

[54] STABLE WAX SIZING COMPOSITION AND METHOD OF SIZING CELLULOSIC FIBER PRODUCTS

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[57] ABSTRACT

A stable aqueous wax emulsion sizing composition comprising a continuous aqueous phase; a waxy material dispersed phase containing up to about 45 percent by weight of wax; about 10–15 percent by weight based on the weight of the waxy material of clay; and a small amount of sulfuric acid. The sizing composition may be applied to a variety of cellulosic products of a fibrous nature to render the finished product water-resistant or waterproof.

7 Claims, No Drawings

STABLE WAX SIZING COMPOSITION AND METHOD OF SIZING CELLULOSIC FIBER PRODUCTS

BACKGROUND OF THE INVENTION

This invention relates to the sizing of cellulosic products of a fibrous nature to provide resultant products such as paper, cardboard, insulation panels and low density wood fiber boards of improved water-resistance. More particularly, the present invention relates to a stable aqueous wax emulsion sizing composition for producing such resultant products.

The usual procedure employed for sizing cellulosic products of a fibrous nature is to contact an aqueous slurry of the fibers with an aqueous dispersion of the size and then precipitate the size on the fibers by adding a suitable precipitant or by contacting the fibers with an emulsion sizing composition containing an organic surface active emulsifier. 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 it is then precipitated on the fiber with paper maker's alum. Further for example, in the manufacture of fiberboard from vegetable fibers such as wood fiber or bagasse, the board or bagasse is formed from an aqueous slurry on a forming machine which may be an Oliver or Fourdrinier or other board-forming machine of conventional type well-known in this art. The sizing agent is added to the aqueous slurry. The formed board or mat, if to be used as a low-density soft-board or semi-hardboard is then conventionally dried in a known manner. If the board or mat is to be used as hardboard, it will additionally be processed under extreme heat and pressure to develop high densities characteristic of such product.

It is advantageous when employing the above methods 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 of the emulsion.

Waxy materials are commonly included as a basic material for sizing compositions due to the water-resisting properties characteristic of them. However waxy materials are not definite and consistent, particularly in the paraffin wax series, especially towards the low end of this series, such as with the so-called "crude-scale wax." This is particularly noticeable in that the wax composition, and performance as a sizing ingredient, will vary from batch to batch; and this has a consequent effect on the uniformity of resulting emulsions. Crude scale wax is a non-crystalline wax on the low order of the paraffin series of waxes, and the more refined grades of this wax are stated to contain up to a maximum of 3% oils. This value is highly variable, especially from batch to batch wherein one batch may have one-half percent oil content while the next batch may have 1½ or 2 percent oil content. The melting point of this more refined grade of crude scale wax material is about 125-140°F. Lower grades of crude scale wax may contain up to about 15 percent oil and have a melting point temperature of about 115°F. The problem of wax consistency and uniformity from batch to batch is not confined to crude scale wax, but this is one commercial example in which the problem is most prevalent.

In emulsifying wax sizing formulations, a number of variably successful approaches have been utilized in-

cluding the use of clay material alone as an emulsifier as well as more expensive formulations including surface active agents of organic nature.

Although the afore-mentioned surface active type of emulsifiers generally provide commercially acceptable sizing formulations, they do have a number of disadvantages. For example, the surface active agents are generally more expensive than the inorganic clay emulsifier. When employing sizing compositions that require a precipitant, it is frequently necessary to adjust the pH of the pulp solution, and frequently to maintain a value from 4.5-5.5 for best sizing results. The attendant greater acidic conditions cause corrosion problems and furnish a medium favoring the growth of certain types of plant life which cause slime and sludge problems.

When utilizing a clay as the emulsifier for the wax, the effects of the variations in wax uniformity and particularly oil content in the waxy materials causes a high incidence of emulsification problems. Quite frequently the resultant emulsion is not stable for any length of time.

SUMMARY OF THE INVENTION

It is therefore one object and advantage of the present invention to provide stable aqueous wax emulsion sizing compositions utilizing a clay emulsifier.

Another object is the provision of stable aqueous wax emulsion sizing compositions utilizing a clay emulsifier, which emulsions are stable regardless of variation in the characteristics in the wax from batch to batch.

A still further object is the provision of aqueous wax emulsion sizing compositions that do not require the employment of organic surface active agents or organic wetting agents in order to produce highly stable emulsions.

Still another object is the provision of improved aqueous wax emulsion sizing compositions which, although including a highly acidic ingredient, do not require lowering of the pH much below neutral.

