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## SIZING COMPOSITIONS

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This invention relates to paper sizing compositions; and more particularly, to paper sizing compositions prepared by adding major amounts of hydrogenated animal fats or mixtures thereof with minor amounts of hydrogenated vegetable fats in combination with minor amounts of fatty acids, fats or oils to a mixture of casein, ammonium hydroxide and an alkali such as caustic soda, which are useful in aqueous dispersions in the beater.

It has been customary to size writing, printing and wrapping papers for many years in order to control the absorption and consequent spreading of inks subsequently applied to the surface of the paper sheet. The uses of casein and aqueous dispersions of rosin for this purpose were developed very early in the history of the paper-making art and rosin sizes are still the most important in commercial use today. Numerous attempts have been made to improve rosin sizes, including the modification of the rosin or the replacement of all, or part, of the rosin with various substances; such as, for example, partially saponified fats, synthetic resins, gums, waxes, bituminous and asphaltic materials. In spite of these efforts to improve rosin sizes, aqueous dispersions of partially saponified rosin have remained the preferred sizing material of the paper industry. These aqueous dispersions are ordinarily added to the suspensions of pulp in the beater engine in amounts sufficient to provide from about one-half to above five percent by weight of rosin based on the dry weight of the pulp. The alkali neutralized rosin is precipitated as, theoretically, free rosin on the surfaces of the pulp fibers.

The above-described standard rosin paper sizes are known to possess certain disadvantages. One of the greatest disadvantages of rosin sizes is that they produce foaming at numerous stages in the paper-making process; including such stages as, for example, the beater engine, the head box or pressure-foaming chamber for depositing the pulp suspensions on the moving screen, and in the "white-water" recirculating system. Aqueous dispersions of rosin or rosin derivatives also have a tendency to cause the blankets in paper machines to become clogged, thus reducing the ability of the blanket to absorb the liquid phase of the pulp suspensions and necessitating shut-down of the machines at regular intervals to clean the blanket. The efficiency of rosin paper sizes is also not as great as is desired. Thus, rosin sizes do not deposit uniformly, throughout the fibers of the paper nor over the surface of the individual particles of fiber and the adhesion of the rosin size to the fibers of the paper is not good. It has also been determined that the rosin size coating on the fibers contains a high percentage of bubbles which are microscopic in size, but which are detrimental to the appearance and uniformity of quality of the paper. Rosin sizes also generally have a dark color which detract from the appearance of the sized paper. Moreover, papers sized with rosin are lacking in brightness and wet opacity; i.e., any opacity imparted to the paper by rosin size is lost when the paper becomes wet. Rosin sizes are also lacking in their ability to impart resistance to water penetration to paper.

It has now been discovered that certain hydrogenated fats possess excellent sizing properties without the disadvantages inherent in rosin sizes. Therefore, hydrogenated fat is not a sticky mass as is rosin size. Moreover, it is brighter in color and more water repellent than

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rosin. However, the proposed use of hydrogenated fat as a paper size gives rise to a major problem, namely how to incorporate the hydrogenated size into a sizing composition so as to allow the hydrogenated fat to be uniformly deposited on the fibers of the pulp. Since hydrogenated fat is extremely insoluble in water, it is impossible merely to disperse it in an aqueous media as may be done with conventional sizes.

It has now been discovered that certain hydrogenated fats may be used in a sizing composition by combining them with an emulsifying or wetting agent in water to provide a stable emulsion of hydrogenated fat in water. Thus, the improved sizing composition comprises water, hydrogenated fat and an emulsifying agent.

Copending application Serial No. 851,242, filed November 6, 1959, and now U.S. Patent No. 3,066,039, describes a size composition which overcomes the disadvantages inherent in conventional sizing compositions such as rosin sizes by providing a preferred means of getting hydrogenated fat into emulsion. The size composition described therein comprises a major amount of a hydrogenated animal fat having a titer in the range of from 45° to about 61° C. or a mixture of a major amount of such a hydrogenated animal fat and a minor amount of a hydrogenated vegetable fat or oil having a titer in the range of from 45° to 70° C.; and in combination therewith, a minor amount of an alkali treated animal, vegetable, or marine animal fat or oil having a melting point above about 30° C. This composition represents a vast improvement over the prior art sizing compositions such as rosin sizes. However, the sizing composition of the copending application does not possess as high a degree of sizing efficiency as would be desirable since it has been found that a small portion of the hydrogenated fat is lost from the pulp with the white water during sizing operation. By sizing efficiency, is meant the degree of sizing accomplished by a certain concentration of sizing composition on a dispersion of pulp and is measured by preparing a sheet from the sized pulp and determining the time required for water to pass through the specimen.

