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PAPER-SIZING COMPOSITION

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This invention relates to a paper-sizing composition and more especially to a rosin-starch composition whose starch component is possessed of such chemical and physical properties as to enable the realization of sized paper products of improved character, for instance, markedly improved water-repellence, improved bursting-strength, tear-resistance, fold-endurance, and other physical characteristics.

In producing rosin-sized papers, it is well known that the water-repelling or sizing effect on the paper sheet is influenced by the composition of the rosin size added to the papermaking stock. Thus, under given conditions, the greater the free rosin content of the rosin size, the greater is the water-repelling or sizing effect attainable in the finished paper product. It is hence understandable why many paper manufacturers have within recent years adopted the practice of using rosin sizes of high free rosin content. Indeed, some rosin sizes being used currently on a commercial scale consist essentially of an aqueous dispersion of substantially only free or unsaponified rosin, the dispersion being stabilized by a relatively very small amount of protective colloid, such as rosin soap and/or alkali-caseinate.

An important aspect of the present invention is the provision of a sizing composition containing besides rosin size a particular kind or form of starch that evidently serves the function of maintaining the free rosin content of the rosin size, whatever such free rosin content may be, at a maximum, and that hence enables the realization of paper products of maximum water-repellence for a particular rosin size usage. More specifically, the sizing composition hereof contains as its starch component a so-called starch-conversion product in acidic condition and exhibiting, among other characteristics, substantial solubility in water and relatively low dextrin content, as determined by a method presently to be indicated. The sizing composition hereof is prepared in an exceedingly simple way, namely, by mere substantially homogeneous admixture of substantially dry, pulverulent, rosin size and substantially dry, pulverulent, starch-conversion product of the particular character already described. The resulting substantially physically homogeneous rosin-starch composition presents the advantages that it can be stored and shipped economically with no significant deterioration, even when exposed to widely varying temperature, humidity, and other atmospheric conditions, and that it can be added directly to papermaking stock, as in a beater engine, and otherwise handled much in the same way as when using rosin size, as ordinarily, in dry or wet forms for sizing papermaking stock.

While we cannot explain with precision the mechanism underlying the improved results attainable through the use of the rosin-starch compositions hereof, yet some factors known to us contribute importantly to these results. To begin with, the admixture of substantially dry rosin size having some rosin soap content with the substantially dry starch-conversion product is attended by an envelopement or coating of the rosin size particles with such product. Upon addition of the composition consisting essentially of starch-coated rosin size particles to an aqueous suspension of paper-making stock, as in the beater engine, the aqueous medium tends to dissolve the soluble content of the converted starch coatings or envelopes before the rosin size particles themselves are acted upon by the aqueous medium and put into solution or dispersion in the aqueous medium. It is accordingly seen that the aqueous medium is, immediately prior to or concurrently with the solution or dispersion of the rosin size particles, put in acid condition by the acidic, converted starch for the solubilizing or dispersing action on the rosin size particles. Our hypothesis is that the converted starch, by reason of its acidic condition, not only controls or influences the kind of solution or dispersion effected upon the rosin size particles in the direction of yielding a solution or dispersion of microscopically fine or colloidal particle size but also preserves or increases the free rosin content of the rosin size. In this latter connection, it must be borne in mind that the acidic, converted starch, as it contacts with and is dissolved at least partially in the aqueous medium along with the rosin soap content of the rosin size, is conducive, if anything, to reaction between the rosin soap and the acidic aqueous medium to form free rosin or abietic acid. It is our further theory that, in the course of adding the rosin-starch composition hereof to papermaking stock, the free rosin content of such composition is preserved, if not increased. Moreover, we have observed that in appying our sizing composition to papermaking stock there is no observable generation in the papermaking stock of agglomerates of rosin size. In other words, the rosin size particles are dissolved or dispersed with no observable formation of palpable rosin particles; and such increase in free rosin as may occur during admixture of the sizing composition hereof with the papermaking stock is evidently in the

form of microscopically or colloidally fine free rosin particles. Whether or not our hypotheses are correct, the fact is that papermaking stocks sized with the composition hereof lead to paper products of higher water-repellence than when sizing is accomplished under similar conditions with similar amounts of the rosin size and converted starch added separately to the papermaking stock and phenomenally higher than when sizing is accomplished under similar conditions with similar amounts of the rosin size and alkali-converted starch added concurrently or separately to the papermaking stock.

