



**WATERLESS SELF-EMULSIFIABLE CHEMICAL
SOFTENING COMPOSITION USEFUL IN FIBROUS
CELLULOSIC MATERIALS**

FIELD OF THE INVENTION

This invention relates to a substantially waterless self-emulsifiable chemical softener composition. More particularly, it relates to substantially waterless self-emulsifiable chemical softener compositions useful for treating fibrous cellulose materials, such as tissue paper webs. The treated tissue webs can be used to make soft, absorbent paper products such as toweling, napkin, facial tissue, and toilet tissue products.

BACKGROUND OF THE INVENTION

Paper webs or sheets, sometimes called tissue or paper tissue webs or sheets, find extensive use in modern society. Such items as paper towels, napkins, facial and toilet tissues are staple items of commerce. It has long been recognized that three important physical attributes of these products are their softness; their absorbency, particularly their absorbency for aqueous systems; and their strength, particularly their strength when wet. Research and development efforts have been directed to the improvement of each of these attributes without seriously affecting the others as well as to the improvement of two or three attributes simultaneously.

Softness is the tactile sensation perceived by the consumer as he/she holds a particular product, rubs it across his/her skin, or crumples it within his/her hand. This tactile sensation is provided by a combination of several physical properties. One of the most important



physical properties related to softness is generally considered by those skilled in the art to be the stiffness of the paper web from which the product is made. Stiffness, in turn, is usually considered to be directly dependent on the dry tensile strength of the web and the stiffness of the fibers which make up the web.

Strength is the ability of the product, and its constituent webs, to maintain physical integrity and to resist tearing, bursting, and shredding under use conditions, particularly when wet.

Absorbency is the measure of the ability of a product, and its constituent webs, to absorb quantities of liquid, particularly aqueous solutions or dispersions. Overall absorbency as perceived by the consumer is generally considered to be a combination of the total quantity of liquid a given mass of tissue paper will absorb at saturation as well as the rate at which the mass absorbs the liquid.

The use of wet strength resins to enhance the strength of a paper web is widely known. For example, Westfelt described a number of such materials and discussed their chemistry in *Cellulose Chemistry and Technology*, Volume 13, at pages 813-825 (1979). Freimark et al. in U.S. Pat. No. 3,755,220 issued August 28, 1973 mention that certain chemical additives known as debonding agents interfere with the natural fiber-to-fiber bonding that occurs during sheet formation in papermaking processes. This reduction in bonding leads to a softer, or less harsh, sheet of paper. Freimark et al. go on to teach the use of wet strength resins in conjunction with the use of debonding agents to offset the undesirable effects of the debonding agents. These debonding agents do reduce both dry tensile strength and wet tensile strength.

Shaw, in U.S. Pat. No. 3,821,068, issued June 28, 1974, also teaches that chemical debonders can be used to reduce the stiffness, and thus enhance the softness, of a tissue paper web.

Chemical debonding agents have been disclosed in various references such as U.S. Pat. No. 3,554,862, issued to Hervey et al. on January 12, 1971. These materials include quaternary ammonium salts such as cocotrimethylammonium chloride, oleyltrimethylammonium chloride, di(hydrogenated)tallow dimethyl ammonium chloride and stearyltrimethyl ammonium chloride.

Emanuelsson et al., in U.S. Pat. No. 4,144,122, issued March 13, 1979, teach the use of complex quaternary ammonium compounds



such as bis(alkoxy(2-hydroxy)propylene) quaternary ammonium chlorides to soften webs. These authors also attempt to overcome any decrease in absorbency caused by the debonders through the use of nonionic surfactants such as ethylene oxide and propylene oxide adducts of fatty alcohols.

Armak Company, of Chicago, Illinois, in their bulletin 76-17 (1977) disclose the use of dimethyl di(hydrogenated)tallow ammonium chloride in combination with fatty acid esters of polyoxyethylene glycols to impart both softness and absorbency to tissue paper webs.

One exemplary result of research directed toward improved paper webs is described in U.S. Pat. No. 3,301,746, issued to Sanford and Sisson on January 31, 1967. Despite the high quality of paper webs made by the process described in this patent, and despite the commercial success of products formed from these webs, research efforts directed to finding improved products have continued.

For example, Becker et al. in U.S. Pat. No. 4,158,594, issued January 19, 1979, describe a method they contend will form a strong, soft, fibrous sheet. More specifically, they teach that the strength of a tissue paper web (which may have been softened by the addition of chemical debonding agents) can be enhanced by adhering, during processing, one surface of the web to a creping surface in a fine patterned arrangement by a bonding material (such as an acrylic latex rubber emulsion, a water soluble resin, or an elastomeric bonding material) which has been adhered to one surface of the web and to the creping surface in the fine patterned arrangement, and creping the web from the creping surface to form a sheet material.

Conventional quaternary ammonium compounds such as the well known dialkyl dimethyl ammonium salts (e.g. ditallow dimethyl ammonium chloride, ditallow dimethyl ammonium methyl sulfate, di(hydrogenated)tallow dimethyl ammonium chloride etc ...) are effective chemical debonding agents. Unfortunately, these quaternary ammonium compounds are not hydrophilic. Applicants have discovered that the chemical softening compositions of the present invention enhance both softness and absorbency rate of fibrous cellulose materials.

Furthermore, providing chemical softening compositions containing these softener compounds in substantially waterless forms,



results in cost saving on shipping the product (less weight), cost savings on packaging material, and cost savings on machinery required for processing the chemical softening compositions (less equipment needed to make-up the aqueous dispersions). In addition, the present invention also provides environmental safety advantages because of the elimination of the organic solvents, especially volatile organic solvents typically used in the preparation of concentrated softening compositions.

It is an object of this invention to provide a substantially waterless self-emulsifiable chemical softening composition useful for treating fibrous cellulose materials.

It is a further object of this invention to provide soft, absorbent tissue paper products.

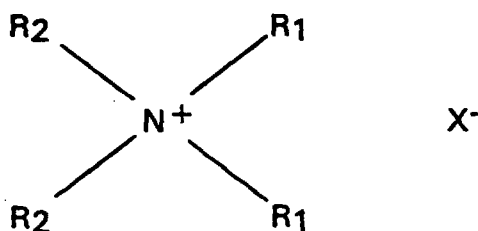
It is also a further object of this invention to provide a process for making soft, absorbent tissue paper products.

These and other objects are obtained using the present invention, as will become readily apparent from a reading of the following disclosure.

SUMMARY OF THE INVENTION

The present invention provides a substantially waterless self-emulsifiable chemical softening composition useful for treating fibrous cellulose materials. Briefly, the waterless self-emulsifiable chemical softening composition comprises a mixture of :

- (a) a quaternary ammonium compound having the formula





wherein each R₂ substituent is a C₁ - C₆ alkyl or hydroxyalkyl group, or mixture thereof; each R₁ substituent is a C₁₄ - C₂₂ hydrocarbyl group, or mixture thereof; and X⁻ is a suitable anion; and

- (b) a polyhydroxy compound selected from the group consisting of glycerol, polyglycerols having a weight average molecular weight of from about 150 to about 800 and polyoxyethylene glycols and polyoxypropylene glycols having a weight average molecular weight from about 200 to 4000;

wherein the weight ratio of the quaternary ammonium compound to the polyhydroxy compound ranges from about 1 : 0.1 to 0.1 : 1; and wherein said polyhydroxy compound is miscible with the quaternary ammonium compound at a temperature of at least 40°C . The chemical softening composition of the present invention is a stable, homogenous, solid or viscous fluid at a temperature greater than or about 20°C . The fluid may have either a liquid or a liquid crystal phase structure. The moisture content of the substantially self-emulsifiable chemical softening composition is less than about 20 % by weight, preferably the moisture content of the chemical softening composition is less than about 10 % by weight and more preferably the moisture content of the chemical softening composition is less than 5 % by weight.

Examples of quaternary ammonium compounds suitable for use in the present invention include the well-known dialkyldimethylammonium salts such as DiTallow DiMethyl Ammonium Chloride (DTDMAC), DiTallow DiMethyl Ammonium Methyl Sulfate (DTDMAMS), Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate (DHTDMAMS), Di(Hydrogenated)Tallow DiMethyl Ammonium Chloride (DHTDMAC).

Examples of polyhydroxy compounds useful in the present invention include glycerol, polyglycerols having a weight average molecular weight of from about 150 to about 800 and polyoxyethylene glycols having a weight average molecular weight of from about 200 to about 4000, with polyoxyethylene glycols having a weight average molecular weight of from about 200 to about 600 being preferred.



Briefly, the process for making the tissue webs of the present invention comprises the steps of formation of a papermaking furnish from the aforementioned components, deposition of the papermaking furnish onto a foraminous surface such as a Fourdrinier wire, and removal of the water from the deposited furnish.

All percentages, ratios and proportions herein are by weight unless otherwise specified.

BRIEF DESCRIPTION OF THE DRAWINGS

While the Specification concludes with claims particularly pointing out and distinctly claiming the present invention, it is believed the invention is better understood from the following description taken in conjunction with the associated drawings, in which :

Figure 1 are the phase diagrams of DiOctadecyl DiMethyl Ammonium Methyl Sulfate (DODMAMS) and of DHTDMAMS.

Figure 2 is a phase diagram of the DODMAMS / PEG-400 system.

Figure 3 is a cryo-transmission photo-micrograph taken at X 63,000 of the 2% dispersion formed by diluting a solid premix of a 1 : 1 by weight ratio of a DHTDMAMS and PEG-400 system.

Figure 4 is a cryo-transmission photo-micrograph taken at X 63,000 of the 2% dispersion formed by diluting a liquid premix of a 1 : 1 by weight ratio of a DHTDMAMS and PEG-400 system.

Figure 5 is a cryo-transmission photo-micrograph taken at X 63,000 of the 2% dispersion formed by diluting a liquid premix of a 1 : 1 by weight ratio of a DHTDMAC and a mixture of glycerol and PEG-400 system.

The present invention is described in more detail below.

DETAILED DESCRIPTION OF THE INVENTION

While this specification concludes with claims particularly pointing out and distinctly claiming the subject matter regarded as the invention, it is believed that the invention can be better understood from a reading of the following detailed description and of the appended examples.