It is the principal object of this invention to provide a paper sizing composition which, when added as an aqueous dispersion to a suspension of paper pulp in a beater, is substantially uniformly distributed throughout the fibers; and, as well, uniformly distributed over the surface of each of the individual particles of fiber and which imparts to the final sized product a high degree of brightness, wet and dry opacity and resistance to water penetration. It is a further object of this invention to provide a sizing composition which combines all the advantages possessed by the sizing composition described in copending application Serial No. 851,242 with a higher degree of sizing efficiency.

The foregoing objects are accomplished by this invention which, briefly, consists of a paper sizing composition prepared by adding a major amount of a hydrogenated animal fat having a titer in the range of from 45° to about 61° C. and preferably about 53° C. to 57° C. or a mixture of a major amount of such a hydrogenated animal fat and a minor amount of a hydrogenated vegetable fat or oil having a titer in the range of from 45° C. to 70° C., and preferably, about 65° C.; and, in combination therewith, a minor amount of a saponifiable animal, vegetable, or marine animal fat or oil or fatty acid containing from 8 to 22 carbon atoms or tall oil to an aqueous premix comprising casein, ammonium hydroxide and an alkali saponifying agent. The mixture, after being formed, is heated and agitated until a smooth uniform mixture is achieved. It is preferred to drive off moisture until solids content is from 60 to 68 percent. By solids content as used throughout this application is meant the sizing solids—i.e., casein, hydrogenated fat and fat, oil or fatty

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acid—and does not include any sodium hydroxide or ammonia in the composition. The casein acts as a binder and aids in fixing the hydrogenated fat to the pulp fibers. The ammonium hydroxide in turn acts as a preservative for the casein.

The product thus obtained may be used in sizing paper by adding it to any desired amount of heated water with agitation, to form an aqueous dispersion of a paper sizing composition. It is preferred to dilute the sizing composition to a 32 percent solution with heating and then to add water to form a 10 percent solution. The paper sizing composition, in the form of an aqueous dispersion, may then be added to the suspension of pulp in the beater in an amount sufficient to provide from about 0.5% to about 5% of size based on the dry weight of the paper pulp, depending on the degree of sizing desired.

The paper sizing compositions comprising this invention are produced by first preparing the mixture of casein, ammonium hydroxide and alkali. This is preferably done by adding one part by weight of casein to from about 7 to 12 parts by weight of water and heating to about 90 to 110° F. for 5 to 15 minutes with mild agitation to prevent foaming. Subsequently, from about .70 to 1.5 parts by weight of alkali saponifying agent, preferably sodium hydroxide, and from about 0.7 to 1.4 parts of ammonium hydroxide are added and the mixture is heated to from 130° to 150° F. and mixed for 20 to 30 minutes. The preferred mixture comprises one part by weight of casein, about 7.1 parts by weight of water, about 0.74 part by weight of sodium hydroxide and 0.29 part by weight of ammonia diluted with water to a 26° Bé. solution (i.e., 1.01 parts by weight of 26° Bé. ammonium hydroxide).

Alternatively, the mixture may be prepared by adding one part by weight of casein to from about 9.5 to about 20 parts by weight of a 10° Bé. sodium hydroxide solution and from about 1.0 to about 2.0 parts by weight ammonium hydroxide. A preferred mixture prepared in this manner comprises one part by weight casein, ten parts by weight 10° Bé. sodium hydroxide solution and two parts by weight 22 Bé. ammonium hydroxide.

Although the mixture prepared by this latter method is generally satisfactory, it is somewhat more difficult to prepare than the mixture obtained by the first described process inasmuch as casein added directly to a mixture of caustic soda solution and ammonium hydroxide tends to ball up and become sticky, making it more difficult to dissolve. By adding casein directly to the water, the granular material is dispersed throughout the solution and will dissolve without balling when caustic and ammonia are added.

