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SIZING FIBROUS CELLULOSIC MATERIALS

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This invention relates to the sizing of fibrous cellulosic materials to provide products such as paper, cardboard, textile threads and fabrics, imitation leather, twines and ropes and other similar materials of cellulose of improved water resistance. More particularly the present invention relates to a new method of sizing cellulosic materials of a fibrous nature in which a new bitumen-in-water type emulsion is employed and to the resultant products.

The usual procedure employed for sizing cellulosic fibrous materials is to contact the fibers with an aqueous dispersion of the size and then precipitate the size on the fibers by adding a suitable precipitant. Thus, for example, in the sizing of paper pulp, the dispersion of size is generally added to the pulp in the beater or Holland machine and is there precipitated on the fibers with papermaker's alum. It is advantageous when employing this method of internal sizing to use a sizing agent which may be prepared as a highly concentrated, stable emulsion having a minimum amount of water. This permits a saving on shipping and storage costs for the emulsion.

A number of sizing agents, such as "T-size," a proprietary rosin size of Hercules Powder Co., have met with commercial acceptance where high size level treatments are not required. If a high degree of sizing is desired, such asphaltic products as "Flintsize 33-C," a proprietary product of The Flintkote Co., and "Bitusize B," a proprietary product of The American Bitumulus and Asphalt Co., are commercially acceptable.

Although the aforementioned commercial sizes are commercially acceptable they do have a number of disadvantages. For example, when employing such sizes for the production of paper, it is necessary to adjust the pH of the pulp solution and control it to maintain a value of from 4.5 to 5.5 for best sizing results. In addition, a precipitating agent such as papermaker's alum is required to develop their sizing effect. The attendant acidic conditions cause corrosion problems and furnish a medium favoring the growth of certain types of plant life such as algae which in turn cause slime and sludge problems.

A further disadvantage is the fact that a large percentage of the paper pulp production is of the kraft type and is therefore on the alkaline side. Since these prior art commercial sizes require an acid pH of from 4.5 to 5.5 in order to function properly, it is apparent that enormous amounts of alum are required to adjust the pH of the alkaline pulp from pH values as high as 10.5 to at least a pH of 5.5.

Cellulosic materials are particularly susceptible to acids since the acids tend to weaken the fibers. Weakening of the fibers causes a decrease in the bursting strength of paper sheets. In order to compensate for the loss in strength of the pulp caused by the acids, it is necessary to increase the amount of beating during fiber preparation. As a result of increasing the amount of beating, power costs and equipment tie-up are increased. Furthermore, increased beating during fiber preparation will not retard the acceleration of aging caused by residual acids trapped in the fibers.

For these reasons it is apparent that it would be desirable to be able to eliminate the requirement for the use of

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a setting agent such as alum and to be able to size throughout the pH range covered in normal cellulosic fiber production, i.e., from approximately 4.5 to 10.5.

Accordingly, it is an object of the present invention to provide sized fibrous cellulosic products characterized by the sizing agents' ability to size on either the alkaline or acid side without the need for a setting or precipitating agent.

A further object of the present invention is to provide a new and improved process for sizing cellulosic materials of fibrous nature, the process being characterized by the ability of the sizing agent to size on either the acid or alkaline side with or without a precipitating or setting agent.

Another object of the present invention is to provide a new and improved method of sizing cellulosic material of a fibrous nature over a wide range of pH thereby alleviating the necessity of critical pH control and permitting the pH range to be varied at will from acid to basic so as to provide means for killing those strains of algae which have acquired an affinity for a particular pH range.

These and other objects of the present invention will become more apparent upon considering the following description.

In accordance with the present invention, I have discovered that the aqueous bitumen-in-water emulsions forming the subject matter of my copending application Serial No. 448,158, filed August 5, 1954, now abandoned, are excellent sizing agents in that they overcome the many difficulties heretofore experienced in employing sizing agents of the type requiring the use of a setting or precipitating agent. I am not only able to prepare sized cellulosic products of a fibrous nature with these sizing agents without the use of a setting or precipitating agent, but also may carry out the process of sizing in acid or alkaline medium, thereby eliminating the heretofore required adjustment of the pH on the acid side and control of this adjustment. As a result, an economical saving results from the elimination of the need for a setting or precipitating aid, the elimination of the need for large volumes of acid (and/or alum) for controlling the pH of sizing, particularly in the case of alkaline pulps of cellulosic fibers, and the elimination of equipment tie-up caused by corrosion problems resulting from sizing in an acid medium of from 4.5 to 5.5 pH level, and slime and sludge problems resulting from algae growth which is favored at a constant pH level. From the foregoing, it will be appreciated that the present invention is concerned with the preparation of sized cellulosic products of a fibrous nature using a bitumen-in-water sizing agent which is of the substantive type, i.e., a bitumen-in-water sizing agent characterized by its ability to size on either the alkaline or acid side without the need for a setting or precipitating agent. Such substantive type bitumen-in-water sizing agents are to be distinguished from the adjective type bitumen-in-water sizing agents of the prior art which are characterized by their inability to size without the need for a setting or precipitating agent, such as alum, and the necessity of closely controlling the pH.

