

UNITED STATES PATENT OFFICE

2,096,129

MANUFACTURE OF SIZED PAPERS

Oscar F. Neitzke, Belmont, Mass., assignor to
Bennett Incorporated, Cambridge, Mass., a
corporation of Massachusetts

No Drawing. Application February 24, 1936,
Serial No. 65,435

12 Claims. (Cl. 92—21)

This invention relates to the manufacture of sized papers. It deals more especially with the manufacture of sized papers involving the use of aqueous sizing compositions containing stably suspended or dispersed therein a mixture of hydrocarbon wax and rosin and the combination of such dispersed material with papermaking stock preparatory to sheeting of the stock on a paper-making machine.

The use of aqueous emulsions or dispersions of wax and wax-rosin mixtures as paper-sizing compositions is now in vogue in many papermaking mills. These emulsions or dispersions are generally stabilized by soap or other precipitable protective colloid so that after the emulsions have been incorporated into the papermaking stock, as in the beater engine, the wax or wax-rosin particles may be fixed or precipitated on the stock by the addition of alum or other salt capable of reacting with the precipitable protective colloid and thus "breaking" the emulsions. One paper-sizing composition widely used at the present time consists of a wax-rosin emulsion at least part of whose rosin content is in the form of rosin soap. The rosin soap thus serves initially as the emulsion-stabilizer and is then precipitated along with the wax and free rosin on the fibers of the papermaking stock into which the emulsion is incorporated at a suitable stage of stock preparation, generally in the beater engine.

In accordance with the present invention, I prepare paper-sizing compositions in the form of aqueous dispersions of hydrocarbon wax-rosin mixtures which, rather than being stabilized by soaps or other precipitable protective colloid, are stabilized by inert or non-precipitable compounds, such as neutral salts of sulphonic acids, preferably sodium or other alkali metal salts of such acids, or water-soluble gums of the nature of gum arabic. Because of the inertness or non-precipitability of the dispersion-stabilizer present in the aqueous dispersions of the present invention, it might be reasoned that they would be ill-adapted for sizing papermaking stock on account of their inherent stability and the absence thereof of any added substance that might be precipitated or flocculated so as to entrain and/or fix the sizing solids, that is, the dispersed wax-rosin mixture on papermaking stock. I have discovered, however, that through control of particle size in the dispersion and control of the proportion of wax in the dispersed wax-rosin mixture, it is possible to attach or fix substantially all of the dispersed particles on papermaking stock by the action of a small amount of alum or equivalent

mordant salt. In other words, despite the inertness of the dispersion toward alum or similar salt, as attested by the fact that no precipitation of the dispersion takes place upon the addition thereto of alum or other salt or electrolyte in the absence of papermaking stock or pulp, it is possible to discharge or attach its dispersed sizing solids practically completely on papermaking stock or pulp, as in the beater engine, by the addition of alum or equivalent mordant salt thereto. I have termed alum as a mordant by reason of the fact that it functions to attach or discharge the dispersed wax-rosin particles on the papermaking stock or fibers without noticeable precipitating or clotting action on the particles; and it is my theory that the alum plays a role similar to that of a mordant salt in the dyeing of fibrous material. The mordanting effect of alum may be readily demonstrated by adding the aqueous wax-rosin dispersions hereof to papermaking stock both in the absence and in the presence of alum and then centrifuging the mixture to form a compact, partially dewatered layer of stock next to the centrifuge wall and a separate layer of aqueous medium inwardly thereof. When centrifugation is performed in the absence of alum, it is found that the separated aqueous medium is of a sizing solids content per unit of volume as great as that of the original dispersion, whereas, on the other hand, when centrifugation is performed in the presence of a small amount of alum, it is found that the separated aqueous medium is substantially clear or devoid of sizing solids, indicating that the sizing solids have attached themselves to the fibers of the papermaking stock.