The above mixtures may be prepared in a steam-jacketed open kettle. Casein derived from any source may be used. It is preferred to use lactic casein of 30 to 60 mesh. Sodium hydroxide is the preferred alkali saponifying agent. However, other alkali saponifying agents may also be used such as calcium, magnesium, or potassium hydroxide or carbonate. The ammonium is preferably handled as aqua ammonia of about 26° Bé., however, more or less concentrated solutions or even anhydrous ammonia may be used.

To the premix prepared as described above there is added 10 parts by weight of hydrogenated fat and 2 to 5 parts by weight of the saponifiable fatty acid, fat or oil. The amount of premix to which the hydrogenated fat and fatty acid, fat or oil are added may vary from 9.0 to 23.0 and preferably 9 to 16 parts by weight depending on the relative amounts of each of the constituents in the premix. The preferred proportions are 9.9 parts of premix to 10 parts hydrogenated fat and 3 parts fatty acid. The hydrogenated fat and the fatty acid, fat or oil may be added either separately or together as a mixture. It is preferred to pre-melt both the hydrogenated fat and the fatty acid, fat or oil before adding to the mixture of casein, sodium hydroxide and ammonium hydroxide. Alternatively, the

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casein mixture may be added to the melted mixture of hydrogenated fat and fatty acid, fat or oil.

The hydrogenated fats or oils employed in the paper sizing compositions comprising this invention consist of hydrogenated animal fats or oils having titer points in the range of from 45° to 61° C., but it is preferred such hydrogenated fats and oils have a titer in the range of from about 55° to 61° C.; and specifically, a titer of about 57° C. The hardened or hydrogenated fats are prepared by the customary commercial method for hydrogenating such fats or oils which consists of hydrogenating in the presence of a reduced nickel catalyst on a kieselguhr or Filtarcel carrier at a temperature in the range of from 175°–190° C. and at a pressure in the range of from 20–40 pounds per square inch. The hydrogenation is continued until test portions show the fat or oil has acquired a titer of at least about 45° C. The hydrogenation forms saturated acids, in part, and also converts linoleic acid into trans and isomeric forms of oleic acid (isooleic) having higher melting points than normal fatty acids. The oil may be filter pressed while hot to remove the catalyst and carrier, and is then cooled. If desired it may be stripped with steam to remove any residual odors and liquid fractions still present. The known methods of hydrogenating fats are described by O. H. Wurster, Ind. Eng. Chem., 32, 1193 (1940), and form no part of this invention but the disclosure thereof is incorporated herein by reference. The preferred hydrogenated animal fats for use in this invention are the tallows, or depot fats of herbivorous animals; sheep and cattle. Thus, it is preferred to hydrogenate beef tallow to a titer of about 53° to 61° C. or mutton tallow to about 57° C.–58.5° C. The titer number of the beef tallow that is hydrogenated is 38–47 and that of the mutton tallow used 39–52. Lard having an average melting point of about 38° C. and titer number of about 36° C. may be hydrogenated until it has a titer in the range of 57°–60° C. to produce what is known as lard flakes which may be used in this invention. The chemical composition of the foregoing fats is given in *The Chemical Constitution of Natural Fats*, by T. P. Hilditch, published by Wiley, New York (1940), the disclosure of which is incorporated herein by reference. Other hydrogenated animal fats including beef marrow fat, bone fat, chicken fat, goose fat and horse fat may be used, but these have little commercial importance and the use thereof is not preferred since the best sizing compositions according to this invention are prepared from the above described very hard beef tallows.