The basic constituent of the emulsions used as sizing agents in accordance with the present invention is a bitumen. By the term "bitumen" is meant various products derived from petroleum by refining such as heavy lubricating oils, reduced crude oils, asphalt, cracked tars, asphaltenes, resins, asphaltic oils and naturally occurring asphalts (bitumens and pyrobitumens) or products obtained by blowing these materials with an oxygen containing gas in the presence or absence of a catalyst. Examples of naturally occurring asphalts include gilsonite, grahamite, wurtzite and native asphalts.

The bitumen-in-water emulsions used as sizing agents

in the present invention may be prepared with the aid of organic emulsifying agents of the type promoting oil-in-water emulsions. When properly prepared these emulsions have an average particle size of less than two microns in diameter, preferably 0.5–1 micron or smaller with substantially no emulsified particles of a diameter greater than 6 microns. It will be appreciated that there are certain preferred procedural steps embodied in the method of preparation of these emulsions and that preferred emulsions are obtained when these preferred procedural steps are carried out.

For the purpose of preparing the sizing agents of the present invention, it is essential that during emulsification the phase volume ratio for the bitumen-in-water system be continuously maintained within the range yielding substantially a maximum viscosity at the temperature of emulsification. For example if the bitumen is a petroleum resin, a viscosity of at least 50,000 centipoises is required when using nonpressurized equipment or colloid mills at room temperature, whereas at a temperature of 180–190° F., it will be of the order of 3,000 to 10,000 centipoises and higher, thus demonstrating the variation in magnitude of viscosity with temperature while maintaining the maximum viscosity necessary for my process.

In general, the emulsions useful for the purposes of this invention may be prepared by the simultaneous and controlled addition of the water and bitumen phases in those ratios so as to continuously maintain the phase volume ratio within the range yielding substantially a maximum viscosity at the temperature of emulsification, or may be prepared by controlled and separate incremental addition of the two phases so as to maintain the phase volume ratio as aforesaid.

In accordance with the second mentioned method, as much bitumen must be added to the starting soap solution as possible before further water is added or the resulting emulsion will have a considerable number of particles of a size greater than 2.0 microns. The need for addition of water is controlled by watching the viscosity. If the last increment of bitumen added to the emulsion results in a slight decrease in viscosity, this indicates a tendency for the emulsion to invert. Thereupon, a small increment of water must be added before further amounts of bitumen are added. If this procedure of maintaining a high viscosity is not followed by alternately adding increments of water and bitumen to thereby maintain the phase volume ratio in the critical zone near the phase reversal point, the resulting emulsion will either invert to give a water-in-oil emulsion or the particles of the final oil-in-water emulsion will be too large. Water may, for example, serve as a vehicle for dissolving the emulsifying agent and introducing it into the bitumen or may be added independently of the emulsifying agent in increments as needed for the maintenance of the proper viscosity, i.e., substantially at a maximum for the system at the temperature of emulsification.

For the purpose of preparing the sizing agents of the present invention in accordance with this second method, it is preferred that the emulsifying agent be admixed with or formed in a minor proportion of the total bitumen to be utilized in the emulsion with a subsequent thorough mixing prior to the addition of the balance of the bitumen. Apparently this technique assures homogeneous distribution of the emulsifying agent throughout the body of the bitumen.

Although the emulsifying agent may be formed in situ, it is preferred to add the already prepared emulsifying agent to the bitumen or vice versa. With this preferred variation of procedure, emulsions with an average particle size of less than 2 microns may be prepared by using as little as 3% by weight of an emulsifying agent based on the weight of bitumen present.

The preferred continuous commercial method of producing my emulsion is to combine the water and bitumen streams just prior to their entering into the agitation

zone, e.g., a colloid mill. The emulsifying agent may be added separately or in admixture with either the water or bitumen streams and in some cases in both streams. I prefer to add the emulsifying agent to the water stream either continuously or in the water supply tank. The percent emulsifier in the water stream may vary from approximately 10 to the upper limit of fluidity, i.e., 40 to 50% with tall oil or rosin soaps, or higher concentrations may be used if provision is made for handling the resulting viscous material.