The fulfillment of these and other objects and advantages of the present invention are accomplished by an aqueous wax emulsion sizing composition comprising a continuous aqueous phase; a waxy material dispersed phase containing up to about 45 percent by weight, based on the weight of the composition, of a wax; about 10-15 percent by weight, based on the weight of the waxy material, of a clay; and a small amount, preferably about ½-1 percent by weight, of sulfuric acid based on the weight of the waxy material. In such an emulsion, the effects of the variations of wax uniformity from batch to batch, and particularly oil content in the waxy material, are inhibited from causing emulsification problems and the resultant emulsion is highly stable over long periods of time. Such emulsions can be used for the sizing of cellulosic products of a fibrous nature to provide products such as paper, cardboard, and low density wood fiberboard and insulation mats of improved water-resistance by adding on the order of about 0.3% or more by weight of the emulsion, based on the weight of the fiber, at any convenient point to the aqueous pulp slurry such as by addition to the head box, stock chest, mixing tank and the like.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The wax component of the emulsion may comprise

any form of petroleum wax, and may therefore be present in the form of a paraffin wax, scale wax or slack wax, as obtained from petroleum distillation processes, petrolatum wax obtained from dewaxing heavy lubricating oilstock or microcrystalline waxes obtained from the petrolatum or from pipe still bottoms or other petroleum residue. Petroleum waxes modified with various polymers such as polyethylene or copolymers such as ethylene-vinyl acetate copolymers, and similar polymeric materials or suitable natural waxes such as beeswax, etc., and mixtures with the foregoing may also be included. The waxes employed in the composition are preferably petroleum waxes or, more preferably, scale waxes, especially those of a crude nature. A principal objective of the present invention is the capability of utilizing a wax ingredient of generally higher oil content. Thus the scale waxes and especially crude scale waxes are particularly pertinent for use in the present invention. Scale wax and crude scale wax is generally the product of a petroleum slop wax or slack wax that has been purified to the extent that it still contains several percent of oil, generally 0.1 to 10 percent or more. Most of the scale waxes produced have a melting point generally of 126°-130°F ASTM melting point.

Thus the word wax is used in the present specification and claims as used in its normal sense to designate any of the plastic, amorphous or crystalline solid compositions generally denominated as having a liquifying point between about 80° and 180°F, the capacity to acquire gloss when rubbed, low viscosity at just above the melting point, low solubility and solvency for fats at room temperatures and capacity to produce emulsions with water. The compositions of the present invention will improve the emulsification capabilities of any of the ordinary materials customarily denominated as waxes, although the compositions are most particularly preferred for increasing the emulsification capability of waxes containing on the higher order of oil contents.

The clay component of the composition may be any of those capable of acting as an emulsifier for aqueous wax emulsions, although it is preferred to use a clay that does not appreciably swell in water. Preferably the clay will contain as a primary constituent a mineral of the group known as montmorillonites; and such clays are generally referred to as bentonites. The clay should be in a finely divided state, generally with the particles having an average particle size of around 200-300 U.S. Standard Tyler Mesh. Substantial quantities of clay particles having a substantially larger size are not recommended as generally tending to settle out of the composition and thus tending to interfere with good emulsification. The amount of the clay component employed in the emulsification will generally be about 10-15 percent based on the weight of the wax; although slightly more or less may be used but without substantial further advantage. Considerably greater quantities would not be economical and considerably lower quantities would provide difficulty in emulsification.

The amount of water employed in the emulsification is not critical, but should be sufficient to yield a fluid emulsion of the oil in water type. As a practical matter, the final emulsion will preferably contain about in the order of 50% water to insure that the water is the continuous phase of the emulsion.

The concentrated sulfuric acid will be present preferably in an amount of $\frac{1}{2}$ -1 percent based on the weight

of the wax present. Substantially lesser amounts will not provide the advantages of the present invention. As the amount of concentrated sulfuric acid is increased over about 1 percent based on the weight of the wax, the concentrated sulfuric acid will have a greater effect on the pH of the composition. It is generally desired that the pH of the composition be maintained around a neutral pH; and about one-half percent based on the weight of the wax will maintain the pH at around 6-7. Any quantities of sulfuric acid much greater than 1 percent based on the weight of the wax will engender corrosion problems without providing substantial improvement in emulsification, unless special handling equipment is provided and then the amount of sulfuric acid may be increased to on the order of 5 percent or more.

At present it is not truly known exactly how the small amounts of sulfuric acid are acting to improve emulsification and also provide easy emulsification of heretofore non-emulsifying batches of aqueous clay-wax dispersions. However it is presently theorized that the small amounts of the highly electrolytic concentrated sulfuric acid are acting upon the clay particles. The clay emulsifier is a strongly ionizing material, and the electrical forces associated with the clay particles apply a net negative charge. It is theorized that the very small amounts of the strongly electrolytic sulfuric acid tend to neutralize the electrical charge on the individual plates within the clay crystal lattice to assist the clay in more efficiently preventing wax droplets from coalescing in the system and to maintain their dispersion in the emulsion. In any event, it is found that by the present invention, ease of emulsification between different batches of heretofore difficult-to-emulsify waxes of variable oil content is greatly increased. The resultant emulsions, on observation, contain much smaller sized wax droplets than without the addition of the sulfuric acid.