As used herein, the term "viscous fluid" refers to a fluid having a viscosity greater than or equal to 10,000 centipoise at 20°C.

As used herein, the term "homogenous mixture" refers to compositions wherein the quaternary ammonium and polyhydroxy compounds are dissolved or dispersed in each other.

As used herein, the term "self-emulsifiable" refers to compositions that will form a uniform colloidal dispersion with a minimum of shear, heat, dispersing aids, etc. ... when added to a liquid carrier such as water.

As used herein, the terms "tissue paper web, paper web, web, paper sheet and paper product" all refer to sheets of paper made by a process comprising the steps of forming an aqueous papermaking furnish, depositing this furnish on a foraminous surface, such as a Fourdrinier wire, and removing the water from the furnish as by gravity or vacuum-assisted drainage, with or without pressing, and by evaporation.

As used herein, an "aqueous papermaking furnish" is an aqueous slurry of papermaking fibers and the chemicals described hereinafter.

The first step in the process of this invention is the forming of an aqueous papermaking furnish. The furnish comprises papermaking fibers (hereinafter sometimes referred to as wood pulp), and a mixture of at least one quaternary ammonium compound and at least one polyhydroxy compound, all of which will be hereinafter described.

It is anticipated that wood pulp in all its varieties will normally comprise the papermaking fibers used in this invention. However, other cellulose fibrous pulps, such as cotton liners, bagasse, rayon, etc., can be used and none are disclaimed. Wood pulps useful herein include chemical pulps such as Kraft, sulfite and sulfate pulps as well as mechanical pulps including for example, ground wood, thermomechanical pulps and chemically modified thermomechanical pulp (CTMP). Pulps derived from both deciduous and coniferous trees can be used. Also applicable to the present invention are fibers derived from recycled paper, which may contain any or all of the above categories as well as other non-fibrous materials such as fillers and adhesives used to facilitate the original papermaking. Preferably, the papermaking fibers used in this invention comprise Kraft pulp derived from northern softwoods.

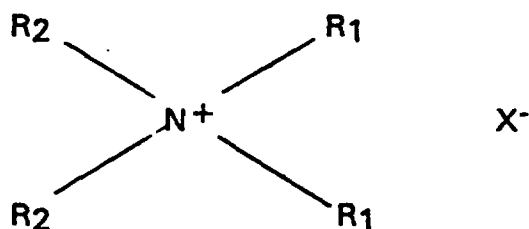
Waterless Self-emulsifiable Chemical Softener Compositions

The present invention contains as an essential component a mixture of a quaternary ammonium compound and a polyhydroxy compound. The ratio of the quaternary ammonium compound to the polyhydroxy compound ranges from about 1 : 0.1 to 0.1 : 1; preferably, the weight ratio of the quaternary ammonium compound to the polyhydroxy compound is about 1 : 0.3 to 0.3 : 1; more preferably, the weight ratio of the quaternary ammonium compound to the polyhydroxy compound is about 1 : 0.7 to 0.7 : 1, although this ratio will vary depending upon the molecular weight of the particular polyhydroxy compound and/or quaternary ammonium compound used.

Each of these types of compounds will be described in detail below.

A. Quaternary Ammonium Compound

The substantially waterless self-emulsifiable chemical softening composition contains as an essential component a quaternary ammonium compound having the formula :



In the structure named above each R₁ is C₁₄-C₂₂ hydrocarbon group, preferably tallow, R₂ is a C₁ - C₆ alkyl or hydroxyalkyl group, preferably C₁-C₃ alkyl, X⁻ is a suitable anion, such as an halide (e.g. chloride or bromide) or methyl sulfate. As discussed in Swern, Ed. in Bailey's Industrial Oil and Fat Products, Third Edition, John Wiley and Sons (New York 1964), tallow is a naturally occurring material having a variable composition. Table 6.13 in the above-identified reference edited by Swern indicates that typically 78% or more of the fatty acids of tallow contain 16 or 18 carbon atoms. Typically, half of the fatty acids present in tallow are unsaturated, primarily in the form of oleic acid. Synthetic as well as natural "tallows" fall within the scope of the present invention. Preferably, each R₁ is C₁₆-C₁₈ alkyl, most preferably each R₁ is straight-chain C₁₈ alkyl. Preferably, each R₂ is methyl and X⁻ is chloride or methyl sulfate.



Examples of quaternary ammonium compounds suitable for use in the present invention include the well-known dialkyldimethylammonium salts such as ditallow dimethyl ammonium chloride, ditallow dimethylammonium methyl sulfate, di(hydrogenated)tallow dimethyl ammonium chloride; with di(hydrogenated)tallow dimethyl ammonium methyl sulfate being preferred. This particular material is available commercially from Sherex Chemical Company Inc. of Dublin, Ohio under the tradename "Varisoft® 137".

B. Polyhydroxy Compound

The chemical softening composition contains as an essential component a polyhydroxy compound.

Examples of polyhydroxy compounds useful in the present invention include glycerol, polyglycerols having a weight average molecular weight of from about 150 to about 800 and polyoxyethylene glycols and polyoxypropylene glycols having a weight average molecular weight of from about 200 to about 4000, preferably from about 200 to about 1000, most preferably from about 200 to about 600. Poxoxyethylene glycols having an weight average molecular weight of from about 200 to about 600 are especially preferred. Mixtures of the above-described polyhydroxy compounds may also be used. For example, mixtures of glycerol and polyoxyethylene glycols having a weight average molecular weight from about 200 to 1000, more preferably from about 200 to 600 are useful in the present invention. Preferably, the weight ratio of glycerol to polyoxyethylene glycol ranges from about 10 : 1 to 1 : 10.

A particularly preferred polyhydroxy compound is polyoxyethylene glycol having an weight average molecular weight of about 400. This material is available commercially from the Union Carbide Company of Danbury, Connecticut under the tradename "PEG-400".

The waterless self-emulsifiable chemical softening composition described above i.e. mixture of a quaternary ammonium compounds and a polyhydroxy compound are preferably diluted to a desired concentration to form a dispersion of the quat and polyhydroxy compounds before being added to the aqueous slurry of papermaking fibers, or furnish, in the wet end of the papermaking machine at some suitable point ahead of the Fourdrinier wire or sheet forming stage.



However, applications of the above described chemical softening composition subsequent to formation of a wet tissue web and prior to drying of the web to completion will also provide significant softness, absorbency, and wet strength benefits and are expressly included within the scope of the present invention.

It has been discovered that the chemical softening composition is more effective when the quaternary ammonium compound and the polyhydroxy compound are first pre-mixed together before being added to the papermaking furnish. A preferred method, as will be described in greater detail hereinafter in Example 1, consists of first heating the polyhydroxy compound to a temperature of about 66°C (150°F), and then adding the quaternary ammonium compound to the hot polyhydroxy compound to form a homogenous fluid. The weight ratio of the quaternary ammonium compound to the polyhydroxy compound ranges from about 1 : 0.1 to 0.1 : 1; preferably, the weight ratio of the quaternary ammonium compound to the compound is about 1 : 0.3 to 0.3 : 1; more preferably, the weight ratio of the quaternary ammonium compound to the compound is about 1 : 0.7 to 0.7 : 1, although this ratio will vary depending upon the molecular weight of the particular compound and/or quaternary ammonium compound used. The moisture content of the chemical softening composition is less than about 20 % by weight, preferably the moisture content of the chemical softening composition is less than about 10 % by weight and more preferably the moisture content of the chemical softening composition is less than 5 % by weight. Importantly, the chemical softening composition is a stable, homogenous, solid or viscous fluid at a temperature greater than or about 20°C .

The substantially waterless self-emulsifiable chemical softener composition can be pre-mixed at the chemical supplier (e.g. Sherex company of Dublin, Ohio). Providing chemical softening compositions containing these softener compounds in substantially waterless forms results in cost saving on shipping the product (less weight), cost savings on packaging material and cost savings on machinery for processing the chemical softening compositions (less equipment needed to make-up the aqueous dispersion). In addition, the present invention also provides environmental safety advantages because of the elimination of the organic solvents, especially volatile organic solvents.



The ultimate users of the chemical softening composition simply dilute the mixture with a liquid carrier (i.e., water) to form an aqueous dispersion of the quaternary ammonium compound / polyhydroxy compound mixture, which is then added to the papermaking furnish. The homogenous mixture of the quaternary ammonium compound and the polyhydroxy compound can exist either in a solid state or in a fluid state before being dispersed in the aqueous media. Preferably, the mixture of the quaternary ammonium compound and polyhydroxy compound is diluted with a liquid carrier such as water to a concentration of from about 0.01% to about 25% by weight of the softening composition before being added to the papermaking furnish. The temperature of the liquid carrier preferably ranges from about 20°C to about 80°C. After mixing, the quaternary ammonium compound and the polyhydroxy compound are present as particles dispersed in the liquid carrier. The average particle size preferably ranges from about 0.01 to 10 microns, most preferably from about 0.1 to about 1.0 micron. As shown in Figures 3 - 5, the dispersed particles are in the form of either closed vesicles or open particles.

It has unexpectedly been found that the adsorption of the polyhydroxy compound onto paper is significantly enhanced when it is premixed with the quaternary ammonium compound and added to the paper by the above described process. In fact, at least 20% of the polyhydroxy compound and the quaternary ammonium compound added to the fibrous cellulose are retained; preferably, the retention level of quaternary ammonium compound and the polyhydroxy compound is from about 50% to about 90% of the added levels.

Importantly, adsorption occurs at a concentration and within a time frame that are practical for use during paper making. In an effort to better understand the surprisingly high retention rate of polyhydroxy compound onto the paper, the physical science of the melted solution and the aqueous dispersion of a Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate (DHTDMAMS), and polyoxyethylene glycol 400 were studied.

Without wishing to be bound by theory, or to otherwise limit the present invention, the following discussion is offered for explaining how the quaternary ammonium compound promotes the adsorption of the polyhydroxy compound onto paper.



Information on the physical state of DHTDMAMS Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate, $R_2N^+(CH_3)_2CH_3OSO_3^-$ and on DODMAMS is provided by X-ray and NMR (Nuclear Magnetic Resonance) data on the commercial mixture. DODMAMS (DiOctadecyl DiMethyl Ammonium Methyl Sulfate, $(C_{18}H_{37})_2N^+(CH_3)_2CH_3OSO_3^-$) is a major component of DHTDMAMS, and serves as a model compound for the commercial mixture. It is useful to consider first the simpler DODMAMS system, and then the more complex commercial DHTDMAMS mixture.