I shall now describe a typical and preferred sizing composition for the purposes of the present invention and how it may be produced. A melting kettle is charged with 70 parts by weight of rosin, for instance, the grade known as G gum rosin and sold to the papermaking industry for making rosin size, and with 30 parts by weight of hydrocarbon wax, for instance, so-called scale wax having a melting point of about 124° to 126° F. The mixture is melted and heated to a temperature of about 220° to 250° F., whereupon it is dispersed in 150 parts by weight of a 1% solution of a neutral salt of sulphonic acid, for example, the salt of this character sold under the trade-mark "Daxad", under conditions to produce a finished dispersion at about 180° to 190° F. The dispersion may to advantage be produced by commingling the melted mixture and the aqueous solution in a high-speed mixer,

for instance, a mixing or dispersing machine such as is described in United States Patent No. 1,792,067. It is unnecessary to cool the materials as they are being commingled or the finished dispersion; and, as already indicated, the dispersion as it is finished may be at a temperature well above the melting point of either the wax or rosin of the dispersed wax-rosin mixture but safely below the boiling point of water, say, about 180° to 190° F. Upon cooling to room temperature, the dispersion, which has a wax-rosin solids content of about 40%, assumes the consistency and appearance of heavy cream. Such a dispersion may be diluted with water to any desired solids content substantially without separation of its dispersed solids, that is, without "breaking".

The dispersion produced as hereinbefore described may be used with excellent results in the beater-sizing of papermaking stock. Thus, it may be added in thick, creamy condition or diluted with water to the papermaking stock and its dispersed wax-rosin particles may be fixed on the fibers with a small amount of alum, which may be added therewith or independently thereof. The papermaking stock may be made to take up various percentages of wax-rosin mixture, for instance, up to 8% or more, based on the dry weight of fiber, the particular percentage fixed on the stock depending upon the water-repellency or sizing value desired in the finished paper product. In the case of a substantially neutral papermaking stock, the use of alum in amount to impart to the stock a pH of about 5 or less ensures the desired retention of the sizing solids by the stock. However, irrespective of the pH of the stock and even when the stock contains various electrolytes, it is possible by the use of about 1% alum, based on the dry weight of fiber, to cause the stock to retain the sizing solids satisfactorily. Indeed, by using such comparatively small amount of alum, I am able to discharge the sizing solids from the dispersion on papermaking stock even when the stock is distinctly on the alkaline side and when the stock contains calcium and other salts such as are apt to occur therein and/or in the slushing water mixed therewith. As already indicated, the dispersed sizing solids are not precipitated on the stock in the sense that the stabilizer associated therewith and initially maintaining them in suspension is chemically destroyed or precipitated. They merely stick to the fibers evidently by reason of their physical attraction, probably electrical, caused by the alum or equivalent mordant salt, such as aluminum chloride, sodium aluminate, ferric sulphate, or the like. The paper-sizing composition hereof is hence practically foolproof, for, whereas the usual aqueous wax dispersion stabilized by soap or other precipitable protective colloid is subject to premature precipitation in papermaking stocks containing salts or other electrolytes tending to precipitate the protective colloids and thereby to induce premature precipitation and attendant aggregation of the wax particles, no such premature precipitation and attendant aggregation of the sizing solids or particles of the composition hereof can or does take place, in consequence of which papers sized with the composition hereof are free from spottiness or irregular and defective sizing arising from aggregates or unduly large particles of the sizing solids.

I have conducted extensive research to determine those factors underlying and contributing

to the results secured hereby. I have established that proper particle size in the dispersions or sizing compositions hereof is vital to their successful use and that it is necessary to produce dispersions wherein the wax-rosin mixture has a particle size averaging upwards of 5 microns in order to realize fixation of the particles to the papermaking stock by alum or equivalent mordant salt. Unlike the present invention, it has heretofore been the objective to produce dispersions of the finest dispersed particle size attainable; and it is hence not surprising that wax sizes or dispersions as heretofore made have had an average particle size but a very small fraction of 5 microns. I have found, however, that the dispersions hereof having an average particle size of 5 microns give perfectly uniform sizing of paper and that satisfactory sizing results are also had when such dispersions have an average particle size ranging from about 5 to 50 microns. When the average particle size of such dispersions is less than 5 microns, satisfactory retentivity of the sizing solids by the papermaking stock is not had no matter how much alum or equivalent mordant salt is used in an attempt to fix such solids on the fibers; and when the average particle size of such dispersions is greater than about 50 microns, they do not yield papers of the desired quality as regards uniform sizing and appearance.