In the sizing operation, the concentrated emulsion is either diluted to insure proper mixing in the pulp slurry or used as is and metered in gradual increments into the pulp slurry. The in use concentration, or dilution, of the emulsion is highly variable depending on the degree of sizing effect desired. Generally the emulsion can be diluted up to 100 fold for satisfactory sizing of low density wood fiber board. No special precautions are necessary with these emulsions either during storage or during the dilution step other than to avoid freezing, and the emulsions will remain stable indefinitely.

The sizing emulsion preferably is added to the aqueous pulp slurry at the head box, stock chest, mixing tanks or other normal point for addition of additives, wherein as a result of contact with the cellulosic fibers the sizing constituents of the emulsion are deposited on the fibers of the cellulosic products.

The emulsions of the present invention have been found to be suitable for sizing of pulps known to the art as jute liner board, sulfate pulp, sulfate and soda pulps, ground wood pulp and the like to provide products such as paper, cardboard and wood fiber board and insulation mats of all types. The emulsions are highly effective for sizing low density wood fiber board and insulation mats, but have a slightly deleterious effect on strength of greatly compressed high density wood fiber hardboard.

EXAMPLES

The following specific examples will serve further to illustrate the practice and advantages of this invention. In the following examples, percentages listed are given on a weight basis, unless otherwise stated. References to ASTM methods are to the 1965 BOOK OF ASTM STANDARDS published by the American Society for Testing and Materials.

EXAMPLE 1

The following example illustrates a preferred composition made in accordance with the preferred method described hereinabove wherein a small amount of concentrated sulfuric acid is added to a crude-scale wax containing 3 percent oil content to produce a stable emulsion having excellent sizing properties.

The sizing emulsion was prepared using a formulation, in parts by weight, as follows:

Crude Scale Wax (Plasticrude 6005 brand by National Wax Co.)	100 grams
Bentonite non-swelling clay (Panther Creek brand by American Colloid)	15 grams
Water	200 grams
Concentrated Sulfuric Acid	1 gram
	<hr/> 316 grams

The emulsion was formulated by adding the wax and clay to the water; and then adding the sulfuric acid with constant mixing. The mixture was first heated to about 180°-200°F. until all of the wax was melted. The mixture was then agitated vigorously until emulsification was completed, as by agitation in a high shear mixer for approximately 10 minutes.

A low density (about 10-15 lb.) wood fiber board was made by forming an aqueous slurry of the wood fibers and diluting with water to about a 1% consistency. The fiber slurry was thoroughly mixed and the above sizing emulsion was added in an amount of about 0.5 percent based on the weight of the wood fiber solids; and mixing continued. Then paper maker's alum was added in an amount of about 0.5 percent based on the weight of the emulsion sizing composition solids; and mixing continued. The thoroughly mixed aqueous slurry was formed into a mat on a forming machine; lightly pressed to expel additional water and dried in an oven to produce the softboard. The finished board had low water absorption properties.

EXAMPLE 2

In a plant-size production evaluation, a number of batches of wax emulsions were made using 615 lbs. of a scale wax, 1230 lbs. of water and from 95 to 120 lbs. of a non-swelling bentonite clay. The emulsions were made by adding the wax to the water and then heating this mixture to 200°F until there was complete melting of the wax. Then mixing was commenced and increased to vigorous agitation at which point the clay was added. Mixing was continued for an additional 15 minutes, at which time emulsion samples were taken and evaluated for capability of mixing with cold water.

It was found in approximately 20 percent of the batches that the emulsion, when cooled down to about 125°F, broke and formed a skin of unemulsified wax particles on the surface or contained large clumps of

unemulsified wax particles. By analyzing the waxes from the various batches, it was found that in the satisfactory batches the wax had an oil content of about 0.1-0.2 percent and a melting point of about 140; while in the unsatisfactory batches the oil content was generally about 2 percent or higher and the average melting point was about 127°F.

EXAMPLE 3

To the unsatisfactory batches obtained in EXAMPLE 2 was added approximately 0.15 percent sulfuric acid based on the amount of wax present in the particular emulsion. As a control measure, aliquots of the unsatisfactory batches did not receive sulfuric acid addition. In comparison, all of the batches which received the sulfuric acid now mixed well with cold water, had excellent emulsion appearance and were storage stable; while the control aliquots continued to form a skin of unemulsified wax particles, or clumps of unemulsified wax particles and generally did not maintain stable emulsification. Further the control aliquots were difficult to re-emulsify without heating and addition of more clay along with strenuous agitation.