Depending on the temperature, DODMAMS may exist in any of four phase states (Figure 1): two polymorphic crystals (X^β and X^α), a lamellar (Lam) liquid crystal, or a liquid phase. The X^β crystal exists from below room temperature to 47°C . At this temperature it is transformed into the polymorphic X^α crystal, which at 72°C is transformed into the Lam liquid crystal phase. This phase, in turn, is transformed into an isotropic liquid at 150°C . DHTDMAMS is expected to resemble DODMAMS in its physical behavior, except that the temperatures of the phase transitions will be lowered and broadened. For example, the transition from the X^β to the X^α crystal occurs at 27°C in DHTDMAMS instead of 47°C as in DODMAMS. Also, calorimetric data indicate that several crystal $\rightarrow$ Lam phase transitions occur in DHTDMAMS rather than one as in DODMAMS. The onset temperature of the highest of these transitions is 56°C , in good agreement with the X-ray data.

DODMAC (DiOctadecyl DiMethyl Ammonium Chloride) displays qualitatively different behavior from DODMAMS in that the Lam liquid crystal phase does not exist in this compound (Laughlin et al., Journal of Physical Chemistry, Physical Science of the Dioctadecyldimethylammonium Chloride-Water System. 1. Equilibrium Phase Behavior, 1990, volume 94, pages 2546-2552, incorporated herein by reference). This difference, however, is believed not to be important to the use of this compound (or its commercial analog DHTDMAC) in the treatment of paper.

Mixtures of DHTDMAMS with PEG-400.

A 1:1 weight ratio mixture of these two materials is studied, and a plausible model for the phase behavior of this system is suggested in Figure 2. In this diagram DODMAMS and PEG are shown to be



immiscible at high temperatures, where they coexist as two liquid phases. As mixtures of the two liquids within this region are cooled, a Lam phase separates from the mixture. This study therefore shows that these two materials, while immiscible at high temperatures do become miscible at lower temperatures within the Lam liquid crystal phase. At still lower temperatures crystal phases are expected to separate from the Lam phase, and the compounds are again immiscible.

These studies therefore suggest that in order to form good dispersions of DHTDMAMS and PEG-400 in water, the premix that is diluted with water should be held within the intermediate temperature range where the two compounds are miscible.

Mixtures of DHTDMAC with PEG-400.

Phase studies of these two materials using the step-wise dilution method demonstrate that their physical behavior is considerably different from that of DHTDMAMS. No liquid crystal phases are found. These compounds are miscible as liquid solution over a wide range of temperatures, which indicates that dispersions may be prepared from these mixtures over a comparable range of temperatures. In particular no upper temperature limit of miscibility exists.

Preparation of dispersions.

Dispersions of either of these materials may be prepared by diluting a premix, that is held at a temperature at which the polyhydroxy compound and the quaternary ammonium salt are miscible, with water. It does not matter greatly whether they are miscible as a liquid crystalline phase (as in the case of DHTDMAMS), or as a liquid phase (as in the case of DHTDMAC). Neither DHTDMAMS nor DHTDMAC are soluble in water, so that dilution of either dry phase with water will precipitate the quaternary ammonium compound as small particles. Both quaternary ammonium compounds will precipitate at elevated temperatures as a liquid-crystal phase in dilute aqueous solutions, regardless of whether the dry solution was liquid or liquid crystalline. The polyhydroxy compound is soluble with water in all proportions, so is not precipitated.

Cryoelectron microscopy demonstrates that the particles present in the dispersion are about 0.1 to 1.0 micrometers in size, and highly varied in structure. Some are sheets (curved or flat), while others are closed vesicles. The membranes of all these particles are bilayers of



molecular dimensions in which the head groups are exposed to water, the tails are together. The PEG is presumed to be associated with these particles. The application of dispersions prepared in this manner to paper results in attachment of the quaternary ammonium ion to the paper, strongly promotes the adsorption of the polyhydroxy compound onto paper, and produces the desired enhancement of softness with retention of wettability.

State of the dispersions.

When the above described dispersions are cooled, the partial crystallization of the material within the colloidal particles may occur. However, it is likely that the attainment of the equilibrium state will require a long time (perhaps months), so that the membranes within those particles that interact with paper are in a disordered state.

It is believed that the vesicles containing DHTDMAMS and PEG break apart upon drying of the fibrous cellulosic material. Once the vesicle is broken, the majority of the PEG component may penetrate into the interior of the cellulose fibers where it enhances the fiber flexibility. Importantly, some of the PEG is retained on the surface of the fiber where it acts to enhance the absorbency rate of the cellulose fibers. Due to ionic interactions, the majority of the DHTDMAMS component stays on the surface of the cellulose fiber, where it enhances the surface feel and softness of the paper product.

The second step in the process of this invention is the depositing of the papermaking furnish using the above described chemical softener composition as an additive on a foraminous surface and the third step is the removing of the water from the furnish so deposited. Techniques and equipment which can be used to accomplish these two processing steps will be readily apparent to those skilled in the papermaking art. Preferred tissue paper embodiments of the present invention contain from about 0.005% to about 5.0%, more preferably from about 0.03% to 0.5% by weight, on a dry fiber basis of the chemical softening composition described herein.

The present invention is applicable to tissue paper in general, including but not limited to conventionally felt-pressed tissue paper; high bulk pattern densified tissue paper; and high bulk, uncompacted tissue paper. The tissue paper may be of a homogenous or multilayered



construction; and tissue paper products made therefrom may be of a single-ply or multi-ply construction. Tissue structures formed from layered paper webs are described in U.S. Patent 3,994,771, Morgan, Jr. et al. issued November 30, 1976, and incorporated herein by reference. In general, a wet-laid composite, soft, bulky and absorbent paper structure is prepared from two or more layers of furnish which are preferably comprised of different fiber types. The layers are preferably formed from the deposition of separate streams of dilute fiber slurries, the fibers typically being relatively long softwood and relatively short hardwood fibers as used in tissue papermaking, upon one or more endless foraminous screens. The layers are subsequently combined to form a layered composite web. The layered web is subsequently caused to conform to the surface of an open mesh drying/imprinting fabric by the application of a fluid force to the web and thereafter thermally predried on said fabric as part of a low density papermaking process. The layered web may be stratified with respect to fiber type or the fiber content of the respective layers may be essentially the same. The tissue paper preferably has a basis weight of between 10 g/m² and about 65 g/m², and density of about 0.60 g/cm³ or less. Preferably, basis weight will be below about 35 g/m² or less; and density will be about 0.30 g/cm³ or less. Most preferably, density will be between 0.04 g/cm³ and about 0.20 g/cm³.

Conventionally pressed tissue paper and methods for making such paper are known in the art. Such paper is typically made by depositing papermaking furnish on a foraminous forming wire. This forming wire is often referred to in the art as a Fourdrinier wire. Once the furnish is deposited on the forming wire, it is referred to as a web. The web is dewatered by transferring to a dewatering felt, pressing the web and drying at elevated temperature. The particular techniques and typical equipment for making webs according to the process just described are well known to those skilled in the art. In a typical process, a low consistency pulp furnish is provided in a pressurized headbox. The headbox has an opening for delivering a thin deposit of pulp furnish onto the Fourdrinier wire to form a wet web. The web is then typically dewatered to a fiber consistency of between about 7% and about 25% (total web weight basis) by vacuum dewatering and further dewatered by pressing operations wherein the web is subjected



to pressure developed by opposing mechanical members, for example, cylindrical rolls.

The dewatered web is then further pressed during transfer and being dried by a stream drum apparatus known in the art as a Yankee dryer. Pressure can be developed at the Yankee dryer by mechanical means such as an opposing cylindrical drum pressing against the web. Vacuum may also be applied to the web as it is pressed against the Yankee surface. Multiple Yankee dryer drums may be employed, whereby additional pressing is optionally incurred between the drums. The tissue paper structures which are formed are referred to hereinafter as conventional, pressed, tissue paper structures. Such sheets are considered to be compacted since the web is subjected to substantial mechanical compression forces while the fibers are moist and are then dried while in a compressed state.

Pattern densified tissue paper is characterized by having a relatively high bulk field of relatively low fiber density and an array of densified zones of relatively high fiber density. The high bulk field is alternatively characterized as a field of pillow regions. The densified zones are alternatively referred to as knuckle regions. The densified zones may be discretely spaced within the high bulk field or may be interconnected, either fully or partially, within the high bulk field. Preferred processes for making pattern densified tissue webs are disclosed in U.S. Patent No. 3,301,746, issued to Sanford and Sisson on January 31, 1967, U.S. Patent No. 3,974,025, issued to Peter G. Ayers on August 10, 1976, and U.S. Patent No. 4,191,609, issued to Paul D. Trokhan on March 4, 1980, and U.S. Patent 4,637,859, issued to Paul D. Trokhan on January 20, 1987; all of which are incorporated herein by reference.

In general, pattern densified webs are preferably prepared by depositing a papermaking furnish on a foraminous forming wire such as a Fourdrinier wire to form a wet web and then juxtaposing the web against an array of supports. The web is pressed against the array of supports, thereby resulting in densified zones in the web at the locations geographically corresponding to the points of contact between the array of supports and the wet web. The remainder of the web not compressed during this operation is referred to as the high bulk field. This high bulk field can be further dedensified by application of fluid



pressure, such as with a vacuum type device or a blow-through dryer. The web is dewatered, and optionally predried, in such a manner so as to substantially avoid compression of the high bulk field. This is preferably accomplished by fluid pressure, such as with a vacuum type device or blow-through dryer, or alternately by mechanically pressing the web against an array of supports wherein the high bulk field is not compressed. The operations of dewatering, optional predrying and formation of the densified zones may be integrated or partially integrated to reduce the total number of processing steps performed. Subsequent to formation of the densified zones, dewatering, and optional predrying, the web is dried to completion, preferably still avoiding mechanical pressing. Preferably, from about 8% to about 55% of the tissue paper surface comprises densified knuckles having a relative density of at least 125% of the density of the high bulk field.

