously used crosslinkers, such as amino resins. For example, melamine formaldehyde resins, urea formaldehyde resins, glyoxal based resins, and the like require a strong acidic catalyst for their reaction with both the polymer of the surface sizing composition and the cellulose of the paper surface which prohibits the use of inexpensive alkaline filler pigments, such as calcium carbonate. These aforementioned resins additionally do not immobilize the surface sizing composition by complex formation, because they do not react in an aqueous environment, thereby causing penetration of the surface sizing composition into the paper or paperboard sheet. They do not complex with pigments. They also emit undesirable formaldehyde vapors into the workplace and environment.

The surface sizing composition of the instant invention provides many advantages for the paper maker. The porosity of the sheet is decreased, thereby improving sizing values. As a result of the more strongly bound surface imparted by the instant invention, the loss of cellulosic fiber and mineral content from the sheet during printing is greatly reduced, resulting in less down time of the printing press. Upon subsequent coating of the paper and paperboard sheets, scratches or streaks are minimized as mentioned later. The amount of mineral filler pigments can be increased in the sheet at the wet end of the paper machine, which reduces the unit cost of the paper and paperboard. The total amount of the surface sizing composition can be reduced because the instant invention allows the surface sizing composition to be used more efficiently, thereby also reducing the level of foam during the sizing operation. The reliance on the internal size for holdout of the surface treatment of the paper sheet is reduced, thereby saving on internal size. The ability to obtain high sizing efficiency with less costly, low viscosity starch such as ammonium persulfate modified starch in the surface sizing composition is an important advantage of the instant invention over previously used processes. The bonds between zirconium ions and polymer in the surface sizing composition as well as between the zirconium ions and the cellulosic fibers, and the zirconium ions and the pigment particles on the surface of the sheet can be broken by a strongly alkaline treatment, thus allowing the paper and paperboard sheet to be repulpable. The zirconium salt orients the carboxylated polymer molecule, such as SMA, in such a way through ionic charges that the hydrophobic portion faces away from the surface of the paper sheet, thereby improving the water resistance and water repellency of the surface sized paper sheet.

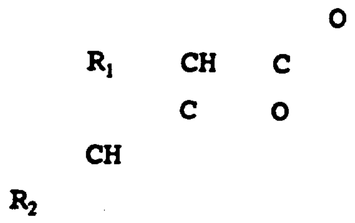
When it is desired to make internal sizing compositions useful in the manufacture of cellulosic products, metal salts such as those selected from the group of metals consisting of zirconium, hafnium titanium and mixtures thereof are mixed with retention aids such as starch used in a composition selected from the group consisting of alkenyl succinic anhydrides, alkyl ketene dimers and mixtures thereof. The amount of metal salt in the sizing compositions of the present invention is typically in the range of 0.1% to 15% by weight, preferably 2% to 12% by weight based upon the retention aid.

Typical retention aids include starches, cationic starches and polyamides. The preferred starches are quaternary cationic starches at dosage levels of 0.4%-0.7% starch solids on dry cellulose (8 to 14 lbs/2000 lbs pulp). The preferred polyamides are cationic polyamide or polyacrylamide dosed typically at 0.5%-2.0% solids on dry pulp (1 to 4 lbs/2000 lbs pulp). Alternatively, a dual retention system comprised of anionic and cationic retention aids often is used to maintain ionic balance required for proper retention. The anionic polymer is normally an anionic polyamide or an anionic polyacrylamide dosed separately from the cationic retention aid.

The amount of alkenyl succinic anhydride or alkyl ketene dimer or mixtures thereof is typically in the range 84% to 30% preferably in the range of 30% to 45% by weight. When mixtures of ASA and AKD are used the amounts of each in the mixtures can be in the range of 1 to 99% by weight.

The substituted succinic anhydride useful for this invention is a hydrophobic molecule. Usually it will have one substituent in the 3-position but it may have substituents in both the 3- and 4-positions. In general, the substituent will be an alkyl, alkenyl or aralkyl group. Other elements may be present in a minor amount, such as a sulfur or ether linkage. The total number of carbon atoms in the substituent is between 6 and 50. A preferred substituent size is between 10 and 30 carbon atoms. More preferred is between 12 and 25 carbon atoms. A preferred embodiment of the contemplated anhydrides is the alkenyl succinic anhydride made by allowing an olefin to react with maleic anhydride. For present purposes, I shall refer to the anhydrides contemplated as "ASA".

Such materials are exemplified by the maleic anhydride copolymers with n-pentadecene-2; n-pentadecene-3; n-pentadecene-6; n-heptadecene-4; n-heptadecene-5; n-heptadecene-8; n-heptadecene-3; n-heptadecene-5; n-heptadecene-7; n-octadecene-3; n-octadecene-4; n-octadecene-9; n-nonadecene-2; n-nonadecene-7; n-eicosene-4; n-eicosene-10; n-heneicosene-3; n-heneicosene-9; n-tetracosene-2; n-tetracosene-5 and n-tetracosene-11. The ketene dimers used in the invention are known per se and have the following general formula:



Wherein $R_1$ and $R_2$ each individually represents an organic hydrophobic hydrocarbon group having about 8-40 carbon atoms.