While the particular mixing or dispersing machine in which the aqueous dispersions or sizing compositions hereof are produced and the conditions of operating such machine determine in some measure the particle size of the dispersions and should hence be adapted for the production of dispersions of the particle size herein desired, yet I have found that wax and rosin proportionality in the wax-rosin mixture most importantly influences the particle size in the dispersions hereof produced from such mixture. Thus, I have ascertained that if the wax-rosin mixture contains more than 50% wax, it is extremely difficult to control the particle size in the resulting dispersion thereof on account of the low viscosity of the melted mixture even when its temperature after mixing with the aqueous dispersing medium is only moderately above its melting point. In such case, despite the fact that dispersion of the mixture is effected at the lowest temperature at which dispersion can be had, the average particle size of the dispersed solids is too small for the purposes herein and the particles are apt to be non-uniform, some, for instance, being altogether too large. On the other hand, I have determined that if the wax-rosin mixture contains less than 20% wax, the viscosity of the melted mixture is too high even when it is heated to such temperature that when mixed with the aqueous dispersing medium, the water practically boils. In such latter case, the average particle size of the dispersed wax-rosin mixture is apt to be too large for the purposes herein and the dispersed particles tend to settle out on standing. By dispersing wax-rosin mixtures containing 20 to 50% of wax it is possible readily to keep the average particle size in the dispersions within the range of 5 to 50 microns and to reproduce such dispersions repeatedly in various mixing or dispersing machines. So, too, the resulting dispersions are stable or non-separating probably because the dispersed particles have a specific gravity closely approximating that of water. In this connection, it is to be noted that the wax having a specific gravity less than water buoys

up the rosin whose specific gravity is greater than water, as will be appreciated from the pronounced settling of free rosin that takes place in the ordinary free rosin-containing sizes used in the papermaking industry. It is possibly because the floating tendency of the wax substantially neutralizes the sinking tendency of the rosin in the dispersed wax-rosin particles so that such particles have a specific gravity approximating unity that they are sensitive to the mordanting or fixing effect of alum on the papermaking stock. That the dispersed particles in the dispersions or sizing compositions hereof are wax-rosin particles of a composition quite similar to that of the molten wax-rosin mixture preparatory to its dispersion is shown by similarity of melting point. Thus, when the dispersed particles are placed under a microscope on a heated support, whose temperature is accurately taken a sharp change in refractive index of the particles, indicating that the particles have melted, takes place at a temperature coinciding almost exactly with the melting point of the wax-rosin mixture preparatory to its dispersion. This observation is, of course, also in line with what I have said about the mutual effect of the wax and rosin upon each other in conducing to dispersed particles of a specific gravity approximating unity.

There are important advantages inhering in the sizing compositions used accordant with the present invention for the production of sized papers, including a saving in alum, the possibility of sizing the papermaking stock in the presence of hard water and at any pH value, the possibility of adding the size to hot beaters, and the improved color of the sized paper products. As to the saving in alum, it might be noted that in the case of ordinary wax sizes stabilized by rosin soap or other precipitable protective colloid, alum must be used in sufficient quantity to ensure the precipitation of such colloid. In all cases of using the sizing composition of the present invention, on the other hand, not more than 1% of alum, based on the weight of the papermaking stock, is necessary to cause the desired fixation of sizing solids on the fibers. With regard to pH value in the stock or the presence of electrolytes therein, it might be observed that ordinary wax sizes are susceptible to premature "breaking" in stock on either side of neutrality and in the presence of hard water, whereas the sizing composition of the present invention is not adversely affected by such stock conditions. As to stock temperature, experience has shown that unless the wax component of the usual soap-stabilized wax dispersions of the prior art is of relatively high melting point, such dispersions cannot be used when the papermaking stock is hot, as is likely to be the case immediately after a beating operation, since elevated temperature tends to "break" the dispersion prematurely and to cause coalescence or aggregation of the dispersed particles. No such difficulty is encountered with the wax-rosin dispersions hereof even when they are made with comparatively inexpensive, low melting point waxes, such as scale wax, since they are unsuceptible to premature precipitation or "breaking" and attendant particle-aggregation under heat such as is likely to be encountered in beaten papermaking stock. The better or whiter color of papers sized with the compositions hereof is a reflection of the absence of rosin soap from such compositions. Experience has shown that the higher the free rosin content of a rosin size or a rosin-wax size, the better or brighter