The array of supports is preferably an imprinting carrier fabric having a patterned displacement of knuckles which operate as the array of supports which facilitate the formation of the densified zones upon application of pressure. The pattern of knuckles constitutes the array of supports previously referred to. Imprinting carrier fabrics are disclosed in U.S. Patent No. 3,301,746, Sanford and Sisson, issued January 31, 1967, U.S. Patent No. 3,821,068, Salvucci, Jr. et al., issued May 21, 1974, U.S. Patent No. 3,974,025, Ayers, issued August 10, 1976, U.S. Patent No. 3,573,164, Friedberg et al., issued March 30, 1971, U.S. Patent No. 3,473,576, Amneus, issued October 21, 1969, U.S. Patent No. 4,239,065, Trokhan, issued December 16, 1980, and U.S. Patent No. 4,528,239, Trokhan, issued July 9, 1985, all of which are incorporated herein by reference.

Preferably, the furnish is first formed into a wet web on a foraminous forming carrier, such as a Fourdrinier wire. The web is dewatered and transferred to an imprinting fabric. The furnish may alternately be initially deposited on a foraminous supporting carrier which also operates as an imprinting fabric. Once formed, the wet web is dewatered and, preferably, thermally predried to a selected fiber consistency of between about 40% and about 80%. Dewatering can be performed with suction boxes or other vacuum devices or with blow-through dryers. The knuckle imprint of the imprinting fabric is impressed in the web as discussed above, prior to drying the web to completion.



One method for accomplishing this is through application of mechanical pressure. This can be done, for example, by pressing a nip roll which supports the imprinting fabric against the face of a drying drum, such as a Yankee dryer, wherein the web is disposed between the nip roll and drying drum. Also, preferably, the web is molded against the imprinting fabric prior to completion of drying by application of fluid pressure with a vacuum device such as a suction box, or with a blow-through dryer. Fluid pressure may be applied to induce impression of densified zones during initial dewatering, in a separate, subsequent process stage, or a combination thereof.

Uncompacted, nonpattern-densified tissue paper structures are described in U.S. Patent No. 3,812,000 issued to Joseph L. Salvucci, Jr. and Peter N. Yiannos on May 21, 1974 and U.S. Patent No. 4,208,459, issued to Henry E. Becker, Albert L. McConnell, and Richard Schutte on June 17, 1980, both of which are incorporated herein by reference. In general, uncompacted, non pattern densified tissue paper structures are prepared by depositing a papermaking furnish on a foraminous forming wire such as a Fourdrinier wire to form a wet web, draining the web and removing additional water without mechanical compression until the web has a fiber consistency of at least 80%, and creping the web. Water is removed from the web by vacuum dewatering and thermal drying. The resulting structure is a soft but weak high bulk sheet of relatively uncompacted fibers. Bonding material is preferably applied to portions of the web prior to creping.

The tissue paper web of this invention can be used in any application where soft, absorbent tissue paper webs are required. Particularly advantageous uses of the tissue paper web of this invention are in paper towel, toilet tissue and facial tissue products. For example, two tissue paper webs of this invention can be embossed and adhesively secured together in face to face relation as taught by U.S. Pat. No. 3,414,459, which issued to Wells on December 3, 1968 and which is incorporated herein by reference, to form 2-ply paper towels.

Molecular Weight Determination

A. Introduction

The essential distinguishing characteristic of polymeric materials is their molecular size. The properties which have enabled polymers to



be used in a diversity of applications derive almost entirely from their macro-molecular nature. In order to characterize fully these materials it is essential to have some means of defining and determining their molecular weights and molecular weight distributions. It is more correct to use the term relative molecular mass rather the molecular weight, but the latter is used more generally in polymer technology. It is not always practical to determine molecular weight distributions. However, this is becoming more common practice using chromatographic techniques. Rather, recourse is made to expressing molecular size in terms of molecular weight averages.

B. Molecular weight averages

If we consider a simple molecular weight distribution which represents the weight fraction (w_i) of molecules having relative molecular mass (M_i), it is possible to define several useful average values. Averaging carried out on the basis of the number of molecules (N_i) of a particular size (M_i) gives the Number Average Molecular Weight

$$\bar{n} = \frac{\sum N_i M_i}{\sum N_i}$$

An important consequence of this definition is that the Number Average Molecular Weight in grams contains Avogadro's Number of molecules. This definition of molecular weight is consistent with that of monodisperse molecular species, i.e. molecules having the same molecular weight. Of more significance is the recognition that if the number of molecules in a given mass of a polydisperse polymer can be determined in some way then $\bar{n}$ can be calculated readily. This is the basis of colligative property measurements.

Averaging on the basis of the weight fractions (W_i) of molecules of a given mass (M_i) leads to the definition of Weight Average Molecular Weights

$$\bar{w} = \frac{\sum W_i N_i}{\sum W_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$



w is a more useful means for expressing polymer molecular weights than n since it reflects more accurately such properties as melt viscosity and mechanical properties of polymers and is therefor used in the present invention.

Analytical and Testing Procedures

Analysis of the amount of treatment chemicals used herein or retained on tissue paper webs can be performed by any method accepted in the applicable art.

A. Quantitative analysis for quaternary ammonium and polyhydroxy compounds

For example, the level of the quaternary ammonium compound, such as Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate (DHTDMAMS) retained by the tissue paper can be determined by solvent extraction of the DHTDMAMS by an organic solvent followed by an anionic/cationic titration using Dimidium Bromide as indicator; the level of the polyhydroxy compound, such as PEG-400, can be determined by extraction in an aqueous solvent such as water followed by gas chromatography or colorimetry techniques to determine the level of PEG-400 in the extract. These methods are exemplary, and are not meant to exclude other methods which may be useful for determining levels of particular components retained by the tissue paper.

B. Hydrophilicity (absorbency)

Hydrophilicity of tissue paper refers, in general, to the propensity of the tissue paper to be wetted with water. Hydrophilicity of tissue paper may be somewhat quantified by determining the period of time required for dry tissue paper to become completely wetted with water. This period of time is referred to as "wetting time". In order to provide a consistent and repeatable test for wetting time, the following procedure may be used for wetting time determinations: first, a conditioned sample unit sheet (the environmental conditions for testing of paper samples are $23 \pm 1^\circ\text{C}$ and $50 \pm 2\%$ R.H. as specified in TAPPI Method T 402), approximately $4\text{-}3/8$ inch x $4\text{-}3/4$ inch (about 11.1 cm x 12 cm) of tissue paper structure is provided; second, the sheet is folded into four (4) juxtaposed quarters, and then crumpled into a ball approximately 0.75 inches (about 1.9 cm) to about 1 inch (about 2.5



cm) in diameter; third, the balled sheet is placed on the surface of a body of distilled water at $23 \pm 1^\circ\text{C}$ and a timer is simultaneously started; fourth, the timer is stopped and read when wetting of the balled sheet is completed. Complete wetting is observed visually.

Hydrophilicity characters of tissue paper embodiments of the present invention may, of course, be determined immediately after manufacture. However, substantial increases in hydrophobicity may occur during the first two weeks after the tissue paper is made: i.e., after the paper has aged two (2) weeks following its manufacture. Thus, the wetting times are preferably measured at the end of such two week period. Accordingly, wetting times measured at the end of a two week aging period at room temperature are referred to as "two week wetting times."

C. Density

The density of tissue paper, as that term is used herein, is the average density calculated as the basis weight of that paper divided by the caliper, with the appropriate unit conversions incorporated therein. Caliper of the tissue paper, as used herein, is the thickness of the paper when subjected to a compressive load of 95 g/in^2 (15.5 g/cm^2).

Optional Ingredients

Other chemicals commonly used in papermaking can be added to the substantially waterless self-emulsifiable chemical softening composition described herein, or to the papermaking furnish so long as they do not significantly and adversely affect the softening, absorbency of the fibrous material, and enhancing actions of the chemical softening composition.

For example, surfactants may be used to treat the tissue paper webs of the present invention. The level of surfactant, if used, is preferably from about 0.01% to about 2.0% by weight, based on the dry fiber weight of the tissue paper. The surfactants preferably have alkyl chains with eight or more carbon atoms. Exemplary anionic surfactants are linear alkyl sulfonates, and alkylbenzene sulfonates. Exemplary nonionic surfactants are alkylglycosides including alkylglycoside esters such as Crodesta SL-40 which is available from Croda, Inc. (New York, NY); alkylglycoside ethers as described in U.S.



Patent 4,011,389, issued to W. K. Langdon, et al. on March 8, 1977; and alkylpolyethoxylated esters such as Pegosperse 200 ML available from Glyco Chemicals, Inc. (Greenwich, CT) and IGEPAL RC-520 available from Rhone Poulenc Corporation (Cranbury, N.J.).

Other types of chemicals which may be added, include dry strength additives to increase the tensile strength of the tissue webs. Examples of dry strength additives include carboxymethyl cellulose, and cationic polymers from the Acco chemical family such as Acco 711 and Acco 514, with the Acco chemical family being preferred. These materials are available commercially from the American Cyanamid Company of Wayne, New Jersey. The level of dry strength additive, if used, is preferably from about 0.01% to about 1.0%, by weight, based on the dry fiber weight of the tissue paper.

Other types of chemicals which may be added, include wet strength additives to increase the wet burst of the tissue webs. The present invention may contain as an optional component from about 0.01% to about 3.0%, more preferably from about 0.3% to about 1.5% by weight, on a dry fiber weight basis, of a water-soluble permanent wet strength resin.

Permanent wet strength resins useful herein can be of several types. Generally, those resins which have previously found and which will hereafter find utility in the papermaking art are useful herein. Numerous examples are shown in the aforementioned paper by Westfelt, incorporated herein by reference.

In the usual case, the wet strength resins are water-soluble, cationic materials. That is to say, the resins are water-soluble at the time they are added to the papermaking furnish. It is quite possible, and even to be expected, that subsequent events such as cross-linking will render the resins insoluble in water. Further, some resins are soluble only under specific conditions, such as over a limited pH range.

Wet strength resins are generally believed to undergo a cross-linking or other curing reactions after they have been deposited on, within, or among the papermaking fibers. Cross-linking or curing does not normally occur so long as substantial amounts of water are present.