Examples of some suitable hydrophobic hydrocarbon groups include alkyl groups, alkenyl groups, aralkyl groups, alkaryl groups, and alkyl substituted cycloalkyl groups. Illustrative of some suitable alkyl groups for $R_1$ and $R_2$ having about 8 to about 40 carbon atoms are decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, tetracosyl, and pentacosyl groups.

The preferred alkyl groups contain from about 12 to about 30 carbon atoms. Some examples of suitable alkenyl groups containing about 8 and 40 carbon atoms include decenyl, tridecenyl, heptadecenyl, octadecnyl, eicosenyl, and tricosenyl groups.

Some suitable aralkyl, alkaryl and alkyl substituted cycloalkyl groups having at least about 8 carbon atoms include 4-tert butylphenyl, octylphenyl, nonylphenyl, dodecylphenyl tridecylphenyl, pentadecylphenyl, octadecylphenyl, heneicosylphenyl, nonycyclopropyl, dodecylcyclobutyl, tridecylcyclopentyl, tetradecylcyclohexyl groups.

It is understood that the alkyl, alkenyl, alkaryl, aralkyl and alkycycloalkyl groups can contain non-interfering, inert substituents as is known to persons skilled in the art. Some examples of inert substituents include ether, carboalkoxy, alkyloxy, aryloxy, aryloxy, arylalkyloxy, keto (carbonyl) tert amide groups and the like. Some radicals which preferably should not be to any large degree in the hydrophobic groups $R_1$ and $R_2$ include hydroxyl groups, amide groups containing amide hydrogen primary and secondary amino groups, unstable halogens and carboxylic groups and other acidic groups. Of course, persons skilled in the art can readily determine which substituents can be employed if it is desired to avoid undesirable side reactions.

Each $R_1$ and $R_2$ individually is preferably an alkyl group containing 8 to 30 carbon atoms. Moreover, mixtures of ketene dimers can be used when desired.

The ketene dimers can be prepared by previously known methods. For instance, the ketene dimers can be obtained by reacting thionyl chloride and carboxylic acid containing the desired hydrophobic hydrocarbon group to produce the corresponding acid chloride, and then dimerizing the acid chloride by hydrogen chloride splitting to produce the desired ketene dimer.

Cationic starch dosage with AKD also is typically above what is required to retain AKD or ASA per se to enhance the sheet strength prior to its being dried (wet web strength). For example, 0.4%-0.5% is adequate for retention, and an additional 0.20% often is added for improved strength.

When it is desired to make an emulsion, and emulsifier may be optionally added, although it is not necessary since materials such as cationic starch which act as a binder may also act as an emulsifier. The emulsifier is typically selected from the group of nonionic, anionic and cationic surfactants. When an emulsion containing a cationic starch is used, the starch in the emulsion is present in the concentration range of 10 to 20% by weight based on the total weight of each of the components of the emulsion. The preferred contact for the cationic starch is 2% to 20% by weight.

The actual use of the sizing agents of the present invention 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 co-addition of chemical dispersing agents to the fiber slurry.

Another important factor in the effective utilization of the sizing agents of this 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 sizing agents herein as well as for bringing the latter into close proximity to pulp fibers. Among the materials which may be employed as cationic agents in the process herein one may list alum, aluminum chloride, long chain fatty amines, sodium aluminate, substituted polyacrylamide, chromic sulfate, animal glue, cationic thermosetting resins and polyamide polymers. Of particular interest for use a 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, these 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 the 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 supped agitators, mechanical 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 the sizing agents, one may list such hydrocolloids as ordinary starches, non-cationic starch derivatives, dextrines, carboxymethyl cellulose, gum arabic, gelatin, and polyvinyl alcohol as well as various surfactants. Examples of such surfactants include polyoxyethylene sorbitan trioleate, polyoxyethylene sorbitol hexaoleate, polyoxyethylene sorbitol laureate, and polyoxyethylene sorbitol oleate-laureate. When such noncationic emulsifiers are used, it is often desirable to separately add a cationic agent to the pulp slurry after the addition to the latter of emulsified sizing agent. In preparing these emulsions with the use of an emulsifier, the latter is usually first dispersed in water and the sizing agent is then introduced along with vigorous agitation.

Further improvements in the water resistance of the paper prepared with these 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. However, it should again be noted that post curing is not essential to the successful operation of this invention.

The sizing agents of this 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 chemiground-wood, 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.

The following examples further describe the invention, and are meant to be illustrative without limiting the cope of the instant invention:

## Example 1

A surface sizing composition was prepared by adding AZC (AZCote$_{5800m}$, supplied by Hopton Technologies, Inc., Albany, Oregon was used), containing about 12 to about 18 percent zirconium as calculated as $ZrO_2$, at 4.5 percent "as received" on the dry content of a solution of low molecular weight starch, which had been converted using ammonium persulfate, after cooking and dissolving. The surface sizing composition was applied in the size press to a sheet of paper containing 12 percent precipitated calcium carbonate, dried and cured. This sheet had previously caused excessive dusting, and had caused contamination by calcium carbonate of an offset printing blanket.