colored is the sized paper. The wax-rosin sizing compositions of the prior art generally contain rosin soap as the stabilizer; and it is evidently the rosin soap content of such compositions that detract from the whiteness of paper sized therewith. It is hence understandable why the sizing compositions of the present invention, which are devoid of rosin soap, may be used to advantage in sizing white papermaking stocks with minimum detracton from the whiteness and brightness of the resulting sized paper. In addition, the sizing compositions hereof possess all of the attributes of the usual wax-rosin sizes, including capability of imparting high water-repellency or sizing value to the papers in which they appear. Because the sizing compositions can be applied accordant with the present invention to papermaking stock without the precipitation of aluminum resinate or other compound and with the use of only a very small amount of alum or other mordant salt practically entirely removed along with the white water during the papermaking operation, the size particles flux better on the hot drum-driers of the papermaking machine; so that, despite the fact that the particle size of such compositions may be much greater than that of prior art sizing compositions, the larger particles are fluxed or fused more perfectly during the drying of the paper. In other words, the sizing particles of wax-rosin mixture are substantially unadulterated, that is, are substantially free from precipitated rosin soap or other compound that modifies or raises their melting point or otherwise interferes with their fluxing on the fibers. In any event, the water-repellent or sized value of papers sized as herein described compares very favorably with the water-repellent value of the prior art papers containing the same amount of wax-rosin sizing solids.

It is to be understood that the principles of the present invention may be embodied in a wide variety of practices and products. For instance, the wax component of the sizing composition hereof may be any one of a large number of hydrocarbon waxes, including the so-called amorphous waxes and paraffin wax. I have mentioned scale wax in the example hereinbefore given because of its low cost compared with such higher melting point waxes as paraffin wax (melting point 132 to 135° F.) and amorphous waxes (melting point 140 to 160° F.). Again, the inert or non-precipitable stabilizer for the sizing compositions hereof might be water-soluble gums, such as gum arabic even though "Daxad" was given in the preceding example on account of its especially high effectiveness as a stabilizer. In fixing the sizing solids of such compositions to papermaking stock it is possible to use salts or electrolytes other than alum, for instance, aluminum chloride, ferric chloride, ferric sulphate, or the like. However, alum being colorless, inexpensive, and highly effective is generally preferable as the fixing agent for the sizing solids. It is probably the case that the fixation of the dispersed sizing solids on the papermaking stock occurs by reason of electrical or electrostatic attraction of such solids to the fibers. I have observed that the particles of the dispersions hereof are negatively charged; and it would appear that the alum or equivalent mordant salt serving to fix such particles imparts to the fibers a positive electrical charge that attracts the dispersed negatively charged particles and fixes them on the fibers. The positive charge imparted to the fibers is evidently a very weak one insufficient to over-

come the intensive Brownian movement of very fine particles but of sufficient potency to attract particles of the average size present in the compositions hereof and possessed of a specific gravity so near to unity that they are sensitive to deposition upon the fibers even as a result of very weak electrical pull or attraction by the fibers.

It is apposite to the present invention to observe that Brownian movement in aqueous wax-rosin dispersions practically stops or is comparatively small when the dispersed particles are of a size greater than 5 microns, as is the case herein. In other words, the aqueous dispersions or sizing compositions hereof are lacking or practically lacking in Brownian movement, whereas wax-rosin dispersions or sizing compositions which were heretofore made with a view toward developing extremely fine particle size, say, about 1 micron, display violent Brownian movement. My hypothesis is, as already suggested, that the retention by papermaking stock of the sizing solids of the dispersions hereof without the need of chemical precipitating action is linked up with the absence or substantial absence of Brownian movement in such dispersions, that is, the presence therein of dispersed solids of sufficiently small average particle size, e. g. 5 to 50 microns, to be maintained stable in suspension and to be uniformly distributable through papermaking stock and the resulting paper but, nevertheless, of average particle size greater than that attended by any display or significant display of Brownian movement.