Of particular utility are the various polyamide-epichlorohydrin resins. These materials are low molecular weight polymers provided with reactive functional groups such as amino, epoxy, and azetidinium



groups. The patent literature is replete with descriptions of processes for making such materials. U.S. Pat. No. 3,700,623, issued to Keim on October 24, 1972 and U.S. Pat. No. 3,772,076, issued to Keim on November 13, 1973 are examples of such patents and both are incorporated herein by reference.

Polyamide-epichlorohydrin resins sold under the trademarks Kymene® 557H and Kymene® 2064 by Hercules Incorporated of Wilmington, Delaware, are particularly useful in this invention. These resins are generally described in the aforementioned patents to Keim.

Base-activated polyamide-epichlorohydrin resins useful in the present invention are sold under the Santo Res trademark, such as Santo Res 31, by Monsanto Company of St. Louis, Missouri. These types of materials are generally described in U.S. Pat. Nos. 3,855,158 issued to Petrovich on December 17, 1974; 3,899,388 issued to Petrovich on August 12, 1975; 4,129,528 issued to Petrovich on December 12, 1978; 4,147,586 issued to Petrovich on April 3, 1979; and 4,222,921 issued to Van Eenam on September 16, 1980, all incorporated herein by reference.

Other water-soluble cationic resins useful herein are the polyacrylamide resins such as those sold under the Parex trademark, such as Parex 631NC, by American Cyanamid Company of Stamford, Connecticut. These materials are generally described in U.S. Pat. Nos. 3,556,932 issued to Coscia et al. on January 19, 1971; and 3,556,933 issued to Williams et al. on January 19, 1971, all incorporated herein by reference.

Other types of water-soluble resins useful in the present invention include acrylic emulsions and anionic styrene-butadiene latexes. Numerous examples of these types of resins are provided in U.S. Patent 3,844,880, Meisel, Jr. et al., issued October 29, 1974, incorporated herein by reference.

Still other water-soluble cationic resins finding utility in this invention are the urea formaldehyde and melamine formaldehyde resins. These polyfunctional, reactive polymers have molecular weights on the order of a few thousand. The more common functional groups include nitrogen containing groups such as amino groups and methylol groups attached to nitrogen.



Although less preferred, polyethylenimine type resins find utility in the present invention.

More complete descriptions of the aforementioned water-soluble resins, including their manufacture, can be found in TAPPI Monograph Series No. 29, *Wet Strength In Paper and Paperboard*, Technical Association of the Pulp and Paper Industry (New York; 1965), incorporated herein by reference. As used herein, the term "permanent wet strength resin" refers to a resin which allows the paper sheet, when placed in an aqueous medium, to keep a majority of its initial wet strength for a period of time greater than at least two minutes.

The above-mentioned wet strength additives typically result in paper products with permanent wet strength, i.e., paper which when placed in an aqueous medium retains a substantial portion of its initial wet strength over time. However, permanent wet strength in some types of paper products can be an unnecessary and undesirable property. Paper products such as toilet tissues, etc., are generally disposed of after brief periods of use into septic systems and the like. Clogging of these systems can result if the paper product permanently retains its hydrolysis-resistant strength properties. More recently, manufacturers have added temporary wet strength additives to paper products for which wet strength is sufficient for the intended use, but which then decays upon soaking in water. Decay of the wet strength facilitates flow of the paper product through septic systems.

Examples of suitable temporary wet strength resins include modified starch temporary wet strength agents, such as National Starch 78-0080, marketed by the National Starch and Chemical Corporation (New York, New York). This type of wet strength agent can be made by reacting dimethoxyethyl-N-methyl-chloroacetamide with cationic starch polymers. Modified starch temporary wet strength agents are also described in U.S. Pat. No. 4,675,394, Solarek, et al., issued June 23, 1987, and incorporated herein by reference. Preferred temporary wet strength resins include those described in U.S. Pat. No. 4,981,557, Bjorkquist, issued January 1, 1991, and incorporated herein by reference.

With respect to the classes and specific examples of both permanent and temporary wet strength resins listed above, it should be



understood that the resins listed are exemplary in nature and are not meant to limit the scope of this invention.

Mixtures of compatible wet strength resins can also be used in the practice of this invention.

The above listings of optional chemical additives is intended to be merely exemplary in nature, and are not meant to limit the scope of the invention.

The following examples illustrate the practice of the present invention but are not intended to be limiting thereof.

EXAMPLE 1

The purpose of this example is to illustrate a method that can be used to make-up a substantially waterless self-emulsifiable chemical softener composition comprising a mixture of Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate (DHTDMAMS) and Polyoxyethylene Glycol 400 (PEG-400).

A waterless self-emulsifiable chemical softener composition is prepared according to the following procedure : 1. An equivalent weight of DHTDMAMS and PEG-400 is weighed separately; 2. PEG is heated up to about 66°C (150°F); 3. DHTDMAMS is dissolved in the PEG to form a melted solution at 66°C (150°F); 4. Adequate mixing is provided to form a homogenous mixture of DHTDMAMS in PEG; 5. The homogenous mixture of (4) is cooled down to a solid form at room temperature.

The substantially waterless self-emulsifiable chemical softener composition of (5) can be pre-mixed (steps 1-5 above) at the chemical supplier (e.g. Sherex company of Dublin, Ohio) and then economically shipped to the ultimate users of the chemical softening composition where it can then be diluted to the desired concentration.

EXAMPLE 2

The purpose of this example is to illustrate a method that can be used to make-up a substantially waterless self-emulsifiable chemical



softener composition which comprises a mixture of Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate (DHTDMAMS) and a mixture of Glycerol and PEG-400.

A substantially waterless self-emulsifiable chemical softener composition is prepared according to the following procedure : 1. A mixture of Glycerol and PEG-400 is blended at 75 : 25 by weight ratio; 2. Equivalent weights of DHTDMAMS and the mixture of (1) are weighted separately; 3. The mixture of (1) is heated up to about 66°C (150°F); 4. DHTDMAMS is dissolved in (3) to form a melted solution at 66°C (150°F); 5. Adequate mixing is provided to form a homogenous mixture of DHTDMAMS in (3); 6. The homogenous mixture of (5) is cooled down to a solid form at room temperature.

The substantially waterless self-emulsifiable chemical softener composition of (6) can be pre-mixed (steps 1-6 above) at the chemical supplier (e.g. Sherex company of Dublin, Ohio) and then economically shipped to the ultimate users of the chemical softening composition where it can then be diluted to the desired concentration.

EXAMPLE 3

The purpose of this example is to illustrate a method using a blow through drying papermaking technique to make soft and absorbent paper towel sheets treated with a substantially waterless self-emulsifiable chemical softener composition comprising a premix of Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate (DHTDMAMS) and a Polyoxyethylene Glycol 400 (PEG-400) in solid state, and a permanent wet strength resin .

A pilot scale Fourdrinier papermaking machine is used in the practice of the present invention. First, the substantially waterless self-emulsifiable chemical softener composition is prepared according to the procedure in Example 1 wherein the homogenous pre-mixed of DHTDMAMS and PEG-400 in solid state is dispersed in a conditioned water tank (Temperature ~ 66°C) to form a sub-micron vesicle dispersion. The particle size of the vesicle dispersion is determined using an optical microscopic technique. The particle size range is from about 0.1 to 1.0 micron. Figure 3 illustrates a cryo-transmission micro-



photograph taken at X 63,000 of a vesicle dispersion of a 1 : 1 by weight ratio of a DHTDMAMS and PEG-400 system. Figure 3 indicates that the particles have membranes one or two bilayers thick, whose geometry ranges from closed/open vesicles; to disc-like structures and sheets.

Second, a 3% by weight aqueous slurry of NSK is made up in a conventional re-pulper. The NSK slurry is refined gently and a 2% solution of a permanent wet strength resin (i.e. Kymene[®] 557H marketed by Hercules Incorporated of Wilmington, DE) is added to the NSK stock pipe at a rate of 1% by weight of the dry fibers. The adsorption of Kymene[®] 557H to NSK is enhanced by an in-line mixer. A 1% solution of Carboxy Methyl Cellulose (CMC) is added after the in-line mixer at a rate of 0.2% by weight of the dry fibers to enhance the dry strength of the fibrous substrate. The adsorption of CMC to NSK can be enhanced by an in-line mixer. Then, a 1% solution of the chemical softener mixture (DHTDMAMS/ PEG) is added to the NSK slurry at a rate of 0.1% by weight of the dry fibers. The adsorption of the chemical softener mixture to NSK can also be enhanced via an in-line mixer. The NSK slurry is diluted to 0.2% by the fan pump.

Third, a 3% by weight aqueous slurry of CTMP is made up in a conventional re-pulper. A non-ionic surfactant (Pegospense) is added to the re-pulper at a rate of 0.2% by weight of dry fibers. A 1% solution of the chemical softener mixture is added to the CTMP stock pipe before the stock pump at a rate of 0.1% by weight of the dry fibers. The adsorption of the chemical softener mixture to CTMP can be enhanced by an in-line mixer. The CTMP slurry is diluted to 0.2% by the fan pump. The treated furnish mixture (NSK / CTMP) is blended in the head box and deposited onto a Fourdrinier wire to form an embryonic web. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and vacuum boxes. The Fourdrinier wire is of a 5-shed, satin weave configuration having 84 machine-direction and 76 cross-machine-direction monofilaments per inch, respectively. The embryonic wet web is transferred from the Fourdrinier wire, at a fiber consistency of about 22% at the point of transfer, to a photo-polymer fabric having 240 linear Idaho cells per square inch, 34 percent knuckle areas and 14 mils of photo-polymer depth. The name "linear Idaho" is based on the fact that the cross-section of conduits from which this



pattern was derived, originally resembled the shape of a potato. The walls of the conduits on four sides, however, are formed by generally straight lines, thus the pattern is referred to as being a "linear" Idaho rather than simply as an Idaho pattern. Further de-watering is accomplished by vacuum assisted drainage until the web has a fiber consistency of about 28%. The patterned web is pre-dried by air blow-through to a fiber consistency of about 65% by weight. The web is then adhered to the surface of a Yankee dryer with a sprayed creping adhesive comprising 0.25% aqueous solution of Polyvinyl Alcohol (PVA). The fiber consistency is increased to an estimated 96% before the dry creping the web with a doctor blade. The doctor blade has a bevel angle of about 25 degrees and is positioned with respect to the Yankee dryer to provide an impact angle of about 81 degrees; the Yankee dryer is operated at about 800 fpm (feet per minute) (about 244 meters per minute). The dry web is formed into roll at a speed of 700 fpm (214 meters per minutes).