After incorporating AZC into the surface sizing composition, dusting and linting of the treated paper sheet were significantly reduced during subsequent paper processing. As a result of reduced dusting, the precipitated calcium carbonate was then increased to 17 percent of the sheet content, causing less dusting and contamination than was experienced printing paper sheets that had a 12 percent calcium carbonate content when AZC was not added to the surface sizing composition.

### Example 2

A surface sizing composition was prepared by adding AZC (AZCote$_{5800m}$), containing about 12 to about 18 percent zirconium as calculated as $ZrO_2$,at a level of 5 percent "as received" on the dry content of an ethylated corn starch. The reverse side of a coated board was then treated with the surface sizing composition to bond cellulosic fibers to the surface, and dried and cured. The paperboard later came into contact with a moisture condensate covered chill roll on the paper machine, causing the starch of the surface size to resolubilize and lose its fiber-lay property before AZC was added to the surface sizing composition. After adding AZC to the surface sizing composition, and treating the same paperboard, fiber linting on an off-set printing blanket was substantially reduced as a result of keeping the surface sizing composition at the surface through immobilization, rather than having the starch penetrate the sheet. On drying and curing the sheet, the starch was crosslinked to also impart water resistance to the sheet, since no resolubilization occurred on a chill roll.

### Example 3

A surface sizing composition was prepared by adding AZC (AZCote$_{5800m}$) and KZC (HTI 5000), both containing about 12 to about 18 percent zirconium as calculated as $ZrO_2$, supplied by Hopton Technologies, Inc., Albany, Oregon) respectively, at 5 percent "as received" on the dry content of a 6 percent solution of ethylated converted corn starch (Penford Gum 260 was used, as supplied by Penford Products), and 5 percent of the sodium salt of SMA (NA SMA) as supplied by Hopton Technologies, Inc., Albany, Oregon as HTI 6620M, and 5 percent of the ammonium salt of SMA ($NH_4$ SMA) as supplied by Hopton Technologies, Inc., Albany, Oregon as HTI 6625, respectively, both amounts on a dry basis to the dry basis of the ethylated converted corn starch, in order to improve strength and reduce porosity through immobilization of the surface sizing composition near the surface of the sheet and subsequent crosslinking by heat. Results are listed in Tables 1 and 2:

TABLE 1

HERCULES SIZE TEST

| | AZC OR KZC not added | AZC added | KZC added |
|---|---|---|---|
| Starch only | 20.8 Seconds | 24.1 Seconds | 22.8 Seconds |
| Starch + $NH_4$ SMA | 24.7 Seconds | 46.5 Seconds | 33.9 Seconds |
| Starch + Na SMA | 20.7 Seconds | 24.8 Seconds | 23.4 Seconds |

HERCULES SIZE TEST METHOD: (HST) (80 percent transmittance, 1 percent ink, 1 percent formic acid (higher value in seconds equals more sizing effect and are, therefore, better) (Tappi Test Method T530-PM83 was used)

TABLE 2

GURLEY VISCOSITY TEST

| | AZC OR KZC not added | AZC added | KZC added |
|---|---|---|---|
| Starch only | 43 Seconds | 47 Seconds | 47 Seconds |
| Starch + $NH_4$ SMA | 53 Seconds | 67 Seconds | 70 Seconds |
| Starch + Na SMA | 66 Seconds | 84 Seconds | 87 Seconds |

GURLEY POROSITY: Number of seconds for volume of air to pass through a sheet. Higher values equal more sizing effect and are, therefore, better. Higher values mean reduced porosity. (Tappi Test Method T536-Om88 was used)

Both HST and Gurley results demonstrate that a performance of a polymer in the surface sizing composition is significantly enhanced by adding either AZC or KZC, and further, that the effect is even more enhanced when SMA is used in conjunction with the starch.

Example 4

A surface sizing composition was prepared by adding AZC (AZCote$_{5800m}$), containing about 12 to about 18 percent zirconium as calculated as $ZrO_2$, to a 7 percent solution of a low molecular weight starch, which had been converted using ammonium persulfate. Paper was sized, dried and cured and the paper was tested (starch + AZC). Next, 4.5 percent (dry basis on starch solids) sodium salt of SMA was added to the surface sizing composition and paper was sized, dried and cured, and the paper was tested (Starch + $NH_4$ SMA). AZC was next added at 4 percent "as received" level, based on the dry content of starch and SMA, to the surface sizing composition; paper was then sized, dried and cured and the paper was tested (Starch + $NH_4$ SMA + AZC). The results obtained are listed in Table 3:

TABLE 3

HST AND COBB SIZING AND GURLEY POROSITY TESTS

| | HST Sizing | Cobb Sizing | Gurley Porosity |
|---|---|---|---|
| Starch + AZC | 72 Seconds | 39 g $H_2O/m^2$ | 42 Seconds |
| Starch + $NH_4$ SMA | 83 Seconds | 33 g $H_2O/m^2$ | 120 Seconds |
| Starch + $Nh_4$ SMA+AZC | 126 Seconds | 31 g $H_2O/m^2$ | 635 Seconds |

*HERCULES SIZE TEST METHOD (HST) (80 percent transmittance, 1 percent ink, 1 percent formic acid) (higher values in seconds equal more sizing effect and are, therefore, better) (Tappi Test Method T530-PM83 was used)

COBB SIZING METHOD (COBB): 70 sec. exposure, weight difference before and after exposure to moisture; lower values equal more sizing effect and are, therefore, better. (Tappi Test Method T441-OM90 was used)

GURLEY POROSITY: Number of seconds for volume of air to pass through a sheet. Higher values equal more sizing effect and are, therefore, better. Higher values mean reduced porosity. (Tappi Test Method T536-OM88 was used)

This example shows again that AZC is very effective when SMA is added to the starch in the surface sizing composition.