The paper sizes of this invention may also be prepared by replacing a minor portion of the hard hydrogenated animal fats; such as, for example, beef tallow, having titers in excess of 50° C., with very hard hydrogenated vegetable fats or oils. Thus, up to 40 percent by weight of the total amount of hydrogenated fat employed may be a hydrogenated vegetable fat or oil having a titer in excess of about 45° C.; and, preferably, of about 65° C. It is preferred to employ either a hydrogenated soybean oil having a titer of about 65° C., or in the range of 64.5° to 66.5° C., or hydrogenated olive oil having a titer of at least about 65° C. Other hydrogenated vegetable fats or oils may be used; such as, for example, hydrogenated cottonseed oil, titer 60° C., and hydrogenated castor oil titer 87° C. Other hydrogenated vegetable oils which may be used include hydrogenated palm oil, peanut oil, or sesame oil. The amount of hydrogenated vegetable fat or oil used with hydrogenated animal fat is preferably in the range of from about 1 to 4 parts by weight of hydrogenated vegetable fat or oil to from 9 to 6 parts by weight of hydrogenated animal fat for a total of 10 parts. It is preferred to use about 3 parts by weight of the hydrogenated vegetable fat or oil to about 7 parts by weight of the hydrogenated animal fat.

The hydrogenated animal fats or mixtures thereof with hydrogenated vegetable fats or oils which have been described above are added to the mixture of casein, am-

monium hydroxide and alkali saponifying agent along with a saponifiable animal, marine animal or vegetable fat or oil or fatty acid derived therefrom or tall oil. The fats and oils which may be used are those preferably from which the free glycerin has been removed. Examples of fats or oils which may be used are animal fats such as mutton or beef tallow and lard; marine animal fats such as menhaden, cod liver, herring or sardine; and vegetable fats or oils such as olive oil, cottonseed oil, peanut oil or castor oil. When soft fats and oils are used, such as olive oil, cottonseed oil and soybean oil, which contain high percentages of unsaturated acids, the sizing composition is more readily dispersible in tepid water. However, paper sized with such a composition is not as crisp as paper sized with a composition containing hard fats such as tallow and which contain high percentages of long chain saturated acids. The preferred fat is beef tallow having a titer of 38-47° C.

The fatty acids which may be used in the practice of this invention are generally speaking, higher aliphatic monobasic acids containing from about 8 to 22 carbon atoms, and preferably 12 to 18 carbon atoms such as lauric, myristic, palmitic, stearic and oleic. These acids may be saturated or unsaturated, branched or unbranched. They may be obtained from the natural fats and oils described in the last paragraph by any of the well known methods of hydrolysis or "splitting." The most popular process is the so-called "Twitchell Process" which involves addition of water and a catalyst such as sulfonated petroleum to the fat or oil followed by steam splitting under pressure. Glycerol is removed leaving the free fatty acid which generally comprises a mixture of fatty acids. In the practice of this invention, this mixture of fatty acids may be used directly, or, alternately, the mixture may be separated into its individual components such as by fractional distillation. It is preferred from a practical standpoint to use the mixture of fatty acids directly. Methods for the manufacture of fatty acids from fats and oils and for the fractionation of mixtures of fatty acids are described in the Kirk-Orthner "Encyclopedia of Chemical Technology," volume 6, pages 231 to 236 (1951), published by the Interscience Encyclopedia, Inc., New York, and form no part of this invention but the disclosure thereof is incorporated herein by reference.

Preferred fatty acids used in the practice of this invention are those derived from animal tallow such as beef tallow fatty acids which contain high percentages of saturated acids. Beef tallow fatty acids comprise about 41.8 percent oleic acid, about 24.9 percent palmitic acid, about 24.1 percent stearic acid, about 1.8 percent linoleic acid, about 3.1 percent myristic acid, about 2.4 percent palmitoleic acid, about 0.2 percent lauric acid, about 0.8 percent arachidic acid and about 0.5 percent linolenic acid. Fatty acids derived from animal tallow using high pressure splitting of the fat and vacuum distillation of the product generally have a titer of from 32.2 to 42.5° C.; an iodine value of from 51 to 85, a saponification value of 180 to 208 and an acid value of 179 to 208. Acids which possess higher acid and saponification values and lower iodine values tend to improve the sizing efficiency of the sizing composition.

The mixture of casein, alkali, ammonium hydroxide, hydrogenated fat and saponifiable fatty acid, fat or oil, is then heated, preferably at about 160 to 180° F., and agitated until a smooth and uniform mixture is achieved. It is preferred to reduce the moisture content to the point at which the solids content of the mixture is from about 60 to 68 percent. The mixture may be used as is or it may be homogenized to make the composition more uniform throughout. This may be accomplished in a Gaulin homogenizer, at a pressure of 2000 to 3000 p.s.i. In order to reduce the volume of the sizing composition to facilitate handling, the solids content may be further increased by spray drying or oven drying by methods well known in the art.