Another important advantage inhering in the sizing composition hereof is its low foaming property even when its rosin size component is of very high rosin soap content. When such rosin size is applied to papermaking stock concurrently with an alkali-converted starch, as in the beater engine, foaming tendency is so pronounced that it becomes necessary to use so much anti-foaming agent, such as kerosene, to avoid "pin holes" and other physical defects in the paper product as to detract seriously from those qualities supposed to be imparted thereto by the rosin size and starch, including water-repellence, bursting-strength, tear-resistance, and fold-endurance. On the other hand, such foaming as may be occasioned by the application of the rosin-starch sizing composition hereof to papermaking stock in the beater engine is so small or inconsequential that no anti-foaming agent whatever need be added to the sized stock in arriving at a paper product of the desired substantial freedom from "pin holes" or other physical defects. The very low or negligible foaming property in the rosin-starch sizing composition hereof is attributable to the fact that, although the rosin-size component may originally be in distinctly alkaline condition, its alkalinity is largely or substantially completely offset or neutralized by the acidic, converted starched component, wherefore, although the rosin-size component by itself induces marked foaming under agitation in water, the compounding therewith of acidic, converted starch largely or substantially completely eliminates such foaming tendency. It might be remarked that it is well known in the papermaking industry that foam formation in an aqueous suspension of papermaking stock is fostered by distinctly alkaline rosin size and that the extent of foaming is related to the degree of alkalinity in the stock or the rosin size added thereto. It is for this reason that the preferred rosin-size composition hereof is prepared with rosin-size and acidic, converted starches in such relative proportions and/or in such conditions of alkalinity and acidity, respectively, as to yield in the papermaking stock prior to the addition of alum or other precipitant for the composition a substantially neutral condition, that is, pH value of substantially 7.

While not limited thereto, the present invention will now be described in terms of exemplary procedure that has been established as yielding a rosin-starch composition satisfactory for the purposes hereof and also in terms of exemplary papermaking procedure involving the use of such rosin-starch composition in the production of a sized paper product of the desired and improved character. In preparing a rosin-starch composition answering the purposes hereof, one may start with any of the known dry rosin sizes of commerce. For instance, the dry rosin size adopted may consist essentially entirely of pulverulent rosin soap; and it may contain only a slight amount of adventitious moisture, say, about 1%. The acidic, converted starch adopted may be a pulverulent material prepared by the heat-treatment or calcination of any suitable form of raw starch, say, tapioca flour; and the heat-treatment or calcination of the raw starch is preferably conducted under combined conditions controlled to yield an acidic, converted starch of the particular solubility and dextrin content desired. The combined conditions of heat-treatment of the raw starch may include not only properly correlated elevated temperature and time factors but also, if desired, the correlation of the elevated temperature and time factors with a catalyzing factor provided in the sphere of the starch-converting reaction by preliminarily moistening or spraying the raw starch granules with an amount of water or acidic, aqueous medium so limited (e. g., in amount less than about 25%, based on the dry weight of the raw starch) as to avoid substantial gelatinization of the starch granules. For preparing the rosin-starch composition hereof, we have found that an acidic, converted starch having substantial solubility, for instance, upwards of about 20%, is desirable; and we have further found that such starch functions conjunctively with the rosin size to best advantage, as regards increasing the water-repellence and improving the bursting-strength, tear-resistance, flex-endurance, and other qualities of the finished paper products, when its dextrin content is downwards of about 60% and is preferably as close to a substantially zero percentage as is possible to achieve by such heat-treatment or calcination as has been described and as will further be described hereinafter. The starch-solubility value given herein for the acidic, converted starch is determined by adding 5 parts of the starch to 100 parts of water at 75° F. and mixing the starch in the water for not less than about 3 hours, at the end of which time the dissolution of the soluble solids is ensured. The water-starch mixture is then filtered through a suitable filter medium, such as filter paper, and the filter medium carrying the undissolved starch-residue accumulation is dried at, say, 230° F., to bone-dryness and weighed. The undissolved starch residue may then be calculated from the original or bone-dry weight of the filter medium and the percentage of the soluble and insoluble solids in the converted starch readily evaluated. It is usually desirable to add to the water-starch mixture a predetermined or weighed amount of suitable adsorbent or so-called filter aid, such as freshly precipitated aluminum hydroxide or "Filtercel," which adsorbs the undissolved but fine solids residue and hence does away with such error as might result from the escape of fine undissolved particles through the filter medium. Whereas escape of undissolved fine particles is evidenced by a cloudy or milky appearance in the filtrate, the addition to the water-starch mixture being filtered of a suitable amount of adsorbent makes for a clear filtrate. The dextrin content given herein for the acidic, converted starch is determined by the method of Babington, Tingle and Watson, as described under the caption "The Examination of Commercial Dextrin and Related Starches" in the Journal of the Society of Chemical Industry, vol. 37 (1918), p. 257. Such solubility and dextrin values as appear in the appended claims