__Example 5__

Six percent solutions of four different types of polyvinyl alcohol (PVOH) were prepared by cooking for 40 minutes at 95°C. AZC (AZCote$_{5800m}$), containing about 12 to about 18 percent zirconium as calculated as $ZrO_2$, was added at 10 percent "as received" AZC to each solution. Each surface sizing composition was applied to a base sheet of bleached white paper with basis weight of 56 Lbs/3000 ft$^2$, internal sizing of 23.3 seconds HST. Each surface sizing composition was applied with a size press (Dow Coater) operating at 30 ft/min. with a nip pressure of 50 psi, and a drum drying temperature of 90 to 100°C. Control runs were conducted without the addition of AZC. A Hercules Size Test was conducted on each paper sheet using 1 percent Formic Acid, Transmittance. The results obtained are listed in Table 4:

Table 4

HERCULES SIZE TEST

| Polyvinyl alcohol Type | Mol. Wt. x 1000 | AZC added | Pick-up (lbs/3000ft$^2$) | HST (sec.) 1 h. | HST(sec) 24 h. |
|---|---|---|---|---|---|
| 97 % hydrolyzed | 44-65 | no | 0.8 lbs | 39.1 | 40.6 |
| | 44-65 | yes | 0.7 lbs | 43.5 | 54.0 |
| 99.3 % hydrolyzed | 44-65 | no | 1.2 lbs | 27.5 | 31.4 |
| | 85-146 | yes | 0.7 lbs | 29.8 | 36.2 |
| 87-89 % hydrolyzed | 15-27 | no | * | 14.9 | 19.4 |
| | 31-50 | yes | * | 19.6 | 21.7 |
| 87-89 % hydrolyzed | 44-65 | no | 1.0 lbs | 37.2 | 37.5 |
| | 85-146 | yes | 0.7 lbs | 44.4 | 45.4 |

* Problems with drier section of the size press prevented obtaining pick-up readings, and sizing values were also reduced.

HERCULES SIZE TEST METHOD (HST) (80 percent transmittance, 1 percent ink, 1 percent formic acid) (higher values in seconds equal more sizing effect and are, therefore, better) (Tappi Test Method T530-PM83 was used)

It should be noted that improved sizing values were obtained, even when the pick-up was low, when AZC was used, due to immobilization of the polyvinyl alcohol containing surface sizing composition. This demonstrates, that reduced levels of the more expensive polyvinyl alcohol may be used in conjunction with AZC to obtain results similar or superior to when using polyvinyl alcohol without the addition of AZC.

## Example 6

Paperboard which is sized using the process of example 5 is coated off-machine at a first coating station equipped with a blade coater for a first clay coating, and at a second coating station, with an air knife coater to apply a second clay coat. A control is run with paper board that has been sized without adding AZC to the surface sizing composition. The control paper board has developed serious scratches and streaks because loose fibers and pigment on the surface of the paper board accumulate behind the coating blade leading to severe scratching and streaking of the surface of the paperboard. The paper board sized with a surface sizing composition with added AZC (AZCote$_{5800m}$) does not develop any scratches or streaks on subsequent clay coating.

The results of a coating trial show the beneficial effect of immobilizing the surface sizing composition by including AZC in the surface sizing composition. Very few scratches or streaks appear in the coated surface of the paperboard.

## Example 7

A surface sizing composition prepared by cooking a 6 percent solution of starch (AMAIZO 791D, manufactured by the American Maize Products Company) was used, adding the same amount of #1 filler clay to the starch solution, that the weight ratio on a dry basis is 50-50 starch and clay, and finally, mixing in AZC (AZCote$_{5800m}$, supplied by Hopton Technologies, Inc., Albany, Oregon), containing about 12 to about 18 percent zirconium as calculated as $ZrO_2$ at 6 percent "as received" on the dry content of starch. A paper sheet with a basis weight of 44 lbs/300 $ft^2$ that was internally sized with alkylketene dimers of long-chain fatty acids, was surface sized on a size press (Dow Laboratory Coater) at 30 feet/minute speed, a nip pressure of 40 psi and a drying drum temperature of 80°C with the surface sizing composition thus prepared. Test results are listed in Table 5:

Table 5

HST and Cobb Sizing and Gurley Porosity Tests

| | HST Sizing | Cobb Sizing | Gurley Porosity |
|---|---|---|---|
| NO AZC added | 55.8 Sec. | 39.8 g $H_2O/m^2$ | 20.1 sec. |
| AZC added | 72.5 Sec. | 38.9 g $H_2O/m^2$ | 23.7 sec. |

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HERCULES SIZE TEST METHOD (HST) (80 percent transmittance, 1 percent ink, 1 percent formic acid) (higher values in seconds equal more sizing effect and are therefore better) (Tappi Test Method T530-PM83 was used)