The paper sizing compositions comprising this invention are dispersed in water and the aqueous dispersions used in the paper-making process in the same manner that aqueous dispersions of partially saponified rosin are used for sizing purposes. A paper sizing composition, prepared as described above, is added to heated water with agitation to provide about a 10% solution based on the dry weight of the size. The aqueous dispersion thus prepared is cooled and is then added to the beater containing the suspension of paper pulp and filler. The aqueous dispersion is used in an amount sufficient to provide between about 0.5 and 5 percent by weight of sizing composition based on the dry weight of the paper pulp. Paper makers alum must be added to the suspension of sizing and pulp in the amount of from about 3 to 4 percent based on the weight of the pulp to provide a pH of between about 4.5 and 5.5; and preferably about 5.

The sizing compositions of this invention may be used to size any type of pulp which is customarily sized with alkaline rosin sizes. The suspensions of paper pulp to which the aqueous dispersion of the sizing compositions of this invention are added may also contain the usual paper fillers; such as, for example, titanium dioxide and pigmentary silica flocs in amounts of about 8 to 10 percent by weight based on the weight of the dry pulp.

Sized pulp is dried preferably at a minimum temperature of 100° C. which is a condition attained on standard paper drying rolls.

The best mode of carrying out this invention is set forth in the following examples:

#### EXAMPLE 1

One part by weight of 60 mesh lactic casein was placed in a steam-jacketed open kettle and 10.48 parts by weight of water were added. The mixture was heated to 105° F. and held there for 15 minutes with mild agitation to prevent foaming. There was then added 1.35 parts by weight of 26° Bé. ammonium hydroxide and 0.737 part by weight of sodium hydroxide and the mixture heated to 140° F. with mixing for 30 minutes. At this point, a mixture of 10 parts by weight of hydrogenated beef tallow having a titer of 57° C. and 3 parts by weight of beef tallow fatty acids which had been premelted by heating at 154° F. was added to the contents in the kettle. The temperature rose as a result of the exothermic reaction to 165° F. The mixture was then heated to 200° F. and held at that temperature with agitation for 40 minutes. The dry solids content of the final product was determined to be 60 percent.

#### EXAMPLE 2

A paper sizing composition was prepared as described in Example 1 with the exception that the premix comprised 1 part by weight casein, 6.07 parts by weight water, 0.737 part by weight sodium hydroxide and 1.35 parts by weight 26° Bé. ammonium hydroxide. The premix was added to the melted fats and the final mixture heated to 168° F. with agitation for 30 minutes. The dry size content of the final product was determined to be 65 percent.

#### EXAMPLE 3

A paper sizing composition was prepared as described in Example 1 except that the premix comprised 1 part by weight casein, 7.16 parts by weight water, 1.01 parts by weight 26° Bé. ammonium hydroxide and 0.737 part by weight sodium hydroxide. The dry size content of the final product was determined to be 64 percent.

Aqueous dispersions of the compositions produced in Examples 1 to 3 were prepared by adding enough water to each sample to give a 10 percent solids content. These dispersions were added at concentrations of 1.5 and 2.0 percent by weight of sizing based on the weight of dry pulp to defibred bleached pine sulfate pulp. The mixtures were stirred thoroughly and sufficient alum added

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to reduce the pH to 4.4. Hand sheets were prepared from the sized suspension of pulp on a standard TAPPI handsheet forming test machine. These handsheets were tested for water penetration by TAPPI standard procedures. The results are set out in Table I, below. For the purpose of comparison, handsheets sized in exactly the same manner but using Pexol, a fortified rosin size supplied by the Hercules Powder Company, were also tested.

Table I

Type Size	Percent Size	Water Penetration, sec.
Pexol.....	1.5	16.9
Pexol.....	2.0	18.4
Example 1.....	1.5	23.3
Example 1.....	2.0	27.7
Example 2.....	1.5	24.1
Example 2.....	2.0	29.8
Example 3.....	1.5	25.0
Example 3.....	2.0	27.9

As can be seen from Table I, the compositions of this invention gave better results in smaller concentration than do the commercial rosin size and far superior results when used in the same concentrations.