Two plies of the web are formed into paper towel products by embossing and laminating them together using PVA adhesive. The paper towel has about 26 #/3M Sq Ft basis weight, contains about 0.2% of the substantially waterless self-emulsifiable chemical softener mixture and about 1.0% of the permanent wet strength resin. The resulting paper towel is soft, absorbent, and very strong when wetted.

EXAMPLE 4

The purpose of this example is to illustrate a method using a blow through drying and layered papermaking techniques to make soft and absorbent toilet tissue paper treated with a substantially waterless self-emulsifiable chemical softener composition comprising a premix of Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate (DHTDMAMS) and a Polyoxyethylene Glycol 400 (PEG-400) in liquid state and a temporary wet strength resin.

A pilot scale Fourdrinier papermaking machine is used in the practice of the present invention. First, the substantially waterless self-emulsifiable chemical softener composition is prepared according to the procedure in Example 1 wherein the homogenous premix of DHTDMAMS and polyhydroxy compounds in solid state is re-melted at a



temperature of about 66°C (150°F). The melted mixture is then dispersed in a conditioned water tank (Temperature ~ 66°C) to form a sub-micron vesicle dispersion. The particle size of the vesicle dispersion is determined using an optical microscopic technique. The particle size range is from about 0.1 to 1.0 micron. Figure 4 illustrates a cryo-transmission micro-photograph taken at X 63,000 of a vesicle dispersion of a 1 : 1 by weight ratio of a DHTDMAMS and polyhydroxy compounds system. Figure 4 indicates that the particles have membranes one or two bilayers thick, whose geometry ranges from closed/open vesicles, to disc-like structures and sheets.

Second, a 3% by weight aqueous slurry of NSK is made up in a conventional re-pulper. The NSK slurry is refined gently and a 2% solution of the temporary wet strength resin (i.e. National starch 78-0080 marketed by National Starch and Chemical corporation of New-York, NY) is added to the NSK stock pipe at a rate of 0.75% by weight of the dry fibers. The adsorption of the temporary wet strength resin onto NSK fibers is enhanced by an in-line mixer. The NSK slurry is diluted to about 0.2% consistency at the fan pump. Third, a 3% by weight aqueous slurry of Eucalyptus fibers is made up in a conventional re-pulper. A 1% solution of the chemical softener mixture is added to the Eucalyptus stock pipe before the stock pump at a rate of 0.2% by weight of the dry fibers. The adsorption of the substantially waterless self-emulsifiable chemical softener mixture to Eucalyptus fibers can be enhanced by an in-line mixer. The Eucalyptus slurry is diluted to about 0.2% consistency at the fan pump.

The treated furnish mixture (30% of NSK / 70% of Eucalyptus) is blended in the head box and deposited onto a Fourdrinier wire to form an embryonic web. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and vacuum boxes. The Fourdrinier wire is of a 5-shed, satin weave configuration having 84 machine-direction and 76 cross-machine-direction monofilaments per inch, respectively. The embryonic wet web is transferred from the photo-polymer wire, at a fiber consistency of about 15% at the point of transfer, to a photo-polymer fabric having 562 Linear Idaho cells per square inch, 40 percent knuckle area and 9 mils of photo-polymer depth. Further dewatering is accomplished by vacuum assisted drainage until the web has a fiber consistency of about 28%. The patterned web is pre-dried



by air blow-through to a fiber consistency of about 65% by weight. The web is then adhered to the surface of a Yankee dryer with a sprayed creping adhesive comprising 0.25% aqueous solution of Polyvinyl Alcohol (PVA). The fiber consistency is increased to an estimated 96% before the dry creping the web with a doctor blade. The doctor blade has a bevel angle of about 25 degrees and is positioned with respect to the Yankee dryer to provide an impact angle of about 81 degrees; the Yankee dryer is operated at about 800 fpm (feet per minute) (about 244 meters per minute). The dry web is formed into roll at a speed of 700 fpm (214 meters per minutes).

The web is converted into a one ply tissue paper product. The tissue paper has about 18 #/3M Sq Ft basis weight, contains about 0.1% of the chemical softener mixture and about 0.2% of the temporary wet strength resin. Importantly, the resulting tissue paper is soft, absorbent and is suitable for use as facial and/or toilet tissues.

EXAMPLE 5

The purpose of this example is to illustrate a method using a blow through drying papermaking technique to make soft and absorbent toilet tissue paper treated with a substantially waterless self-emulsifiable chemical softener composition comprising a premix of Di(Hydrogenated)Tallow DiMethyl Ammonium Chloride (DHTDMAC) and a mixture of polyhydroxy compound (Glycerol / PEG-400) in liquid state and a dry strength additive resin.

A pilot scale Fourdrinier papermaking machine is used in the practice of the present invention. First, the substantially waterless self-emulsifiable chemical softener composition is prepared according to the procedure in Example 2 wherein the homogenous premix of DHTDMAC and polyhydroxy compounds in solid state is re-melted at a temperature of about 66°C (150°F). The melted mixture is then dispersed in a conditioned water tank (Temperature ~ 66°C) to form a sub-micron vesicle dispersion. The particle size of the vesicle dispersion is determined using an optical microscopic technique. The particle size range is from about 0.1 to 1.0 micron. Figure 5 illustrates a cryo-transmission micro-photograph taken at X 63,000 of a vesicle dispersion of a 1 : 1 by weight ratio of a DHTDMAC and polyhydroxy



compounds system. Figure 5 indicates that the particles have membranes one or two bilayers thick, whose geometry ranges from closed/open vesicles, to disc-like structures and sheets.

Second, a 3% by weight aqueous slurry of NSK is made up in a conventional re-pulper. The NSK slurry is refined gently and a 2% solution of the dry strength resin (i.e. Acco 514, Acco 711 marketed by American Cyanamid company of Fairfield, OH) is added to the NSK stock pipe at a rate of 0.2% by weight of the dry fibers. The adsorption of the dry strength resin onto NSK fibers is enhanced by an in-line mixer. The NSK slurry is diluted to about 0.2% consistency at the fan pump. Third, a 3% by weight aqueous slurry of Eucalyptus fibers is made up in a conventional re-pulper. A 1% solution of the chemical softener mixture is added to the Eucalyptus stock pipe before the stock pump at a rate of 0.2% by weight of the dry fibers. The adsorption of the substantially waterless self-emulsifiable chemical softener mixture to Eucalyptus fibers can be enhanced by an in-line mixer. The Eucalyptus slurry is diluted to about 0.2% consistency at the fan pump.

The treated furnish mixture (30% of NSK / 70% of Eucalyptus) is blended in the head box and deposited onto a Fourdrinier wire to form an embryonic web. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and vacuum boxes. The Fourdrinier wire is of a 5-shed, satin weave configuration having 84 machine-direction and 76 cross-machine-direction monofilaments per inch, respectively. The embryonic wet web is transferred from the photo-polymer wire, at a fiber consistency of about 15% at the point of transfer, to a photo-polymer fabric having 562 Linear Idaho cells per square inch, 40 percent knuckle area and 9 mils of photo-polymer depth. Further dewatering is accomplished by vacuum assisted drainage until the web has a fiber consistency of about 28%. The patterned web is pre-dried by air blow-through to a fiber consistency of about 65% by weight. The web is then adhered to the surface of a Yankee dryer with a sprayed creping adhesive comprising 0.25% aqueous solution of Polyvinyl Alcohol (PVA). The fiber consistency is increased to an estimated 96% before the dry creping the web with a doctor blade. The doctor blade has a bevel angle of about 25 degrees and is positioned with respect to the Yankee dryer to provide an impact angle



of about 81 degrees; the Yankee dryer is operated at about 800 fpm (feet per minute) (about 244 meters per minute). The dry web is formed into roll at a speed of 700 fpm (214 meters per minutes).

Two plies of the web are formed into tissue paper products and laminating them together using ply bonded technique. The tissue paper has about 23 #/3M Sq Ft basis weight, contains about 0.1% of the substantially waterless self-emulsifiable chemical softener mixture and about 0.1% of the dry strength resin. Importantly, the resulting tissue paper is soft, absorbent and is suitable for use as facial and/or toilet tissues.

EXAMPLE 6

The purpose of this example is to illustrate a method using a conventional drying papermaking technique to make soft and absorbent toilet tissue paper treated with a substantially waterless self-emulsifiable chemical softener composition comprising a premix of Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate (DHTDMAMS) and a Polyoxyethylene Glycol 400 (PEG-400) in solid state and a dry strength additive resin .

A pilot scale Fourdrinier papermaking machine is used in the practice of the present invention. First, the substantially waterless self-emulsifiable chemical softener composition is prepared according to the procedure in Example 1 wherein the homogenous premix of DHTDMAMS and PEG-400 in solid state is dispersed in a conditioned water tank (Temperature ~ 66°C) to form a sub-micron vesicle dispersion. The particle size of the vesicle dispersion is determined using an optical microscopic technique. The particle size range is from about 0.1 to 1.0 micron. Figure 3 illustrates a cryo-transmission microphotograph taken at X 63,000 of a vesicle dispersion of a 1 : 1 by weight ratio of a DHTDMAMS and PEG-400 system. Figure 3 indicates that the particles have membranes one or two bilayers thick, whose geometry ranges from closed/open vesicles, to disc-like structures and sheets.

Second, a 3% by weight aqueous slurry of NSK is made up in a conventional re-pulper. The NSK slurry is refined gently and a 2% solution of the dry strength resin (i.e. Acco 514, Acco 711 marketed by



American Cyanamid company of Wayne, New Jersey) is added to the NSK stock pipe at a rate of 0.2% by weight of the dry fibers. The adsorption of the dry strength resin onto NSK fibers is enhanced by an in-line mixer. The NSK slurry is diluted to about 0.2% consistency at the fan pump. Third, a 3% by weight aqueous slurry of Eucalyptus fibers is made up in a conventional re-pulper. A 1% solution of the chemical softener mixture is added to the Eucalyptus stock pipe before the stock pump at a rate of 0.2% by weight of the dry fibers. The adsorption of the chemical softener mixture to Eucalyptus fibers can be enhanced by an in-line mixer. The Eucalyptus slurry is diluted to about 0.2% consistency at the fan pump.