COBB SIZING METHOD (COBB): 70 sec. exposure, weight difference before and after exposure to moisture; lower values equal more sizing effect and therefore better. (Tappi Test Method T441-OM90 was used)

GURLEY POROSITY: Number of seconds for volume of air to pass through a sheet. Higher values equal more sizing effect and therefore better- Higher values mean reduced porosity. (Tappi Test Method T536-OM88 was used)

It can be seen from the results that the ink in the HST test is retained longer on the surface when AZC was used in the surface sizing composition, which shows the beneficial effect of AZC. Often a mottled ink effect is observed in the HST test when no AZC is used in the surface sizing composition, indicating a non uniform surface of the sheet because the starch surface size penetrated the sheet unevenly. This is prevented when using AZC in the surface sizing composition.

Example 8

## Hydrogen Peroxide Test

1. Cut a 30 x 30 centimeter sample off the reel at the end of the paper machine.
2. Condition the samples at 60% Relative Humidity (92° C Dry Bolt, 81°C Wet Bolt temperatures).
3. Measure and record the caliper.
4. Cover both sides of the sample with $H_2O_2$ resistant adhesive tape. Use a roller or putty knife to ensure uniform contact of adhesive to sample surface.
5. Cut into samples measuring 1.5" x 5 1/16" (inches). Be sure to use sharp knife. Use roller or putty knife to press the adhesive tape to surface along cut edges, such that the only exposed area is the edge of the sample. This should yield four (4) samples from the 30 x 30 centimeter sheet.
6. Weight each 1.5" x 5 1/16 sample.
7. Using a wide, shallow Pyrex vessel, prepare a bath of water at 83°C. Place another, smaller, Pyrex vessel in the water bath, and add 70°C $H_2O_2$ (35% active) (Caution: Corrosive) to a depth of 10 centimeters. Be sure that the surface water in the bath is at or above the surface of the $H_2O_2$ bath.
8. Insert the 1.5" x 5 1/16" samples in the $H_2O_2$ bath for ten (10) minutes. Using a glass rod if necessary, be sure that the samples are 10 centimeters below the surface of the $H_2O_2$ solution. Cover the $H_2O_2$ bath to prevent evaporation.
9. After the 10 minutes of immersion has elapsed, move the samples to a blot paper, and then further dry on a second sheet of dry blotting paper.
10. Weigh the test samples, and compare against weight of samples prior to immersion.
11. Convert the weight gain to kilograms/meter$^2$.

An emulsion of AKD was prepared as follows:

200 gallons (1,668 pounds) of water
166.8 pounds of AKD wax
333.6 pounds (dry basis) oxidized cationic potato starch
20 pounds ("as received") of AZCote$_{5800m}$ Ammonium zirconium Carbonate (6% based upon the weight of the Starch)

The ingredients were mixed and homogenized to form an emulsion.

Another emulsion was prepared in the same manner as above, but the AZC was omitted.

The resulting emulsions were applied at 0.15% of paper furnish or 3.0 pounds per ton (2000 pounds) of paper furnish in a 144 lbs/3000 ft$^2$ sheet. A quaternary cationic potato starch was used at 6.7 dry pounds/ton of fiber to retain the AKD in the sheet. The resulting paper sheet samples were tested for comparative $H_2O_2$ absorption using the above described Test Method.

Results:

| | With AZC | Without AZC |
|---|---|---|
| $H_2O_2$ absorption | 0.5 Kg/Mt$^2$ | 0.71 Kg/Mt$^2$ |

### Example 9

An emulsion of ASA was prepared as follows:

200 gallons (1,668 pounds) of water
66.0 pounds of cationic potato starch
4.6 pounds of AZCote$_{5800M}$ Ammonium Zirconium Carbonate
220.0 pounds of ASA

The ingredients were mixed and homogenized to form an emulsion.

Another emulsion was prepared in the same manner as above, but the AZC was omitted.

The resulting emulsions were applied simultaneously with the emulsion prepared in Example 9 described above, in a ratio of 2 parts ASA emulsion: 1 part AKD emulsion, with the total dosage of AKD + ASA emulsion at 3.0 pounds/ton of paper furnish in a 144 lbs 3000 ft$^2$ sheet. The emulsions with AZC were dosed in one paper sheet sample, and the emulsions without AZC were dosed in another paper sheet sample. A quaternary cationic potato starch was used at 6.7 dry pounds per ton of fiber to retain the two emulsions in the sheet. The resulting paper sheet samples were tested for comparative $H_2O_2$ absorption.

Results:

| | With AZC | Without AZC |
|---|---|---|
| $H_2O_2$ absorption | 0.5 Kg/Mt$^2$ | 6 Kg/Mt$^2$ |

Example 10

Another two co-emulsions of ASA and AKD were prepared as described above in Example 9, but with a ratio of 75%/25% AKD/ASA and applied in the manner in the previous Example.

Results:

| | With AZC | Without AZC |
|---|---|---|
| $H_2O_2$ absorption | 0.5 $Kg/Mt^2$ | 0.68 $Kg/Mt^2$ |

Example 11

Two AKD emulsions were prepared in the manner described in Example 9 above, and applied to a 20 pound/1500 $ft^2$ test sheet at a dosage level of 1.5#/ton. A quaternary cationic potato starch was used at 6.7 dry pounds per ton of fiber to retain the two emulsions in the sheet. The sizing values were tested, using the Hercules Sizing Test ("HST") (TAPPI Test Method T530-PM83).