should hence be understood as having been determined by the particular methods herein prescribed.

The substantially dry rosin-starch composition hereof may be produced in an ordinary dry mixer or churn by adding the substantially dry rosin size and the substantially dry acidic, converted starch to the mixer and operating the mixer until substantial physical homogeneity in the resulting composition is ensured. While the composition hereof may have a dry rosin size content ranging from about 10% to 90%, based on the dry weight of the composition, and a dry starch content ranging from about 10% to 90%, based on the dry weight of the composition, the composition is especially advantageous when it has a rosin size content and a starch content each ranging from about 40% to 60%. The ease and simplicity of preparing the composition hereof will be appreciated from the fact that in a suitable dry mixer, for instance, a "Day" mixer, the substantial physical homogeneity desired in the composition is reached in a mixing period of only about one-half hour. The resulting composition may be shipped in bulk, as in barrels; or it may be put up into package form, for instance, in sealed paper bags each holding, say, five pounds and hence useful for sizing a particular portion or weight of papermaking stock in the beater engine. Assuming, for example, that a beater engine is to be charged or furnished with a thousand pounds of papermaking stock on a dry basis and that it is desired to produce from such stock a finished paper product of a sizing solids content of substantially 3%, the beater operator can proceed to add to the engine, along with the papermaking stock, six sealed bags or units of the sizing composition hereof, whereupon he can start the engine along with the necessary amount of circulating water and continue beating the stock until it has acquired the hydration or consistency desired for papermaking. During the beating operation, the paper bags are disintegrated or pulped along with the papermaking stock so that the resulting stock has the substantial homogeneity or consistency necessary for papermaking. It might be noted that the retention of the sizing solids of the composition hereof by the papermaking stock and their sizing or water-repellent value in the finished paper product are not significantly impaired as a result of their having been beaten or manipulated along with the papermaking stock. It is probably by virtue of the microscopically fine or colloidal condition of the sizing solids and their non-coalescing character that the functions desired thereof remain substantially unimpaired during the beating operation, for, in ordinary papermaking practice, it is customary to add rosin or other size when the beating operation is nearing completion or has been completed so as to realize the desired maximum from the size. It is plain, therefore, that one aspect of the present invention is that it makes possible the minimization of costs in the papermaking mill, since it becomes unnecessary to weigh out the sizing composition or handle it in loose, dusty condition as heretofore. On the contrary, the sealed bags or units of the composition hereof may be dumped as such into the beater engine and, being units of sufficiently small size to be disintegrated or reduced as they enter into the ingress afforded by the bed plate and the beater roll of the engine along with the papermaking stock, the distribution or dispersion of the sizing solids occurs at the same time as the papermaking stock is being hydrated and otherwise conditioned for papermaking. In other words, the present invention does away with a size-mixing period subsequent to the beating operation such as has been usual in the practice of sizing papermaking stock in the beater engine. Again, the sealed bags or units of the sizing composition hereof are drawn into the zone of the beater-roll action and under the aqueous medium associated with the papermaking stock, wherefore, dissolution and dispersion of the sizing solids take place rapidly under water throughout the papermaking stock and there is hence no tendency, as in ordinary papermaking practice, for the sizing solids to stick to the walls or other parts of the beater engine, or to fly away as dry dust into the atmosphere of the beater room and thus cause nuisance as well as constitute a loss.