The treated furnish mixture (30% of NSK / 70% of Eucalyptus) is blended in the head box and deposited onto a Fourdrinier wire to form an embryonic web. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and vacuum boxes. The Fourdrinier wire is of a 5-shed, satin weave configuration having 84 machine-direction and 76 cross-machine-direction monofilaments per inch, respectively. The embryonic wet web is transferred from the Fourdrinier wire, at a fiber consistency of about 15% at the point of transfer, to a conventional felt. Further de-watering is accomplished by vacuum assisted drainage until the web has a fiber consistency of about 35%. The web is then adhered to the surface of a Yankee dryer. The fiber consistency is increased to an estimated 96% before the dry creping the web with a doctor blade. The doctor blade has a bevel angle of about 25 degrees and is positioned with respect to the Yankee dryer to provide an impact angle of about 81 degrees; the Yankee dryer is operated at about 800 fpm (feet per minute) (about 244 meters per minute). The dry web is formed into roll at a speed of 700 fpm (214 meters per minutes).

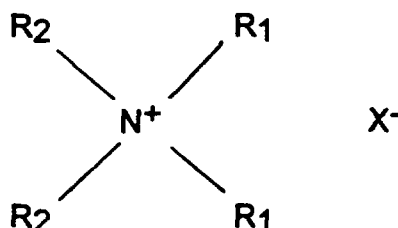
Two plies of the web are formed into tissue paper products and laminating them together using ply bonded technique. The tissue paper has about 23 #/3M Sq. Ft. basis weight, contains about 0.1% of the substantially waterless self-emulsifiable chemical softener mixture and about 0.1% of the dry strength resin. Importantly, the resulting tissue paper is soft, absorbent and is suitable for use as a facial and/or toilet tissues.



What is claimed is:

1. A substantially waterless self-emulsifiable chemical softening composition characterized in that it comprises a mixture of:

(a) a quaternary ammonium compound having the formula



wherein each R₂ substituent is a C1 - C6 alkyl or hydroxyalkyl group, or mixture thereof, preferably C1 - C3 alkyl, most preferably methyl; each R₁ substituent is a C14 - C22 hydrocarbonyl group, or mixture thereof, preferably C16 - C18 alkyl; and X⁻ is a suitable anion, preferably chloride or methyl sulfate; and

- (b) a polyhydroxy compound selected from glycerol, polyglycerols having a weight average molecular weight of from 150 to 800 and polyoxyethylene glycols and polyoxypropylene glycols having a weight average molecular weight from 200 to 4000, preferably from 200 to 1000, most preferably from 200 to 600;

wherein the weight ratio of the quaternary ammonium compound to the polyhydroxy compound ranges from 1 : 0.1 to 0.1 : 1, preferably from 1:0.3 to 3:1, most preferably from 1:0.7 to 0.7:1, wherein said polyhydroxy compound is mixed with said quaternary ammonium compound at a temperature wherein said quaternary ammonium compound and said polyhydroxy compound are miscible, and wherein the moisture content of said chemical softening composition is less than 20 % by weight.

2. The substantially waterless self-emulsifiable chemical softening composition of Claim 1 wherein the chemical softening composition is a stable, homogenous, solid or viscous fluid at a temperature of greater than 20°C.





3. The substantially waterless self-emulsifiable chemical softening composition of Claim 1 or 2 wherein the quaternary ammonium compound is di(hydrogenated)tallow dimethyl ammonium chloride or di(hydrogenated)tallow dimethyl ammonium methyl sulfate.
4. The substantially waterless self-emulsifiable chemical softening composition of any of Claims 1 - 3 wherein the quaternary ammonium compound is mixed with the polyhydroxy compound at a temperature of at least 40°C, preferably from 56°C to 68°C.
5. The substantially waterless self-emulsifiable chemical softening composition of any of Claims 1 - 4 wherein said quaternary ammonium compound is in a liquid-crystal state or in a liquid state when mixed with said polyhydroxy compound.
6. An aqueous dispersion comprising the substantially waterless self-emulsifiable chemical softening composition of any of Claims 1 - 5 and an aqueous media wherein said homogenous mixture of said quaternary ammonium compound and said polyhydroxy compounds self-disperses in said aqueous media to form a sub-micron vesicle dispersion.
7. The aqueous dispersion of Claim 6 wherein the temperature of the aqueous media is at least 20°C.
8. The aqueous dispersion of Claim 6 or 7 wherein said homogenous mixture of quaternary ammonium and polyhydroxy compounds is in a solid state before being dispersed in said aqueous media.
9. The aqueous dispersion of Claim 6 or 7 wherein said homogenous mixture of quaternary ammonium and polyhydroxy compounds is in a liquid state before being dispersed in said aqueous media.
10. The substantially waterless self-emulsifiable chemical softening composition of any of Claims 1 - 5 wherein the moisture content of said chemical softening is less than 10 % by weight.