Another noteworthy quality of the aqueous wax-rosin dispersions or compositions used for the purposes hereof is that their rosin content is substantially wholly unsaponified. The substantially unsaponified state of the rosin of such dispersions is attributable to the use therein of a stabilizer that is incapable of saponifying the rosin as well as being inert toward electrolytes. The substantially neutral salts of sulphonic acid answer admirably, as already indicated, the requirements of a stabilizer herein, for solutions of such salts do not react measurably or significantly with wax-rosin mixtures even when mixed therewith under the elevated temperatures hereinbefore described as being necessary for producing the aqueous dispersions or sizing compositions hereof; and these salts are, moreover, inert toward the electrolytes apt to be present in papermaking stocks or those electrolytes, such as aluminum sulphate, aluminum chloride, sodium aluminate, ferric chloride, ferric sulphate, or the like, preferably added for the purpose of fixing dispersed sizing solids, for instance, the dispersed sizing solids of the sizing compositions hereof, on papermaking stock. It is hence to be understood that in characterizing the stabilizers used herein as being inert or substantially inert toward electrolytes, such characterization is not meant in an absolute sense to indicate that there are no electrolytes capable of reacting upon such stabilizers but more especially in a sense applicable to the papermaking art to indicate that such stabilizers are inert to the electrolytes usually occurring in papermaking stock, or electrolytes, like alum, added to the papermaking stock to fix the sizing solids thereon.

It is to be understood that the sizing composition hereof may be employed in sizing all sorts of fibrous materials or papermaking stocks, for instance, rag pulps, wood pulps, asbestos fiber, wool fiber, or mixtures of such fibers, to be formed

into all classes of papers, including thin or lightweight papers, such as writing, printing, magazine, and book papers, or thick papers or paperboards, such as are used for sheathing and insulating purposes or for making water-repellent containers or cartons for foodstuffs and many other substances. Papermaking stock sized as herein described may also be used in making various molded articles, such as milk bottles, pie plates, and other molded articles generally classified as paper products.

While not limited thereto, the substantially neutral sodium or other alkali metal salts of the sulphonic acids useful herein as stabilizers may be such salts as are prepared from the sludges separated as by-products after mineral oils have been purified or refined by intimate admixture or washing with concentrated sulphuric acid. The acid sludges separated from the refined oil are rich in sulphonic acids of complex variety, which acids are formed by the reaction of the concentrated sulphuric acid on impurities associated with the oil. By neutralizing the sulphonic acid sludges with caustic soda or equivalent alkali, such salts as are herein used as stabilizers may be prepared; or the neutralized sludges may be treated with concentrated mineral acid to liberate the complex sulphonic acids which, after separation from the resulting mineral acid salt and, in some instances, the excess mineral acid, may be neutralized with caustic soda or equivalent alkali to produce the substantially neutral sulphonic acid salts herein used as stabilizers. In addition to the substantially neutral sulphonic acid salts available on the market under the trade-mark "Daxad", I may use other trade-marked salts of similar nature, for instance, such salts as are being sold under the trade-mark "Dipex". Of course, sulphonic acid salts that are synthesized or are derived from sources other than mineral oils may be used as the stabilizers herein, but I have dwelt more especially on the use herein of the by-product sulphonic acid salts by reason of their availability on the market at comparatively low cost and the excellence of their performance in the respects herein desired.

I claim:—

1. A process of making a sized paper product involving the use of a hydrocarbon wax-rosin mixture as the sizing material, which comprises dispersing such wax-rosin mixture in molten condition as particles of a size greater than those exhibiting Brownian movement in an aqueous medium containing dissolved therein as the dispersion-stabilizer substantially only soluble dispersion-stabilizer inert toward and non-precipitable by such electrolytes as aluminum sulphate, aluminum chloride, sodium aluminate, ferric chloride, and ferric sulphate, incorporating the resulting dispersion into fibrous pulp in the presence of an electrolyte capable of causing and in amount sufficient to cause the pulp fibers to attract and retain the dispersed particles, and forming the resulting pulp, to which the dispersed particles have been attached substantially only by said electrolyte, into a paper product.

2. A process of making a sized paper product involving the use of a hydrocarbon wax-rosin mixture as the sizing material, which comprises dispersing such wax-rosin mixture in molten condition as particles of a size greater than those exhibiting Brownian movement in an aqueous solution containing dissolved therein as the dispersion-stabilizer substantially only a substan-

tionally neutral salt of sulphonic acid capable of stabilizing the dispersed particles but inert toward and non-precipitable by such electrolytes as aluminum sulphate, aluminum chloride, sodium aluminate, ferric chloride, and ferric sulphate, incorporating the resulting dispersion into fibrous pulp in the presence of an electrolyte capable of causing and in amount sufficient to cause the pulp fibers to attract and retain the dispersed particles, and forming the resulting pulp, to which the dispersed particles have been attached substantially only by said electrolyte, into a paper product.