Using specifically the rosin-starch composition hereof at a rosin size and starch solids content of 50% each in producing a sized paper product of a sizing solids content of substantially 3%, the procedure may be along the lines hereinbefore indicated. That is to say, sealed bags or units of the substantially dry sizing composition hereof may be added along with the starting papermaking stock to the beater engine, 30 parts by weight of such composition and 1000 pounds of papermaking stock on a dry basis constituting the beater furnish. On the other hand, it is, of course, possible to add the sizing composition hereof after the papermaking stock has been beaten or hydrated to the desired consistency. Irrespective of the particular stage of the beating operation at which the sizing composition is added, one arrives at a substantially physically homogeneous, sized papermaking stock conditioned for the addition of alum or equivalent precipitant capable of throwing down and fixing the sizing solids on the fibers. The alum is added in amount to precipitate and fix substantially all the fixable, dispersed sizing solids associated with the papermaking stock, for instance, in amount predetermined to impart a distinctly acid condition to the beater water, say, a pH value of about 5. We have observed that the ultra-finely or colloidally dispersed phase of sizing solids hereof is precipitated and fixed substantially entirely in the desired very fine particle size upon the fibers of the papermaking stock when the appropriate amount of alum is admixed with the stock, insomuch that the beater water is practically water-white or clear. That the sizing solids of the composition hereof are retained substantially in their entirety by the papermaking stock is also evidenced by the substantial clarity of the white water drained from the papermaking machine. Of course, the sized papermaking stock is, after dilution to the desired fiber content as ordinarily, delivered to the papermaking machine; and, with the stock at diluted or papermaking consistency, fine sizing solids would, unless properly fixed to or retained by the stock, be carried away with the excess water drained from the papermaking machine, as is the case when, for example, raw starch is added to papermaking stock in accordance with prior art practice.

When a papermaking stock, such as kraft pulp, is sized in the manner just described and is converted into a paper of a thickness and basis weight comparable to ordinary kraft wrapping

paper, for instance, a thickness of substantially .007" and a basis weight of substantially 70 pounds (i. e., the weight of 480 sheets whose dimensions are 24" x 36"), it is found that the resulting dried paper sheet has phenomenally high water-repellence, as tested by the usual water-ink floatation method. Thus, the finished paper sheet hereof, when floated on a bath of water-soluble ink or dye, displayed no sign of stain-through of the ink from the under face of the sheet to the upper face for a period longer than two hours. On the other hand, when a dried starch previously alkalinized or gelatinized in alkali solution is compounded with substantially dry rosin size under the same conditions as those used in the preparation of the rosin-starch composition hereof and then put to use for sizing papermaking stock under the same conditions, including proportionality of both rosin and starch to the papermaking stock, as those prevailing in the foregoing example of procedure hereof, it is found that a finished paper product having a thickness of substantially .007" and a basis weight of substantially 70 pounds is of comparatively very low water-repellence, since it exhibits a stain-through period not exceeding about 30 minutes by the usual water-ink floatation method. Comparable marked improvement in the water-repellence of paper products is attainable pursuant to the present invention in the production of papers of various thicknesses and/or basis weights and/or rosin-starch sizing solids contents. It might be further observed that paper products prepared accordant with the present invention are also of superior bursting-strength, tear-resistance, and fold-endurance. Such latter improved physical properties are probably traceable to the high bonding effectiveness of the acidic, converted starch entering into the rosin-starch composition hereof. So far as concerns uniformity of distribution of the rosin and starch sizing solids in the paper products hereof, it is noteworthy that such products are practically free from such defects as resin specks or starch "shiners" observable with the naked eye, which specks or "shiners" bespeak the presence of agglomerates or unduly coarse particles of rosin size or starch in the papermaking stock. It is evidently the case that not only is the acidic, converted starch of the rosin-starch composition hereof substantially uniformly dispersed as ultra-fine or colloidal particles throughout the papermaking stock but further that the dissolved or colloidally suspended starch particles influence through their protective colloidal effect the precipitation of the rosin in the sense that the precipitated rosin particles are substantially uniformly thrown down on the papermaking fibers in very fine or colloidal particle form.