I prefer to feed a stream of water containing the emulsifier to the colloid mill and immediately thereafter starting feeding the fluidized bitumen stream, to the colloid mill, the preferred method of fluidizing the bitumen being by means of a solvent rather than by heat alone. The rate at which water containing the emulsifier is fed to the colloid mill should be greater than the bitumen feed rate at the start. Then the rate of feed of bitumen is increased as long as the viscosity of the emulsion increases. When the bitumen to water ratio exceeds a certain value, the viscosity no longer increases, but shows a decrease, indicating the incipient reversal point. A slight adjustment in the bitumen-water ratio is made to maintain the viscosity of the bitumen-in-water emulsion at substantially maximum and near the incipient reversal point. Then the feed rates of water to bitumen are maintained at this ratio in the incipient reversal zone to produce my emulsion.

The preferred fluid bituminous materials for the purposes of the present invention are asphaltic oils. The solid bituminous material of the sizing agents of the present invention are those having ring and ball softening points (ASTM Test D36–26) too soft to 400° F. and will vary from tacky, black glossy materials to non-tacky, friable ones. Those bituminous materials preferred for use as the basic constituent of the sizing agents will have ring and ball softening points of 125–200° F. and penetrations at 77° F. (ASTM Test D5–25) of 0 to 30. It has been found desirable when using a bitumen of 140° F. or greater softening point to either cut the bitumen back with a suitable solvent to obtain a working fluidity at the desired temperature or resort to pressurized emulsification. The inclusion of a solvent in no way affects the sizing ability of the finished emulsion, as the solvent is volatilized during the drying operation incident to the formation of the final form of dry cellulosic product.

Since the most preferred bitumens, petroleum resins, have softening points in the range of 150 to 180° F. and penetrations in the range of from 0 to 5 at 77° F., it is desirable to emulsify the petroleum resins in water at the highest practical temperature to prevent them from congealing too fast. Practical temperature limitations are somewhat governed by the selection of the solvent used for cutting back the petroleum resins.

Among the many satisfactory volatile-type solvents that may be used are kerosene, gasoline, high-flash naphtha solvents, aromatic solvents, etc. Mineral spirits, an essentially non-aromatic material, is a preferred volatile-type solvent since it possesses a high flash point and a relatively narrow boiling range. The high flash point offers a safety feature and the boiling range of from approximately 300 to 400° F. permits easy evaporation of the solvent when the emulsions are used as sizing agents.

Among the many satisfactory relatively non-volatile type solvents that may be used are solvents such as cracked recycle oils, gas oils, and light lube stock. Such solvents are preferred in some instances where the emulsion formulation contains hard bitumens. The hard bitumens remain plasticized by the non-volatile solvent and better TAPPI size values may be obtained at lower drying temperatures when the emulsions are used as sizing agents.

Another reason for employing cutback bitumens such as petroleum resins or asphalts is for ease of handling.

By cutting back a petroleum resin with a solvent, its viscosity is lowered, thereby facilitating its incorporation into the water emulsion without boiling the water.

The ability of a solvent to lower the viscosity of a particular bitumen over a particular temperature range is influenced to a degree by the viscosity change with temperature exhibited by this solvent. For example, a highly paraffinic solvent would give a smaller change in viscosity with temperature than an aromatic type solvent. Therefore, the viscosity of a cutback bitumen over a particular temperature range is a function of the percent bitumen and cutback present in the mixture and their respective natures.

The solvent apparently serves to help adjust the hydrophilic and hydrophobic nature of the emulsifier by increasing or decreasing the relative solubility of the emulsifier in the cutback bitumen. As an illustration, "Vinsol" (the petroleum (paraffinic) insoluble product derived from pine wood and identified by its manufacturer, Hercules Powder Company, as a polymerized abietic acid containing appreciable phenolic content), is essentially insoluble in mineral spirits but has appreciable solubility in a very high aromatic solvent, such as fortified aromatic spirits. Therefore, if "Vinsol" soaps are used as emulsifying agents, aromatic type cutbacks will tend to facilitate the ease of production of bitumen-in-water type emulsions while non-aromatic type solvents will tend to cause water-in-oil emulsions to be formed.