## EXAMPLE 4

To 9.97 parts by weight of water in a steam-jacketed open kettle was added 1 part by weight of 30 mesh casein. The composition was mixed thoroughly to disperse the casein and 0.759 part by weight of sodium hydroxide and 1.32 parts by weight 26° Bé. ammonium hydroxide were added and the mixture was heated to 170° F. until the casein had all dissolved. At this point, a melted mixture of 6 parts by weight of hydrogenated beef tallow having a titer of 58.5° C., 4 parts by weight of a hydrogenated soybean oil and having a titer of 64.5° C. and 3 parts by weight of tallow fatty acids having a titer of about 41, an acid value of about 200, an iodine value of about 53 and a saponification value of about 205 (Emery 531) was added and the mixture heated with agitation to 162° F. for one hour. The composition was then allowed to cool. The dry size content of the final product was determined to be 65 percent.

## EXAMPLE 5

A paper sizing composition was prepared as described in Example 4 except that the final product was homogenized.

Aqueous dispersions of the compositions produced in Examples 4 and 5 were prepared by adding sufficient water to a sample of each composition to give a 10 percent solids content. These dispersions were used to prepare sized hand-sheets of defibred bleached sulfate pulp. These handsheets were tested for water penetration and tear strength by TAPPI standard procedure. For the purpose of comparison, tests were also made on a handsheet containing no size and one treated with alum. The results of these tests are set out in Table II, below.

Table II

Type Size	Percent Size	Water Penetration
Control—no size, no alum.....	0	Instantaneous.
Control—alum only.....	0	Instantaneous.
Example 4.....	1	15.6 secs.
Example 5.....	1	11.3 secs.

This data illustrates the remarkable improvement obtained in water resistance obtained by using the sizing compositions of this invention.

## EXAMPLE 6

One part by weight of 30 mesh casein was added to a mixture of 10.76 parts by weight of 10° Bé. sodium hy-

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droxide in a steam-jacketed kettle having a rotary stirrer. The mixture was heated and stirred until the casein was thoroughly dissolved at which time a premelted mixture of 10 parts by weight of hydrogenated beef tallow having a titer of 53° C. and 3 parts by weight of tallow fatty acids having a titer of about 35° C., an iodine value of about 70, an acid value of about 185 and a saponification value of about 185 (Emery 500) were added. This mixture was heated at 160° F. and stirred until the dry size content of the mixture was 62.5 percent. The mixture was then allowed to cool.

## EXAMPLE 7

A sizing composition was prepared as described in Example 6 with the exception that one part by weight casein was first added to 9.9 parts by weight water, the mixture was thoroughly stirred, and subsequently, 0.725 part by weight sodium hydroxide and 1.84 parts by weight ammonium hydroxide were added. The dry size content of the mixture was determined to be 62.6 percent.

Aqueous dispersions of the composition produced in Examples 6 and 7 were prepared by adding sufficient water to a sample of each composition to give a 10 percent solids content. These dispersions were added to defibred bleached sulfate pulp having a freeness of 645 ml. in one case and 590 ml. in another set, the freeness being determined by TAPPI Standard No. T-227m-50. The dispersions were added in the proportion of one percent of size based on the dry fiber weight of the pulp. Alum was added to reduce the pH to 5.3 and handsheets were made from the sized pulp according to TAPPI Standard No. T-205m-58. These handsheets were evaluated for water penetration by the dry indicator method as described in TAPPI Standard No. T-433m-44. For the purpose of comparison, handsheets sized with a composition, prepared as described in compending application Serial No. 851,242 by adding 10.76 parts by weight sodium hydroxide to a melted mixture of 10 parts by weight of hydrogenated beef tallow and 3 parts by weight of the fatty acid used in Example 6 and heating at 160° F. until the mixture became heavy and stiff, were also tested. The results are set out in Table III, below.

Table III

Size Sample	Amount Size, percent	Pulp Free-ness, 645 ml. Water Penetration, secs.	Pulp Free-ness, 590 ml. Water Penetration, secs.
Example 6.....	1	22.45	13.8
Example 7.....	1	22.7	13.8
Comparative Example (no Casein).....	1	9.7	3.4

It will be noted that the results obtained by using sizing compositions prepared in accordance with this invention produce far superior results to those obtained by using a similar composition but containing no casein.