From the standpoint of developing the very best physical qualities in the paper products hereof, it is highly desirable to use an acidic, starch conversion product whose acidity is developed during a heat-treatment or calcination of raw starch under conditions controlled to yield an acidic, starch-conversion product possessed of the properties of solubility and dextrin content already indicated. However, it is also possible to use for the purposes hereof an acidic starch-conversion product whose acidity is generated during the hydrolysis of raw starch in suspension in an acidified aqueous medium, as is known to those skilled in the art. When such latter acidic, hydrolyzed, starch-conversion product is used in preparing the rosin-starch composition hereof, it should be understood that the acid-hydrolyzed, aqueous starch solution is, as by spray-drying or drum-drying treatment, brought to the substantially dry, pulverulent form required for compounding with the rosin size. The acid-hydrolyzing treatment of the raw starch in aqueous suspension may be performed with one or more suitable acidic reagents, such as hydrochloric acid, acetic acid, etc., at the desired temperature, preferably at an elevated temperature up to the boiling point of water. The acidic, hydrolyzed, starch-conversion product thus produced by treating the raw starch in suspension in an acidified aqueous medium will be termed hereinafter a "hydrolyzed, acidic, starch-conversion product," as distinguished from the expressions "acidic, converted starch" or "acidic, starch-conversion product," which are used herein to denote both an acidic, hydrolyzed, starch-conversion product and a starch-conversion product prepared by heat-treating or calcining essentially dry or solid raw starch under controlled conditions either in the absence or presence of a limited amount of water or acidic catalyzing agent, which agent in the form of an aqueous or liquid solution of appropriate strength may be applied, as by spraying, substantially uniformly to the raw starch for the purpose of moistening the latter for the heat-treatment. A distinctly preferred acidic catalyzing agent for preparing acidic, heat-treated or calcined starch-conversion products useful for the purposes hereof consists essentially of an aqueous solution of hydrochloric acid, acetic acid, and formaldehyde. Such solution may be advantageously applied to the raw starch in amount to associate substantially uniformly with the starch granules about 0.03% to 0.5% hydrochloric acid, about 0.01% to 0.5% acetic acid, and about 0.03% to 2.0% formaldehyde, based on the dry weight of the starch. However, as above stated, any suitable acidic catalyzing agent may be used in the calcining treatment of the raw starch, according to the particular results desired; and the resulting acidic, calcined, starch-conversion product may be used in the preparation of the sizing compositions hereof. The acidic, heat-treated or calcined starch-conversion product used for the purposes hereof, which has been prepared in the absence of hydrolyzing treatment of the raw starch in suspension in aqueous acidic medium, will be termed hereinafter "acidic, calcined, starch-conversion product" so as to distinguish from the expressions "acidic, hydrolyzed, starch-conversion product" and "acidic, starch-conversion product" or "acidic, converted starch." The acidic, calcined, starch-conversion product used for the purposes hereof is characterized by its swellability or gelatinizing property in water to yield highly viscous or gel-like aqueous solutions when mixed with about 1 to 4 times its weight of water at 70° F.; and such property of swellability has been found to go hand in hand with the development of the best physical properties in paper products sized with the rosin-starch sizing composition hereof. On the other hand, the acidic, hydrolyzed, starch-conversion product yields relatively very thin or highly fluent aqueous solutions when admixed with about 1 to 4 parts of its own weight of water at 70° F.; and, when it constitutes the starch component of the rosin-starch composition hereof, the paper products sized with such composition are of definitely lower physical properties than the sized paper

products whose starch-sizing solids are derived from a rosin-starch composition hereof containing as its starch component an acidic, calcined, starch-conversion product. It is likely the case that acid-hydrolyzing treatment of raw starch in suspension in acidic aqueous medium so degenerates or degrades the starch molecule that its bonding tenacity or power in cementing together the paper fibers is definitely impaired. The measure of impairment can usually be forecast in terms of the relatively low viscosity, or vice versa, the relatively high fluidity of such hydrolyzed or degenerated starch-conversion product. While it may be possible to control or repress the hydrolyzing reaction on raw starch in suspension in acidic aqueous medium so as to arrive at an acidic, hydrolyzed starch-conversion product possessed of a composition and physical characteristics approximating that of an acidic, calcined, starch-conversion product, nevertheless such control presents difficulties and, in any event, an acidic, calcined, starch-conversion product is far more economical of production, since no such after-treatments as dewatering, drying, and pulverization or the expensive apparatus, labor, and other costs incident to these after-treatments figure in the preparation of such latter starch-conversion product.