Another means of varying the balance between the hydrophilic and hydrophobic groups of an emulsifier is to change the nature of the basic constituent which reacts with the acidic portion. To illustrate this concept, if potassium is substituted for sodium in the soap of stearic acid, I have found that potassium stearate is more amenable to my method of emulsification than sodium stearate. I believe this is due to the better balance between the hydrophilic and hydrophobic groups of the emulsifying agent which has the effect of permitting a greater variation in the bitumen to water phase volume ratio in the zone of emulsification near the incipient reversal point. With an emulsifying agent which I prefer to refer to as having a proper balance between the hydrophilic and hydrophobic groups, I find it relatively easy to adjust the phase volume ratio to maintain a substantially maximum viscosity near the incipient reversal point. With an emulsifying agent which has poor balance between the hydrophobic and hydrophilic groups, the phase volume ratio is so critical that the task of maintaining a substantially maximum viscosity near the incipient reversal point becomes extremely difficult, and in some cases almost impossible. The difference in ease of effecting emulsification in the zone near incipient reversal between a proper and a poorly balanced emulsifying agent is such as to lead me to believe there is a plateau effect with the properly balanced emulsifier and a peak effect with the poorly balanced one. Otherwise, I am unable to explain the apparent difference in sensitivity to change in phase volume ratio near the incipient reversal point.

The maximum viscosity obtainable during the preparation of these sizing agents varies with temperature. For example when the emulsification occurs at 120° F. with the formulation of Example III of my aforesaid pending application the maximum viscosity is in the neighborhood of 50,000 centipoises or higher while if emulsification occurs at 190° F. the maximum viscosity would be of the order of 3,000 to 10,000 centipoises or higher. I have found that if the emulsions prepared at 190° F. are allowed to cool to room temperature the viscosity will be in the neighborhood of 50,000 centipoises or higher (extrapolation indicates values up to 500,000 centipoises or higher may be obtained at 80 to 90° F. in some cases).

Considerable thought has been given to deriving a satisfactory mathematical expression for the interrelationship

of particle size, phase volume ratio, the viscosity of the internal phase and the viscosity of external phase to the bulk viscosity exhibited by these sizing agents at various temperatures. It is obvious that the viscosities of the external phase, the internal phase and the emulsion must decrease with increased temperature. Therefore, if the rate of change in viscosity with increasing temperature exhibited by the internal phase is greater than that exhibited by the external phase, then at the higher temperature just to maintain a balance of the forces in the emulsion (i.e., the condition existing at the incipient reversal point), more internal phase must be added than when the rate of change in viscosity with temperature exhibited by the internal phase is less than that of the external phase. Just how the particle size of the emulsion relates to these factors, I am unable to say other than to indicate that the maximum viscosity for the bitumen-in-water system the particle size is found to be the smallest. It might be added that various emulsifiers have a tendency to effect the viscosity of the external phase (water). By way of example, a water solution of sodium stearate and a water solution of potassium stearate exhibit very different viscosities even though both solutions contain identical concentrations of their respective stearates. Sodium stearate solutions also tend to gel at lower concentrations than potassium stearate solutions.

The organic emulsifiers of the sizing agents used in this invention are the ones known in the art as promoters of oil-in-water emulsions such as water soluble soaps made from fatty acids or fatty acid mixtures or their glycerides. Examples of fatty acids include oleic, palmitic, stearic, lauric, naphthenic, oxidized higher hydrocarbons (waxes) containing carboxylic groups, tall oil, and rosin acid (primarily abietic acid or its derivatives) and mixtures thereof containing from 0 to 20% unsaponifiable matter, the unsaponifiable matter comprising the sterols, higher alcohols and terpenoid-like substances usually considered as being formed by decarboxylation of fatty and rosin acids by heat or chemicals. The preferred emulsifier is a rosin or tall oil water soluble soap.

The water soluble emulsifiers used in the preparation of the sizing agents of this invention are prepared by reacting the fatty acids, i.e., either the acid or its glyceride, with a basic substance including alkalis and lower organic amines having less than 6 carbon atoms in the chain. The alkalis suitable for forming water soluble soaps are sodium, potassium and ammonium. Examples of suitable organic amines include ethanol amine, morpholine and ethyl amine. The alkali oxides, hydroxides and carbonates may be used instead of the higher priced metal. The preferred basic material for forming water soluble soaps useful as emulsifiers is sodium hydroxide. This preference is primarily of an economic nature for it would not be preferred in the case of the stearic acid soap already referred to, as potassium is better in this case. When ammonium soaps are used, an excess of free ammonia or ammonium hydroxide is normally used because of the pronounced tendency of ammonia to be volatilized during the emulsification process.

Certain organic bodying agents such as the cellulose derivatives, proteinaceous matter, and certain natural gums may be used in conjunction with the sizing agents of this invention.