3. A process of making a sized paper product involving the use of a hydrocarbon wax-rosin mixture as the sizing material, which comprises dispersing such wax-rosin mixture in molten condition as particles of a size greater than those exhibiting Brownian movement in an aqueous medium containing dissolved therein as the stabilizer for the dispersed particles substantially only a substantially neutral salt inert toward and non-precipitable by such electrolytes as aluminum sulphate, aluminum chloride, sodium aluminate, ferric chloride, and ferric sulphate and incapable of saponifying the rosin, incorporating the resulting dispersion in the substantial absence of rosin soap into fibrous pulp in the presence of an electrolyte capable of causing and in amount sufficient to cause the pulp fibers to attract and retain the dispersed particles, and forming the resulting pulp, to which the dispersed particles have been attached substantially only by said electrolyte, into a paper product.

4. A process of making a sized paper product involving the use of a hydrocarbon wax-rosin mixture as the sizing material, which comprises dispersing such wax-rosin mixture in molten condition in an aqueous medium containing dissolved therein as the dispersion-stabilizer substantially only soluble dispersion-stabilizer inert toward and non-precipitable by such electrolytes as aluminum sulphate, aluminum chloride, sodium aluminate, ferric chloride, and ferric sulphate while maintaining the average particle size of the stabilized dispersion within a range of about five to fifty microns, incorporating the resulting dispersion into fibrous pulp in the presence of an electrolyte capable of causing and in amount sufficient to cause the pulp fibers to attract and retain the dispersed particles, and forming the resulting pulp, to which the dispersed particles have been attached substantially only by said electrolyte, into a paper product.

5. A process of making a sized paper product involving the use of a hydrocarbon wax-rosin mixture as the sizing material, which comprises dispersing such wax-rosin mixture in molten condition in an aqueous solution containing dissolved therein as the dispersion-stabilizer substantially only a substantially neutral salt of sulphonic acid capable of stabilizing the dispersed particles but inert toward and non-precipitable by such electrolytes as aluminum sulphate, aluminum chloride, sodium aluminate, ferric chloride, and ferric sulphate, while maintaining the average particle size of the stabilized dispersion within a range of about five to fifty microns, incorporating the resulting dispersion into fibrous pulp in the presence of an electrolyte capable of causing and in amount sufficient to cause the pulp fibers to attract and retain the dispersed particles, and forming the resulting pulp, to which the dispersed particles have been

attached substantially only by said electrolyte, into a paper product.

6. A process of making a sized paper product involving the use of hydrocarbon wax-rosin mixture as the sizing material, which comprises dispersing such wax-rosin mixture in molten condition in an aqueous medium containing dissolved therein as the stabilizer for the dispersion particles substantially only a substantially neutral salt inert toward and non-precipitable by such electrolytes as aluminum sulphate, aluminum chloride, sodium aluminate, ferric chloride, and ferric sulphate and incapable of saponifying the rosin while maintaining the average particle size of the stabilized dispersion within a range of about five to fifty microns, incorporating the resulting dispersion into fibrous pulp in the substantial absence of rosin soap but in the presence of an electrolyte capable of causing and in amount sufficient to cause the pulp fibers to attract and retain the dispersed particles, and forming the resulting pulp, to which the dispersed particles have been attached substantially only by said electrolyte, into a paper product.

7. A process of making a sized paper product involving the use of a hydrocarbon wax-rosin mixture as the sizing material, which comprises dispersing such wax-rosin mixture in molten condition and at a wax content of about 20% to 50% as particles of a size greater than those exhibiting Brownian movement in an aqueous medium containing dissolved therein soluble dispersion-stabilizer inert toward and non-precipitable by such electrolytes as aluminum sulphate, aluminum chloride, sodium aluminate, ferric chloride, and ferric sulphate, incorporating the resulting dispersion into fibrous pulp in the presence of an electrolyte capable of causing and in amount sufficient to cause the pulp fibers to attract and retain the dispersed particles, and forming the resulting pulp, to which the dispersed particles have been attached substantially only by said electrolyte, into a paper product.