It was further observed that the aliquots containing sulfuric acid appeared to have a much finer particle size of the wax and the emulsion. Although analytical particle size measurements were not taken, the batches containing sulfuric acid were much lighter in color; and this lightness in color is a general indication of the fineness of the wax particle and the wax emulsion. In contrast, the aliquots not containing sulfuric acid were quite dark in color, generally indicating large particle size of the wax particles.

EXAMPLE 4

A series of low density wood fiber insulation mats were made and compared for 2-hour water absorption properties by the method set forth in ASTM C209. In all instances the sizing emulsion was added in an amount of 1 percent by weight of the solids in the insulation mat, and the insulation mats were identical with the exception of the character of the sizing emulsion, as follows:

Sizing Emulsion	Two-Hour Water Absorption
33% crude scale wax (2% oil) + 15% Bentonite clay	4.7%
33% crude scale wax (2% oil) + 15% Bentonite clay + 1/2% H ₂ SO ₄	3.7%
standard commercial rosin size	5.0%
standard commercial asphalt emulsion	4.5%

EXAMPLE 5

Two different batches of crude scale wax were compared for emulsion quality and stability by observation over a 48-hour period and also for 2-hour water absorption by method ASTM C209.

One batch of the crude scale wax (hereinafter identified as WAX A) had an oil content of 2 percent and a melting point of 125°F. The second wax sample (hereinafter identified as WAX B) had an oil content of 9.1 percent and a melting point of 118°F. Aliquots of these different waxes were formed into emulsions containing 30.7 percent wax, 15 percent clay and 55 percent wa-

ter. Mats of pine furnish were also made using these emulsions, the emulsions were added to the furnish in an amount of 0.5 percent, and the mats evaluated for water absorption by method ASTM C209.

For evaluation of emulsion quality and stability by observation, the following rating scale was applied:

Excellent = The emulsion rapidly diluted with cold water without forming oil spots or a wax film on the surface of the emulsion, without the formation of a third phase, and without breaking.

Good = The emulsion was easily and thoroughly diluted with cold water, forming only a few small oil spots, without breaking or forming a third phase and without observable coalescence of wax droplets.

Poor = The emulsion broke, or formed a third phase, or would not dilute with cold water without extensive coalescence of wax droplets.

Exemplary results of these evaluations with varying amounts of sulfuric acid addition to the different crude scale wax batches are as follows:

Formulation	Observed Emulsion Quality	24-Hour Water Absorption
WAX A	Good	15.4%
WAX A + 1.5% H ₂ SO ₄	Excellent	7.5 - 7.9%
WAX B (high oil content)	Poor	7.2%
WAX B + 0.5% H ₂ SO ₄	Good	7.9%
do. 1.0% do.	Good +	7.5%
do. 1.5% do.	Excellent	7.5%
do. 5.0% do.	Excellent	7.4%

While the present invention has been described and exemplified with respect to certain embodiments, it is not to be considered limited thereto; and it is understood that variations and modifications thereof, obvious to those skilled in the art, may be made without de-

parting from the spirit or scope of this invention.

What is claimed is:

1. A stable, aqueous wax emulsion sizing composition consisting essentially of:

- a continuous aqueous phase;
- a dispersed waxy material phase containing up to about 45 percent by weight, based on the weight of the composition, of scale wax;
- about 10-15 percent by weight, based on the weight of the waxy material, of clay; and
- an amount of sulfuric acid effective to facilitate emulsification of said wax.

2. A stable, aqueous wax emulsion as set forth in claim 1, wherein the wax comprises a crude scale wax.

3. A stable, aqueous wax emulsion as set forth in claim 2 wherein the crude scale wax contains about 0.1 to about 10 percent oil content.

4. A stable, aqueous wax emulsion as set forth in claim 2 wherein the crude scale wax contains more than about 2 percent oil content.

5. A stable, aqueous wax emulsion as set forth in claim 1, wherein the clay is a non-swelling bentonite clay.

6. A stable, aqueous wax emulsion as set forth in claim 1, wherein the amount of sulfuric acid is in the order of about ½ to about 1 percent by weight, based on the weight of the waxy material.

7. A stable, aqueous wax emulsion sizing composition consisting essentially of a continuous aqueous phase; up to about 45 percent by weight, based on the weight of the composition, of a crude scale wax containing on the order of about 2 to about 10 percent by weight oil content; about 10-15 percent by weight, based on the weight of the wax, of non-swelling bentonite clay; and on the order of about ½ to about 1 percent by weight, based on the weight of the wax, of sulfuric acid.

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