A preferred formulation for the production of emulsions used as sizing agents in the present invention is as follows:

	Percent
Bitumen or a constituent thereof	40-60
Solvent (cutback)	0-20
Emulsifying agent	0.5-8
Water	30-40

This is not intended to preclude the use of higher percentages of emulsifying agent since as much as 20% by

weight of fatty acid soap will form satisfactory emulsions. In addition, the higher the percent by weight of emulsifying agent, i.e., even above 8%, the more nearly the paper sized on the acid or alkaline side approaches the other in TAPPI value.

An example of a typical emulsion suitable as a sizing agent is as follows:

	Pounds
Petroleum resin, S.P., 178° F.-----	42.9
Mineral spirits-----	21.4
Refined tall oil-----	3.2
Caustic soda-----	0.3
Water-----	32.2

The tall oil is placed in a mixing vessel of 80 quarts capacity and slowly stirred. The caustic soda is dissolved in 4.8 pounds of water and added to the tall oil. No heat is supplied other than the heat of reaction itself, which is sufficient to raise the temperature of the mass to 160–180° F. At the end of a half hour, the reaction is essentially complete, a neutral sodium soap of tall oil, or sodium tallate, having been produced.

The petroleum resin is heated to 400° F., and to this material is slowly added with stirring the mineral spirits of 300–400° F. boiling range. The resultant mixture will have a temperature of 300° F. which should be maintained during addition of the cutback resin to the body of the emulsion.

The petroleum resin mixture is now slowly added to the tall oil soap with vigorous agitation. The mixer (a conventional bakery mixer may be used) should be capable of developing high torque at low speed, and should be so designed that it will sweep the entire mixing area of the vessel. The resin will be incorporated in the soap to form an oil-in-water type of emulsion. Initially the viscosity of the mixture will increase upon addition of the resin, but after the addition of a portion of the resin, usually one-quarter to one-third of the total resin to be added, the viscosity will show a tendency to decrease, indicating a tendency toward incipient reversal of the mixture to form a water-in-oil type emulsion. It is this emulsion which contains a fractional portion of the total bitumen to be emulsified and which is at substantially a maximum viscosity for the system at its temperature that I refer to as being a "preformed emulsion." At this point it is necessary to begin the incremental addition of water preferably at ambient temperature. The water will accomplish two things: prevent the undesirable reversal of the emulsion, and maintain the viscosity of the mixture at substantially the highest point. Maintaining the mixture at substantially its maximum viscosity at its temperature of emulsification is essential to produce the fine particle size of the instant invention. In this example, the water, at the rate of 1 lb. water to 2.3 pounds cutback resin, may be added either alternately with the resin or simultaneously to maintain the necessary high viscosity. Visual observation of the mass is perhaps the best way of determining its viscosity, since the viscous mixture has the consistency of a very heavy paste, and any decrease in its viscosity can be readily observed. The operator is cautioned not to add too much water at this point as this will have an ultimate thinning effect due simply to the increase in volume of the external phase of the emulsion. The ratio of water to the resin-solvent mixture that must be added during the preparation of an emulsion is a critical property of each particular system, and must be determined for each different formulation, but ordinarily will be about one pound of water to each two to seven pounds of resin-solvent mixture depending on the temperature of emulsification.

After all the resin has been incorporated in the mixture, the emulsification is completed, and additional water may be added in order to thin the mixture to a pumpable consistency. The thinning may be enhanced by the addition of small amounts of surface active agents. A final resin-

solvent to water ratio in the range of 6:4 to 4:6 results in a mixture possessing good stability characteristics on standing, a workable consistency, and a sufficiently high concentration of resin to make economically feasible the shipment of the finished product over long distances.

During the batch preparation of the emulsion, the temperature will stay in the range of 120–130° F. No outside source of heat is necessary during the mixing, since the resin-solvent mixture will be added at approximately 300° F.

The finished emulsion will have a particle size in the microscopically observable range of 0.1 to 2.0 microns, with 95% of the observable particles less than 1.0 micron and substantially no particles larger than 6 microns with 99% of particles under 4 microns.

A variation of the above method, known as the nascent soap method may be used. In this method the soap to be used as an emulsifier and stabilizer is prepared in situ by first adding the unreacted tall oil to a portion of the cutback resin, preferably to about 10% of the cutback resin. This mixture, at 250° F., is placed in the kettle and agitated. Into this mixture is poured all the caustic soda dissolved in sufficient water to make a concentrated solution, preferably about 20% caustic soda in water. Upon the addition of the caustic solution, a soap is immediately formed with the tall oil present, in which the cutback resin is emulsified, giving a concentrated cutback resin-in-water emulsion referred to as a "preformed emulsion." At this point the incremental addition of resin and water is begun and the procedure is carried along as before, with due diligence on the part of the operator to insure that water-resin ratio is so maintained that the emulsification takes place at substantially the maximum viscosity of the mixture.