8. A process of making a sized paper product involving the use of a hydrocarbon wax-rosin mixture as the sizing material, which comprises dispersing such wax-rosin mixture in molten condition and at a wax content of about 20% to 50% as particles of a size greater than those exhibiting Brownian movement in an aqueous solution containing dissolved therein as the dispersion-stabilizer substantially only a substantially neutral salt of sulphonic acid capable of stabilizing the dispersed particles but inert toward and non-precipitable by such electrolytes as aluminum sulphate, aluminum chloride, sodium aluminate, ferric chloride, and ferric sulphate incorporating the resulting dispersion into fibrous pulp in the presence of an electrolyte capable of causing and in amount sufficient to cause the said pulp fibers to attract and retain the dispersed particles, and forming the resulting pulp, to which the dispersed particles have been attached substantially only by said electrolyte, into a paper product.

9. A process of making a sized paper product involving the use of a hydrocarbon wax-rosin mixture as the sizing material, which comprises dispersing such wax-rosin mixture in molten condition and at a wax content of about 20% to 50% as particles of a size greater than those exhibiting Brownian movement in an aqueous medium containing dissolved therein as the stabilizer for the dispersed particles substantially only a substantially neutral salt inert toward and non-precipitable by such electrolytes as aluminum sul-

phate, aluminum chloride, sodium aluminate, ferric chloride, and ferric sulphate and incapable of saponifying the rosin, incorporating the resulting dispersion into fibrous pulp in the substantial absence of rosin soap but in the presence of an electrolyte capable of causing and in amount sufficient to cause the pulp fibers to attract and retain the dispersed particles, and forming the resulting pulp, to which the dispersed particles have been attached substantially only by said electrolyte, into a paper product.

10 A process of making a sized paper product involving the use of a hydrocarbon wax-rosin mixture as the sizing material, which comprises
15 dispersing such wax-rosin mixture in molten condition and at a wax content of about 20% to 50% in an aqueous medium containing dissolved therein as the dispersion-stabilizer substantially only soluble dispersion-stabilizer inert toward and
20 non-precipitable by such electrolytes as aluminum sulphate, aluminum chloride, sodium aluminate, ferric chloride, and ferric sulphate while maintaining the average particle size of the stabilized dispersion within a range of about five to
25 fifty microns, incorporating the resulting dispersion into fibrous pulp in the presence of alum in amount sufficient to cause the pulp fibers to attract and retain the dispersed particles, and forming the resulting pulp, to which said dispersed particles have been attached substantially only by said alum, into a paper product.

11. A process of making a sized paper product involving the use of a hydrocarbon wax-rosin mixture as the sizing material, which comprises
35 dispersing such wax-rosin mixture in molten condition and at a wax content of about 20% to 50% in an aqueous solution containing dissolved therein as the dispersion-stabilizer substantially

only a substantially neutral salt of sulphonic acid capable of stabilizing the dispersed particles but inert toward and non-precipitable by such electrolytes as aluminum sulphate, aluminum chloride, sodium aluminate, ferric chloride, and ferric sulphate while maintaining the average particle size of the stabilized dispersion within a range of about five to fifty microns, incorporating the resulting dispersion into fibrous pulp in the presence of alum in amount sufficient to cause the pulp fibers to attract and retain the dispersed particles, and forming the resulting pulp, to which said dispersed particles have been attached substantially only by said alum, into a paper product.

12. A process of making a sized paper product involving the use of a hydrocarbon wax-rosin mixture as the sizing material, which comprises dispersing such wax-rosin mixture in molten condition and at a wax content of about 20% to 50% in an aqueous medium containing dissolved therein as the stabilizer for the dispersed particles substantially only a substantially neutral salt inert toward and non-precipitable by such electrolytes as aluminum sulphate, aluminum chloride, sodium aluminate, ferric chloride, and ferric sulphate and incapable of saponifying the rosin while maintaining the average particle size of the stabilized dispersion within a range of about five to fifty microns, incorporating the resulting dispersion into fibrous pulp in the substantial absence of rosin soap but in the presence of alum in amount sufficient to cause the pulp fibers to attract and retain dispersed particles, and forming the resulting pulp, to which said dispersed particles have been attached substantially only by said alum, into a paper product.

OSCAR F. NETZKE.