## EXAMPLE 8

One part by weight of 60 mesh lactic casein was added to 12 parts by weight 10° Bé. sodium hydroxide solution and 1.84 parts by weight of 22° Bé. ammonium hydroxide. The mixture was heated to 140° F. and agitated until all the casein was dissolved. To this mixture was added 10 parts by weight of hydrogenated lard having a titer of 58° C. and 4 parts by weight of crude tall oil. The mixture was heated and agitated at 160° F. for one hour. At this point, the dry solids content was determined to be 60 percent. This composition was used to size paper pulp as described in the foregoing examples. Handsheets prepared therefrom were of high quality.

When the compositions prepared in accordance with this invention are added to pulp slurries, no foaming occurred as was experienced when using rosin sizes. Paper sized with the compositions of this invention had a much higher degree of brightness and wet and dry opacity than

paper sized with an equal amount of standard rosin size. The sizing in the handsheets was found to be substantially uniformly distributed throughout the body of the sheet.

I claim:

1. A paper sizing composition prepared by adding about 10 parts by weight of a hydrogenated fat selected from the group consisting of hydrogenated animal fats having a titer of from 45° to 61° C. and mixtures consisting of not less than 60% by weight of hydrogenated animal fat having a titer of from 45° to 61° C. and not more than 40% by weight of hydrogenated vegetable fats having a titer of from 45° C. to 70° C.; in combination with from about 2 to about 5 parts by weight of a non-hydrogenated, saponifiable compound selected from the group consisting of animal, vegetable and marine animal fats and oils, fatty acids containing from 8 to 22 carbon atoms and tall oil; to from 9.0 to 23.0 parts by weight of an aqueous premix consisting essentially of one part by weight of casein, from about 7 to 20 parts by weight of water, from about 0.70 to 1.5 parts by weight of an alkali and from about 0.7 to 2.0 parts by weight of ammonium hydroxide; and heating the mixture till the solids content is from 60 to 68 percent.

2. A paper sizing composition as set forth in claim 1 wherein said premix consisting essentially of one part by weight casein, from about 7 to 12 parts by weight of water, from about .70 to 1.5 parts by weight sodium hydroxide and from about 0.7 to 1.4 parts by weight ammonium hydroxide.

3. A paper sizing composition as set forth in claim 1 wherein 10 parts by weight of said hydrogenated fat and from 2 to 5 parts by weight of said saponifiable compound are added to from 9.0 to 16.0 parts by weight of said premix.

4. A paper sizing composition as set forth in claim 1 wherein said hydrogenated fat consists of a mixture of at least six parts by weight of hydrogenated animal fat

having a titer of from 55° to 61° C. and up to four parts by weight of hydrogenated vegetable fat having a titer of about 65° C.

5. A paper sizing composition as set forth in claim 1 wherein said hydrogenated fat consists of hydrogenated beef tallow having a titer of about 57° C.

6. A paper sizing composition as set forth in claim 1 wherein said saponifiable compound consists of beef tallow fatty acids.

7. A paper sizing composition as set forth in claim 1 wherein said saponifiable substance is tall oil.

8. A paper sizing composition prepared by adding 10 parts by weight of hydrogenated beef tallow having a titer of 57° C. and 3 parts by weight of beef tallow fatty acids to a premix consisting essentially of one part by weight casein, about 7.1 parts by weight water, about 0.74 part by weight sodium hydroxide and about 1.01 parts by weight 26° Bé. ammonium hydroxide, and heating the mixture till the solids content is from 60 to 68 percent.

9. The method of preparing a paper sizing composition which comprises mixing one part by weight casein, about 7.1 parts by weight water, about 0.74 part by weight sodium hydroxide and about 1.01 parts by weight 26° Bé. ammonium hydroxide; heating to from 130° F. to 150° F. for 5 to 15 minutes; and subsequently adding 10 parts by weight of a hydrogenated animal fat having a titer of from 55° to 61° C. and 3 parts by weight of a fatty acid containing from 12 to 18 carbon atoms; and heating the mixture till the solids content is from 60 to 68 percent.

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