As an alternate method to the above preparation in a batch kettle, a colloid mill or other dispersion machine capable of handling viscous mixtures may be used to effect the emulsification. The soap is preferably prepared as before and pumped to the reservoir of the colloid mill. The soap is circulated from the reservoir through a pump to the colloid mill and back to the reservoir. Solvent cutback resin is added to the soap mixture just prior to the entry into the colloid mill to give a preformed emulsion. As the soap continues to circulate, the resin content is slowly built up as long as the mixture coming from the mill shows an increase in viscosity. In the instance of a closed system such as a colloid mill, it is necessary to have adequate pumping capacity at the maximum viscosity characteristic of this temperature. When the viscosity levels off or begins to fall, which may be determined by visual observation of the material in the reservoir, water preferably containing the rest of the emulsifying agent, at room temperature is slowly introduced to the mixture at a rate sufficient to maintain substantially the maximum viscosity for this temperature without producing a thinning effect due to dilution of the external phase and thereby maintain the phase volume ratio near the incipient reversal point. The water may be added concurrently with the resin or alternatively thereto. The addition of cutback resin and water to the mixture must be closely controlled to prevent the hot resin from causing the water to boil and vapor lock the system or the water from cooling the resin to the point where it solidifies and is no longer readily dispersible. This can best be prevented by adding the resin at some point just prior to the passage of the mixture through the colloid mill, and adding the water to the mass of material up-stream therefrom. When all the resin has been added, sufficient extra water may be added to permit the emulsion to be more readily pumped to storage. By careful operation, an emulsion can be produced of which 95% of the particles are less than 2 microns in size, normally less than 1.

If it is undesirable to incorporate a solvent in the mixture when working with high softening point mate-

rials, the above procedure may be varied by operating the colloid mill under pressures of, for example, 100 p.s.i.g. This allows the resin to be heated to temperatures such that it possesses the proper fluidity characteristics and yet will not permit boiling of the water phase in the colloid mill. In such a pressurized system, it is necessary to allow the finished material to cool under pressure to a temperature well below the boiling point of water, preferably 140° F. For purposes of controlling the viscosity, a viscosimeter of the Ultra-Viscoson type can be installed in the flow line leading from the colloid mill to the pressurized reservoir.

Additional examples of the preparation of bitumen emulsion suitable for use as sizing agents in accordance with the present invention appear in my aforesaid copending application and are incorporated herein by reference. These examples as well as the foregoing example relate to emulsions prepared in the concentrated form to facilitate handling and storage and to save shipping costs. When it is desired to use these emulsions as sizing agents in accordance with the present invention, they are preferably "let down" by dilution with water to give for example a 5 percent emulsion (percent solids) or some other strength preferred by the sizing operator.

As an example of a specific and preferred embodiment of the present invention I have selected the sizing of paper pulp. The invention however is applicable to the sizing of any other fibrous cellulosic material for the production in final manufactured form of cardboard, textile threads and fabrics, imitation leather, twine, rope, etc. Consequently, the term "cellulosic product of a fibrous nature" as used in the claims is not limited to the production of paper but includes the production of any product made from cellulosic fibers and requiring sizing to impart water resistance.

Prior to the sizing operation, the concentrated emulsion prepared as described above and containing, for example, 50 to 60 percent bituminous solids is preferably diluted with about ten parts of water to insure proper mixing in the pulp and to avoid interference with the customary paper making procedures. No special precautions are necessary with these emulsions during the dilution step and the diluted emulsions will remain stable indefinitely. The diluted size is preferably then added to the beater or Jordan engines during the beating process wherein as a result of intimate contact with the cellulosic fibers, the sizing constituents of the bitumen-in-water emulsion are deposited on the fibers of the cellulose. Although it is preferred to add the size to the beaters or Jordan engines, addition of the size at any point prior to the formation of the sheet up to and including the head box of the paper machine, will give satisfactory results under normal operating conditions.

Depending upon the method used for producing or obtaining the paper pulp, the pH may vary from a value of 4.5 to approximately 10.5. As the specific examples will show hereinafter the sizing agents used in the present invention do not require that the pH be adjusted to any particular value in order to obtain satisfactory results. Furthermore, a setting or precipitating agent is not required. In other words the sizes of the present invention give satisfactory results when sizing on either the alkaline or acid side and do not require the use of alum or any other setting or precipitating agent. In contrast, other sizes such as "T-size," "Flintsize" and "Bitusize" will obtain satisfactory results only when sizing on the acid side at a controlled pH level providing alum or another suitable size precipitating agent is employed.