Results:

| | With AZC | Without AZC |
|---|---|---|
| HST | 29 Seconds | 22 Seconds |

Example 12

The AKD emulsion prepared in Example 9 without AZC was added to a 20 pound per 1500 $ft^2$ paper sample at a dosage of 1.5 pounds/ton. AZC was dosed into the AKD emulsion at 7% (as received basis) AZC on the emulsion solids as the emulsion was added to the furnish. A quaternary cationic potato starch was used at 6.7 dry pounds per ton of fiber to retain the AKD emulsion in the sheet samples.

Results:

| | With AZC | Without AZC |
|---|---|---|
| HST | 26 Seconds | 22 Seconds |

Example 13

Two ASA emulsions were prepared in the manner described above in Example 10, one sample having AZC, the other without AZC. Using a quaternary cationic potato starch at 14 pounds/ton. Both sheets were tested for HST.

Results:

| | With AZC | Without AZC |
|---|---|---|
| HST | 32 Seconds | 24 Seconds |

Example 14

The ASA emulsion prepared in Example 10 without AZC was added at a dosage of 1.0 pounds/ton to a 20 pound per 1500 ft$^2$ paper sample. AZC was dosed into the ASA emulsion at 7% (as received basis) AZC on the emulsion solids as the emulsion was added to the furnish. A quaternary cationic potato starch was used at 6.7 dry pounds per ton of fiber to retain the ASA emulsion in the sheet samples.

Results:

| | With AZC | Without AZC |
|---|---|---|
| HST | 30 Seconds | 24 Seconds |

Example 15

A typical formula as provided to an end user is a follows:

| | |
|---|---|
| AKD or ASA | 0.15% on pulp |
| Cationic starch | 0.50% on pulp |
| AZC (7% wet on dry starch) | 0.0035% |
| Pulp (dry) | 99.3465% |
| TOTAL | 100% |

The following additional tests illustrate the effectiveness of the invention:

1. $H_2O_2$ Test on paper for liquid packaging (milk, juice, etc.):

The following paper sheets were subjected to the $H_2O_2$ Test described on pages 31-32 hereof. Each sheet was 144 pounds/3000 square feet, produced from bleached pulp. AKD Dosage was four (4) pounds per ton of paper furnish.

Sample 1: Standard (AKD without AZC): 1.2 Kg/Mt$^2$ $H_2O_2$ Test Result

Sample 2: AZC was added at 7% (as received) on Starch Solids prior to emulsifying with AKD: 0.9 Kg/Mt$^2$ $H_2O_2$ Test Result

Sample 3: AZC was added at 7% (as received) on Starch Solids prior to emulsifying with AKD and ASA used in combination at 4 pounds per ton dosage: 0.5 Kg/Mt$^2$$H_2O_2$ Test Result

2. Hercules Sizing Test (TAPPI TEST METHOD T530-PM83):

20 pound/1500 square feet sheets of paper were sized with 0.75 pounds/ton with AKD and ASA, respectively. AZC dosed at 7% "as received" on solids of starch used during emulsification of the AKD or ASA. The results using the Hercules Sizing Test ("HST") Method:

Sample 1: ASA at 0.75#/ton dosage. HST result:24

Sample 2: ASA at 0.75#/ton, with AZC added to starch prior to emulsification: HST result: 32

Sample 3: ASA at 0.75#/ton, with AZC added to ASA + Starch after emulsification: HST results: 30

Sample 4: AKD at 0.75#/ton dosage: HST results: 22

Sample 5: AKD at 0.75#/ton, with AZC added to starch prior to emulsification, HST results: 29

Sample 6: AKD at 0.75#/ton, with AZC added to AKD + Starch after emulsification: HST results: 26.

What is claimed is:

1. A sizing composition comprising: (a) a compound selected from the group consisting of alkenyl succinic anhydrides, alkyl ketene dimers and mixtures thereof and (b) an amount of a metal salt selected from the group of metals consisting of zirconium, hafnium, titanium and mixtures thereof effective to cause crosslinking and immobilization on a substrate to be sized.

2. The composition of claim 1 wherein the alkenyl moiety in the alkenyl succinic anhydride contains from 6 to 50 carbon atoms.

3. The composition of claim 1 wherein the alkyl moiety in the alkyl ketene dimer has from 8 to 40 carbon atoms.

4. The composition of claim 1 wherein component (a) is a mixture of alkenyl succinic anhydrides and alkyl ketene dimers.

5. The composition of claim 1 wherein component (b) is selected from the group consisting of ammonium zirconium carbonate (AZC); ammonium zirconium sulfate; ammonium zirconium lactate; ammonium zirconium glycolate; zirconium oxynitrate; zirconium nitrate; zirconium hydroxychloride; zirconium orthosulfate; zirconium acetate; potassium zirconium carbonate (KZC); zirconium mandelate; tripotassium zirconium sulfate; trisodium zirconium carbonate; zirconium glycolate; monosodium zirconium glycolate; zirconium sulfate; zirconium carbonate, and mixtures thereof.