So efficacious is an acidic, calcined starch-conversion product along with rosin size in enhancing the physical properties of rosin-sized paper products, including the water-repellence of such products, that it need not necessarily be applied to or incorporated into the papermaking stock concurrently with or as protective coatings about the substantially dry rosin size. The fact is that another important phase of the present invention involves the admixture with papermaking stock at a suitable stage of its beating or after its beating has been completed of the rosin size and the water swellable or water-gelatinizable, acidic, calcined starch-conversion product as an entity separate or distinct from the rosin size, which latter size may even be used in wet or water-dispersed form. It may be preferable to admix with the papermaking stock the acidic, calcined, starch-conversion product preparatory to the incorporation throughout the stock of the rosin size so as to enjoy such benefit as may accrue from the acidity of the starch in increasing the free rosin content of the size as particles of appropriate fineness throughout the stock. However, irrespective of whether the acidic, calcined, starch-conversion product is admixed with the stock before or after the dispersion of the rosin size throughout the stock, one arrives at desirably improved paper products as regards such qualities as increased bursting-strength, tear-resistance, and fold-endurance coupled with substantial absence of rosin specks or starch "shiners" in such products. The point is that so long as the water-swellable, acidic, calcined, starch-conversion product has been dissolved or dispersed substantially uniformly throughout the papermaking stock along with the rosin size prior to the addition to the stock of the alum or equivalent precipitant, both the starch and rosin are substantially completely precipitated or fixed in the desired ultra-fine or colloidal condition substantially uniformly throughout the stock, the swollen or gelatinized starch particles evidently exerting the desired influence in the precipitating or reacting sphere to maintain the precipitated rosin particles in the desired uniformly ultra-fine or colloidal condition. When the rosin size is applied independently of the water-swellable, acidic, calcined, starch-conversion product to the papermaking stock in the form of an aqueous or water-dispersed composition, it may be advantageous to use rosin size of especially high free rosin content, for instance, a free rosin content so high as to constitute the major portion, if not substantially the entire, sizing solids content of the rosin-sizing composition, in which case such composition may contain an extraneous stabilizer or protective colloid, such as casein. In other words, when the principles of the present invention are utilized in such manner as not to increase the free rosin content of the rosin-sizing composition used for the purposes hereof, it may be preferable, as when using aqueous rosin-sizing composition, to provide sufficient free rosin in the original rosin-sizing composition to develop the desired very high water-repellence in the paper products hereof while maintaining the rosin-sizing solids substantially completely at such ultra-fineness or colloidality as is consonant with the substantial absence of rosin specks or agglomerates observable to the naked eye in the paper products. Apropos of the matter of using rosin size of high free rosin content, papermaking mills sometimes experience trouble with such size because hardness in the water or extraneous contaminations in the papermaking stock tend to induce premature precipitation and agglomeration of the free rosin particles into unduly coarse particles. Such trouble is avoided when such rosin size is added pursuant to the present invention more particularly after the stock has been infused substantially uniformly with an acidic, calcined, starch-conversion product.

The term "starch" is used in the foregoing description and in the appended claims in its comprehensive sense to include starches of various derivations, for instance, such amylaceous substances as tapioca or sago flour, the starches of maize, wheat, potato, etc., and starches containing more or less protein or other matter. Again, the expression "rosin size" is used herein and in the appended claims in its comprehensive sense to include not only straight rosin sizes or soaps and rosin sizes containing more or less free rosin but also compounded rosin sizes, for instance, rosin-wax sizes. It should be understood that various kinds of cellulosic fibers may constitute the papermaking stock hereof, including wood pulps, such as kraft, sulphite, soda, and mechanical wood pulp; also cotton fiber or rag halfstuff. So, too, various non-cellulosic fibers, such as the various animal and mineral fibers, may form part of the papermaking stock together with such customary papermaking ingredients as fillers, colors, dyestuffs, etc.

The present invention may be applied in ways other than those already described. For instance, the rosin-starch sizing composition hereof may be admixed with the papermaking stock and precipitated or fixed thereon at any suitable stage of papermaking beyond the beater engine, say, while it is on its way to the papermaking machine. It is also possible for the papermaker to dissolve or disperse in an appropriate amount of water the substantially dry rosin-starch composition hereof before such composition is admixed with and precipitated or fixed on the papermaking stock. In other words, when added to the stock, such composition may be in wet-compounded condition (i. e., in already-dissolved or water-dispersed condition) rather than being added in preferably dry-compounded condition to the

water associated with the papermaking stock or being preferably wet-compounded in situ in the aqueous component of the papermaking stock. In some instances, as when the papermaker has equipment for preparing aqueous size compositions, dry-compounding of the rosin-starch composition hereof may be dispensed with in favor of admixing the rosin size in the presence of water (e. g., an aqueous rosin-size composition containing a substantial amount of free rosin) with an acidic, starch-conversion product of the kind hereinbefore described, incorporating the resulting wet-compounded, rosin-starch composition into the papermaking stock, and precipitating or fixing the composition on the stock. In such instances, the use of an acidic, calcined, starch-conversion product is also preferred for the reasons already stated. It is possible to utilize the principles of the present invention in other ways without departing from the spirit or scope of the invention as defined in the appended claims.