Upon the completion of the deposition of the sizing constituents of the sizing agent on the cellulosic fibers, the pulp is formed into sheet form, couched, pressed, and dried in accordance with the usual paper making techniques. In the case of producing sized cellulosic

products other than paper, normal finishing operations after sizing may be carried out.

The emulsions of the present invention have been found suitable for sizing sulfite pulp, sulfate and soda pulps, ground wood pulp, and semi-chemical pulps. For example, hard wood soda, hard wood semi-chemical and ground wood pulps give TAPPI's from 20 to 46 at a pH of 8+ and corresponding TAPPI's on the acid side at 4-5 pH using alum. Soft wood sulfite pulp gives TAPPI's of 15 and 21 respectively at 8+ and 4-5 pH. Certain special reclaimed stocks (jute liner board) which have been subjected to extremely severe Asplund refining type treatments respond poorly when sizing on the alkaline side, but sizing improves as such stocks are aged.

In the sizing of pulp known to the art as jute liner board, it is preferred practice of the art to size on the acid side, i.e., less than 7.0 pH by use of a fixative such as alum to set the size and then adjust the pH to the alkaline side, preferably above 8.0 pH with an alkaline material before the sheeting operation. By means of this process they are able to avail themselves of the benefits of sizing on the acid side and sheet formation on the alkaline side to obtain a finished material having certain desired properties. My emulsion size gives excellent results with jute liner board when this method of sizing is followed.

The following specific examples are for the purpose of illustrating this invention and are not limiting to the scope thereof which is set forth in the claims.

EXAMPLE I

Samples of unbleached jack pine, Douglas fir and southern pine kraft pulps were reduced in freeness by beating to 1.5-2.0 percent consistency in a 1.5 pound Valley beater and then dewatered to about 25 percent oven dry content. Individual (20 grams) batches of pulp so prepared were diluted to 2 liters and stirred in a British disintegrator. After removing a sample for a freeness test, the remaining pulp was diluted to about 0.15 percent consistency and handsheets were formed on a British sheet mold. The sheets were couched, pressed, dried and tested. Normal drying conditions were 240° F. for 5 minutes.

The particular sizing agent employed in an amount of 2 percent size solids had a formulation in parts by weight as follows:

Petroleum resin (softening point, 178° F.)	42.9
Mineral spirits (cutback solvent)	21.4
Tall oil, refined	3.2
Sodium hydroxide	0.3
Water	32.2

The emulsion was prepared as described above and was then diluted with 10 parts by weight of water. The point of addition of this sizing agent to the pulp was as indicated in Table I below.

Table I

Pulp (Kraft)	Schopper Riegler Freeness, cc.	Point Sizing Added	pH	Bursting Strength, pt./100#	TAPPI Size, Sec.
Jack Pine	650	None	8.9	143	2
Do	620	After Beater	8.9	127	35
Do	770	In Beater	8.9	125	30
Do	630	In Beater	8.9	135	34
Do	600	None	10.5	136	2
Do	580	After Beater	10.5	131	25
Do	635	In Beater	10.5	136	35
Douglas Fir	545	None	8.9	101	2
Do	515	After Beater	8.9	94	31
Do	510	In Beater	8.9	94	28
Do	465	None	10.5	100	2
Do	460	After Beater	10.5	96	24
Do	420	In Beater	10.5	96	31
Southern Pine	665	None	8.9	101	3
Do	605	After Beater	8.9	92	31
Do	615	In Beater	8.9	92	26
Do	600	None	10.5	96	2
Do	590	After Beater	10.5	98	25
Do	480	In Beater	10.5	101	25

TAPPI size values of over 20 seconds are rated as satisfactory and indicative of sizing. Values of over 30 seconds are rated very satisfactory, exceptionally hard sized products being obtained.

Satisfactory size values were also obtained when alkali organic sulfonates, such as the alkyl aryl sulfonates marketed by Atlas Powder Company under the designation G-3300, were substituted for tall oil and sodium hydroxide in the formulation for the foregoing emulsion.

EXAMPLE II

A Douglas fir kraft pulp having its pH adjusted to 5 ± 0.5 with alum was sized in accordance with the method outlined above in Example I employing as sizing agents the sizing agent of Example I and "T-size." The amount of size used for each test in percent solids as well as the results obtained are set forth below in Table II.