6. The composition of claim 1 wherein the content of component (a) is in the range of 30% to 84% by weight.

7. An aqueous emulsion suitable for sizing cellulosic materials comprising:

(a) water;

(b) at least one emulsifier agent selected from the group consisting of anionic, nonionic and cationic emulsifiers;

(c) a compound selected from the group consisting of alkenyl succinic anhydrides, alkyl ketene dimers and mixtures thereof;

(d) a metal salt selected from the group of metals consisting of zirconium, hafnium, titanium and mixtures thereof, in an amount effective to cause crosslinking and immobilization on cellulosic material; and

(e) a polymer selected from the group consisting of water soluble hydroxylated polymer, water soluble carboxylated polymer, and mixtures thereof.

8. The emulsion of claim 7 wherein the emulsifier is a nonionic emulsifier.

9. The emulsion of claim 7 wherein the alkenyl moiety in the alkenyl succinic anhydride has from 6 to 50 carbon atoms.

10. The emulsion of claim 7 wherein the alkyl moiety in the alkyl ketene dimer has from 8 to 40 carbon atoms.

11. The emulsion of claim 7 wherein the metal salt is selected from the group consisting of ammonium zirconium carbonate (AZC); ammonium zirconium sulfate; ammonium zirconium lactate; ammonium zirconium glycolate; zirconium oxynitrate; zirconium nitrate; zirconium hydroxychloride; zirconium orthosulfate; zirconium acetate; potassium zirconium carbonate (KZC); zirconium mandelate; tripotassium zirconium sulfate; trisodium zirconium carbonate; zirconium glycolate; monosodium zirconium glycolate; zirconium sulfate; zirconium carbonate, and mixtures thereof.

12. The composition of claim 7 wherein said water soluble polyhydroxylated polymer is a cationic starch.

13. A method of sizing cellulosic materials which comprises the step of intimately dispersing within the wet pulp, prior to the ultimate conversion of said pulp into a dry web, the composition of claim 1.

14. A cellulosic article of manufacture having incorporated therein a sizing composition comprising (a) a compound selected from the group consisting of alkenyl succinic anhydrides, alkyl ketene dimers and mixtures thereof and (b) an amount of a metal salt selected from the group of metals consisting of zirconium, hafnium, titanium and mixtures thereof effective to cause crosslinking and immobilization on a sized surface of said article.

15. The cellulosic article of manufacture of claim 14 wherein component (a) is an alkenyl succinic anhydric having 6 to 50 carbon atoms in the alkenyl moiety.

16. The cellulosic article of manufacture of claim 14 wherein component (a) is an alkyl ketene dimer having 8 to 40 carbon atoms in the alkyl moiety.

17. The cellulosic article of manufacture of claim 14 wherein component (a) is a mixture of 1-99% by weight of an alkenyl succinic anhydride and 99 to 1% by weight of an alkyl ketene dimer.

18. The cellulosic article of manufacture of claim 14 wherein said metal salt is an ammonium zirconium carbonate (AZC).

19. The cellulosic article of manufacture of claim 18 wherein said AZC is present in a concentration of 0.1% to 15% by weight.

20. The sizing composition of claim 1 further comprising a retention aid.

21. A sizing composition according to claim 20 wherein the retention aid is dosed on dry cellulose or dry pulp between o.4% to 2.0%.

22. The composition of claim 21 wherein the content of component (b) is in the range of 0.1% to 15% by weight based the retention aid.

23. An aqueous surface sizing composition for sizing paper or paperboard consisting essentially of

50-70 parts water soluble hydroxylated polymer

an amount of a water soluble carboxylated polymer, such that said carboxylated polymer is present relative to said water soluble hydroxylated polymer in a ratio of 0.5:99.5 to 4:96, and not exceeding 7 parts

0.3-3 parts alkali salt of zirconium carbonate (calculated as $ZrO_2$)

0-7 parts polymeric additive

0-2 parts aqueous alkali

0-80 parts pigment

and enough water to obtain from 1.5 to 20 percent total solids and, optionally, an effective amount of a defoamer.

24. The aqueous surface sizing composition according to Claim 23, wherein said water soluble hydroxylated polymer is selected from the group consisting of corn starch, potato starch, rice starch, tapioca starch and polyvinyl alcohol.

25. The aqueous surface sizing composition according to Claim 23, wherein said water soluble hydroxylated polymer is a chemically or biologically modified starch.

26. The aqueous surface sizing composition according to Claim 23, wherein said water soluble hydroxylated polymer is selected from the group consisting of sodium alginate, carrageenan, guar gum, gum arabic, gum ghatti, gum karaya, gum tragacanth, locust bean gum, pectin, xanthan gum, and tamarind gum.

27. The aqueous surface sizing composition according to Claim 23, wherein said water soluble hydroxylated polymer is a chemically modified cellulose.

28. The aqueous surface sizing composition according to Claim 23, wherein said water soluble carboxylated polymer is selected from the group consisting of salts of styrene-maleic anhydride interpolymer, salts of styrene-acrylic acid interpolymer, salts of acrylic or methacrylic acid, salts of vinyl acetate-crotonic acid interpolymer, and salts of ethylene-acrylic acid interpolymer.