We claim:

1. A substantially dry composition particularly adapted for sizing papermaking stock and comprising substantially dry rosin size particles enveloped by substantially dry, acidic, calcined starch-conversion product having a dextrin content downwards of about 60% and substantial solubility in water at 70° F.

2. A substantially dry composition particularly adapted for sizing papermaking stock and comprising substantially dry rosin size particles enveloped by substantially dry, acidic, calcined starch-conversion product having a solubility in water at 70° F. upwards of about 20%.

3. A substantially dry composition particularly adapted for sizing papermaking stock and comprising substantially dry rosin size particles enveloped by substantially dry, acidic, calcined starch-conversion product having a dextrin content downwards of about 60% and a solubility in water at 70° F. upwards of about 20%.

4. A substantially dry composition particularly adapted for sizing papermaking stock and comprising substantially dry rosin size particles enveloped by substantially dry, acidic, calcined starch-conversion product capable of yielding when admixed with about 1 to 4 times its own weight of water at 70° F. a highly viscous solution.

5. A substantially dry composition particularly adapted for sizing papermaking stock and comprising substantially dry rosin size particles enveloped by substantially dry, acidic, calcined, starch-conversion product having at least about 20% solubility in water at 70° F. and capable of yielding when admixed with about 1 to 4 times its own weight of water at 70° F. a highly viscous solution.

6. A substantially dry composition particularly adapted for sizing papermaking stock and comprising substantially dry rosin size particles enveloped by substantially dry, acidic, calcined, starch-conversion product having a dextrin content downwards of about 60%, a solubility in water at 70° F. upwards of about 20%, and capable of yielding when admixed with about 1 to 4 times its own weight of water at 70° F. a highly viscous solution.

7. A substantially dry composition particularly adapted for sizing papermaking stock and comprising substantially dry rosin size particles enveloped by substantially dry, acidic, calcined starch-conversion product, said rosin size and said starch-conversion product each being present in said composition in amount ranging from about 40% to 60%, based on the dry weight of said composition.

8. A substantially dry composition particularly adapted for sizing papermaking stock and comprising substantially dry rosin size particles enveloped by substantially dry, acidic, calcined starch-conversion product having a dextrin content downwards of about 60% and a solubility in water at 70° F. upwards of about 20%, said rosin size and said starch-conversion product each being present in said composition in amount ranging from about 40% to 60%, based on the dry weight of said composition.

9. A substantially dry composition particularly adapted for sizing papermaking stock and comprising substantially dry rosin size particles enveloped by substantially dry, acidic, calcined, starch-conversion product having a solubility in water at 70° F. upwards of about 20% and capable of yielding when admixed with about 1 to 4 times its own weight of water at 70° F. a highly viscous solution, said rosin size and said starch-conversion product each being present in said composition in amount ranging from about 40% to 60%, based on the dry weight of said composition.

10. A substantially dry composition particularly adapted for sizing papermaking stock and comprising substantially dry rosin size particles enveloped by substantially dry, acidic, calcined, starch-conversion product having a dextrin content downwards of about 60%, a solubility in water at 70° F. upwards of about 20%, and capable of yielding when admixed with about 1 to 4 times its own weight of water at 70° F. a highly viscous solution, said rosin size and said starch-conversion product each being present in said composition in amount ranging from about 40% to 60%, based on the dry weight of said composition, and said composition affording when admixed with water a substantially neutral aqueous medium.

11. A composition especially adapted for sizing papermaking stock and comprising rosin size particles enveloped by an acidic, calcined starch-conversion product having a dextrin content downwards of about 60% and a solubility in water at 70° F. upwards of about 20%.

12. A composition especially adapted for sizing papermaking stock and comprising rosin size particles enveloped by an acidic, calcined starch-conversion product having a dextrin content downwards of about 60%, a solubility in water at 70° F. upwards of about 20%, and a capability of yielding when admixed with about 1 to 4 times its own weight of water at 70° F. a highly viscous solution.

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