Table II

Size	Schopper Riegler Free- ness, cc.	Percent Solids	Bursting Strength, pt./100#	TAPPI Size, Seconds	Fluo- rescent Size, Sec.
None.....	660	-----	76	Inst.	2
Example I.....	680	1	68	25	67
Do.....	680	3	69	32	82
T-size.....	690	1	73	23	49
Do.....	670	3	70	24	46

I claim:

1. The process for sizing a cellulosic product of a fibrous nature which comprises the steps of depositing on the fibers of the cellulose active sizing constituents of a substantive bitumen-in-water emulsion by intimately contacting the cellulosic fibers with the emulsion; the active sizing constituents of the emulsion being deposited on the cellulosic fibers in the absence of a precipitating agent; the dispersed phase of the emulsion consisting essentially of bitumen; the emulsion being characterized by having as an emulsifying agent an organic emulsifier which promotes the formation of oil-in-water emulsions, not less than 95% of the particles having a size of 0.1-1.0 micron, not less than 99% of the particles having a size under 4 microns, substantially no particles having a size larger than 6 microns, and average particle size of less than 1.0 micron, an ability to size the cellulosic fibers on the acid side and the alkaline side, and the emulsion being produced by emulsifying the bitumen and water in the presence of the emulsifying agent by dispersing the bitumen in the water in a ratio to produce an emulsion having substantially the maximum viscosity for the bitumen-in-water system at the temperature of emulsification; and subsequently forming the resultant sized fibers into manufactured form.

2. The process of sizing a cellulosic product of a fibrous nature as set forth in claim 1 wherein the bitumen is of petroleum origin.

3. The process of sizing a cellulosic product of a fibrous nature as set forth in claim 1 wherein the bitumen is a liquid petroleum oil having a viscosity within the lubricating range.

4. The process of sizing a cellulosic product of a fibrous nature as set forth in claim 1 wherein the bitu-

men is selected from the group consisting of asphalt, resins, asphaltenes and oils.

5. The product produced by the process of claim 1.

6. The process for sizing a cellulosic product of a fibrous nature which comprises the steps of intimately contacting cellulosic fibers of kraft pulp with a substantive bitumen-in-water emulsion to deposit active sizing constituents of the emulsion on the fibers; the cellulosic fibers being contacted with the emulsion at a pH higher than 7.0; the active sizing constituents of the emulsion being deposited on the cellulosic fibers in the absence of a precipitating agent; the dispersed phase of the emulsion consisting essentially of bitumen; the emulsion being characterized by having as an emulsifying agent an organic emulsifier which promotes the formation of oil-in-water emulsions, not less than 95% of the particles having a size of 0.1-1.0 micron, not less than 99% of the particles having a size under 4 microns, substantially no particles having a size larger than 6 microns, an average particle size of less than 1.0 micron, an ability to size the cellulosic fibers on the acid side and the alkaline side, and the emulsion being produced by emulsifying the bitumen and water in the presence of the emulsifying agent by dispersing the bitumen in the water in a ratio to produce an emulsion having substantially the maximum viscosity for the bitumen-in-water system at the temperature of emulsification; and subsequently forming the resultant sized fibers into manufactured form.

7. The process of claim 6 wherein the emulsion is contacted with the cellulosic fibers at a pH higher than 7.0 and up to about 10.5.

8. The process of sizing a cellulosic product of a fibrous nature as set forth in claim 6 wherein the bitumen is of petroleum origin.

9. The process of sizing a cellulosic product of a fibrous nature as set forth in claim 6 wherein the emulsifying agent is a water-soluble fatty acid soap and the fatty acid portion thereof is selected from the group consisting of oleic acid, palmitic acid, stearic acid, lauric acid, rosin acid, tall oil, abietic acid and naphthenic acid.

10. The process of sizing a cellulosic product of a fibrous nature as set forth in claim 9 wherein the cationic portion of said soap is selected from the group consisting of sodium ion, potassium ion, ammonium ion, and a lower organic amine having less than 6 carbon atoms present in the chain.

11. The process of sizing a cellulosic product of a fibrous nature as set forth in claim 9 wherein 0.5 to 20 percent by weight of the water-soluble fatty acid soap is present in the bitumen-in-water emulsion.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,954,313

September 27, 1960

Eugene E. Woodward

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 20, for "effect" read -- affect --; column 8, line 59, for "alternatively" read -- alternately --; column 10, lines 7, 8, and 10, for "TAPPI's", each occurrence, read -- TAPPIs --.

Signed and sealed this 11th day of April 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

ARTHUR W. CROCKER
Acting Commissioner of Patents