29. The aqueous surface sizing composition according to Claim 23, wherein said polymeric additive is selected from the group consisting of polyurethanes, polyesters, polyamides, and epoxy resins.

30. The aqueous surface sizing composition according to Claim 23, wherein said alkali salt of zirconium carbonate is selected from the group consisting of potassium zirconium carbonate and ammonium zirconium carbonate.

31. The aqueous surface sizing composition according to Claim 23, wherein said pigment is selected from the group consisting of calcium carbonate, clay, titanium dioxide, talc, and silica.

32. The aqueous surface sizing composition according to Claim 23, wherein said aqueous alkali is selected from the group

consisting of aqueous solutions of ammonium hydroxide, sodium hydroxide, potassium hydroxide, and sodium carbonate.

33. The aqueous surface sizing composition according to Claim 23, wherein said water soluble hydroxylated polymer is a partially hydrolyzed polyvinyl alcohol.

34. The aqueous surface sizing composition according to Claim 23, wherein said water soluble hydroxylated polymer is a fully hydrolyzed polyvinyl alcohol.

35. The aqueous surface sizing composition according to Claim 23, wherein said water soluble hydroxylated polymer is an ethylated converted corn starch.

36. The aqueous surface sizing composition according to Claim 23, wherein said water soluble hydroxylated polymer is a low molecular weight starch, which has been converted using ammonium persulfate.

37. The aqueous surface sizing composition according to Claim 23, wherein said pigment is calcium carbonate.

38. The aqueous surface sizing composition according to Claim 23, wherein said composition has a pH between 5 and 10.5.

39. An aqueous surface sizing composition for sizing paper of paperboard consisting essentially of

50-70 parts water soluble hydroxylated polymer

an amount of a water soluble carboxylated polymer, such that said carboxylated polymer is present relative to said water soluble hydroxylated polymer in a ratio of 0.5:99.5 to 4:96, and not exceeding 7 parts

0.3-3 parts alkali salt of Group IV metal selected from the group consisting of zirconium, hafnium and titanium

0-7 parts polymeric additive

0-2 parts aqueous alkali

0-80 parts pigment

and enough water to obtain from 1.5 to 20 percent total solids and, optionally, an effective amount of a defoamer.

40. The aqueous surface sizing composition according to Claim 39 wherein said alkali salt of a Group IV metal is a zirconium salt selected from the group consisting of ammonium

zirconium carbonate (AZC); ammonium zirconium sulfate; ammonium zirconium lactate; ammonium zirconium glycolate; zirconium oxynitrate; zirconium nitrate; zirconium hydroxychloride; zirconium orthosulfate; zirconium acetate; potassium zirconium carbonate (KZC); zirconium mandelate; tripotassium zirconium sulfate; trisodium zirconium carbonate; zirconium glycolate; monosodium zirconium glycolate; zirconium sulfate; and zirconium carbonate.

41. The aqueous surface sizing composition according to Claim 39 wherein said alkali salt of a Group IV metal is a hafnium salt selected from the group consisting of ammonium hafnium carbonate; ammonium hafnium sulfate; ammonium hafnium lactate; ammonium hafnium glycolate; hafnium oxynitrate; hafnium nitrate; hafnium hydroxychloride; hafnium orthosulfate; hafnium acetate; potassium hafnium carbonate; hafnium mandelate; tripotassium hafnium sulfate; trisodium hafnium carbonate; hafnium glycolate; monosodium hafnium glycolate; hafnium sulfate; and hafnium carbonate.

42. The aqueous surface sizing composition according to Claim 39 wherein said alkali salt of a Group IV metal is a titanium salt selected from the group consisting of ammonium titanium carbonate; ammonium titanium sulfate; ammonium titanium lactate; ammonium titanium glycolate; titanium oxynitrate; titanium nitrate; titanium hydroxychloride; titanium orthosulfate; titanium acetate; potassium titanium carbonate; titanium mandelate; tripotassium titanium sulfate; trisodium titanium carbonate; titanium glycolate; monosodium titanium glycolate; titanium sulfate; and titanium carbonate.

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/10283

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C08L 1/08
US CL :106/194, 205, 210
According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 106/194, 205, 210

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS
search terms: succinic, ketene, zirconium, hafnium, size?, alkenyl, dimer

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US, A, 4,872,951 (MALICZYSZYN ET AL.) 10 October 1989. | |
| A | US, A, 4,687,519 (TRZASKO ET AL.) 18 August 1987. | |
| A | US, A, 4,222,820 (HISKENS ET AL.) 16 September 1980. | |
| A | US, A, 4,207,142 (SHEPERD) 10 June 1980. | |
| A | US, A, 2,780,555 (BUDEWITZ) 05 February 1957. | |
| A | US, A, 3,137,588 (TAYLOR) 16 June 1964. | |
| A | US, A, 3,332,794 (HART) 25 July 1967. | |

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

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# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/10283

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US, A, 2,758,102 (GRUMMITT ET AL.) 07 August 1956. | |
| A | US, A, 3,930,074 (DRELICH ET AL.) 30 December 1975. | |
| A | US, A, 4,400,440 (SHAW) 23 August 1983. | |