1/4

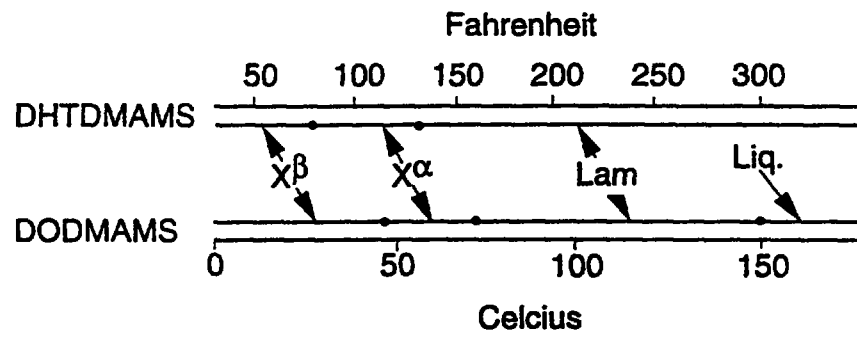


Fig. 1

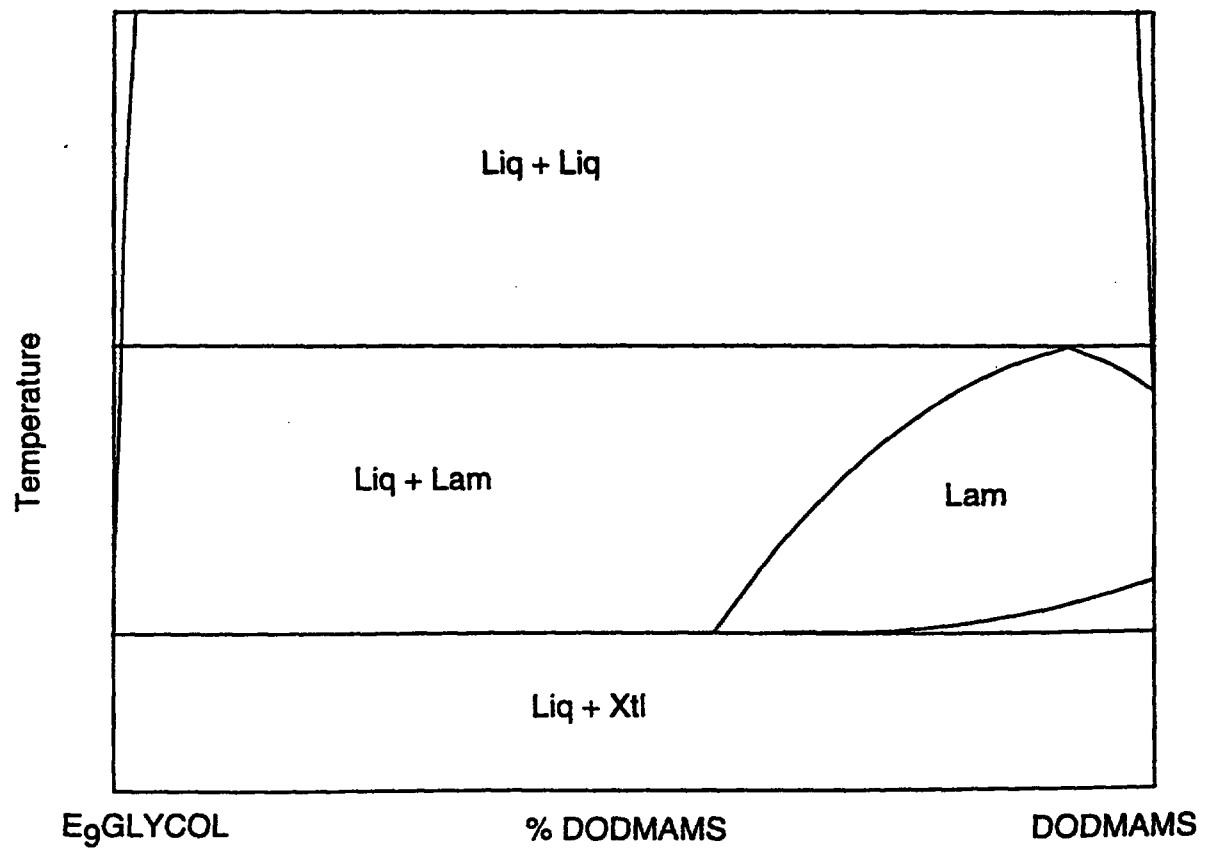


Fig. 2



THIS SHEET HAS BEEN
REPLACED

2/4

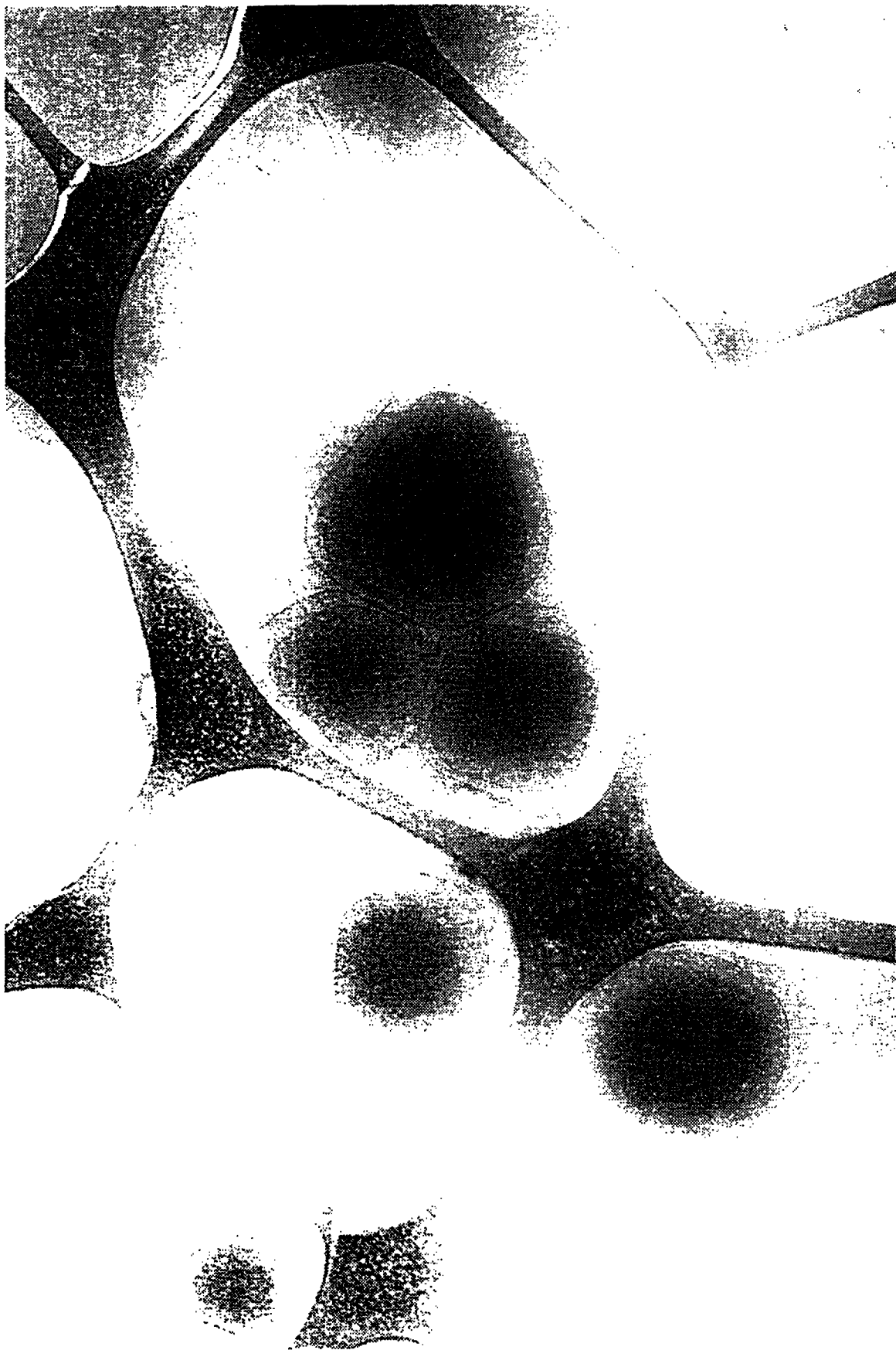


Fig. 3

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

3/4

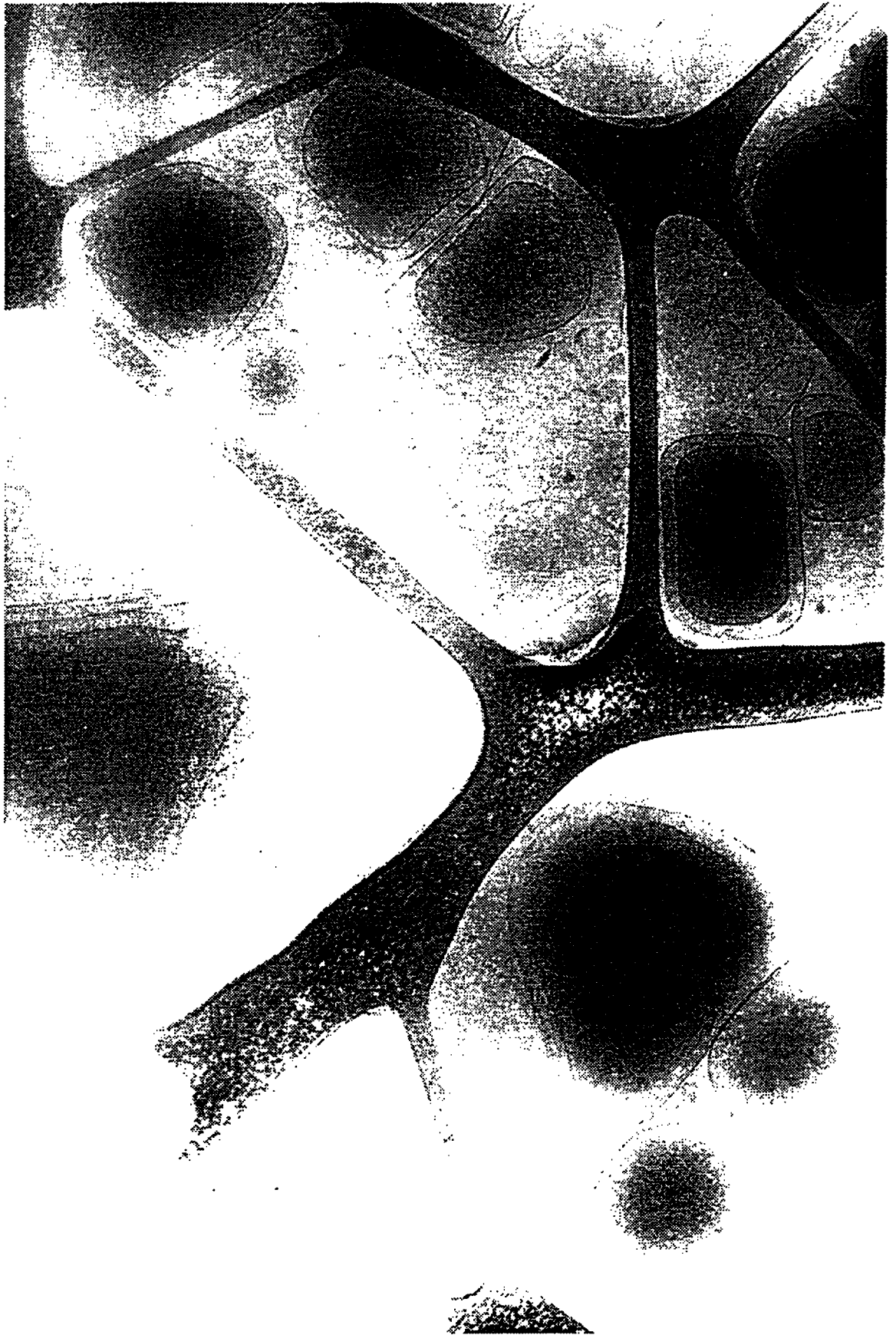


Fig. 4

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

4/4



Fig. 5



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : D21H 17/06, 17/07, 21/24	A1	(11) International Publication Number: WO 94/29520 (43) International Publication Date: 22 December 1994 (22.12.94)
(21) International Application Number: PCT/US94/05777 (22) International Filing Date: 23 May 1994 (23.05.94) (30) Priority Data: 08/072,299 3 June 1993 (03.06.93) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: LAUGHLIN, Robert, Gene; 11641 Bank Road, Cincinnati, OH 45251 (US). PHAN, Dean, Van; 6512 Tylers Crossing, West Chester, OH 45069 (US). TROKHAN, Paul, Dennis; 1356 Warvel Road, Hamilton, OH 45013 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45202 (US).		(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.

(54) Title: WATERLESS SELF-EMULSIFIABLE CHEMICAL SOFTENING COMPOSITION USEFUL IN FIBROUS CELLULOSIC MATERIALS

(57) Abstract

Substantially waterless self-emulsifiable chemical softening compositions are provided comprising a mixture of a quaternary ammonium compound and a polyhydroxy compound. Preferred quaternary ammonium compounds include dialkyl dimethyl ammonium salts such as di(hydrogenated)tallow dimethyl ammonium chloride, di(hydrogenated)tallow dimethyl ammonium methyl sulfate. Preferred polyhydroxy compounds are selected from the group consisting of glycerol, polyglycerols having a weight average molecular weight of from about 150 to about 800 and polyoxyethylene glycols and polyoxypropylene glycols having a weight average molecular weight from about 200 to 4,000. The substantially waterless self-emulsifiable chemical softening compositions are prepared by mixing the quaternary ammonium compound with the polyhydroxy compound at a specific temperature range wherein the polyhydroxy compound is miscible with the quaternary ammonium compound. The resulting stable solid or concentrated fluid mixture can then be economically shipped to the consumer or ultimate user. The ultimate users of the chemical softening composition simply dilute the mixture with a liquid carrier (e.g., water) to form an aqueous dispersion suitable for treating fibrous cellulosic materials. The substantially waterless self-emulsifiable chemical softening compositions disclosed herein are primarily intended for softening disposable paper products such as tissues and towels.

This Sheet Has Been Replaced



26 AUG 1996

**WATERLESS SELF-EMULSIFIABLE CHEMICAL
SOFTENING COMPOSITION USEFUL IN FIBROUS
CELLULOSIC MATERIALS**

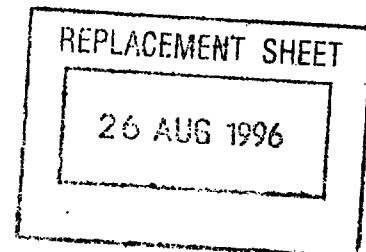
FIELD OF THE INVENTION

This invention relates to a substantially waterless self-emulsifiable chemical softener composition. More particularly, it relates to substantially waterless self-emulsifiable chemical softener compositions useful for treating fibrous cellulose materials, such as tissue paper webs. The treated tissue webs can be used to make soft, absorbent paper products such as toweling, napkin, facial tissue, and toilet tissue products.

BACKGROUND OF THE INVENTION

Paper webs or sheets, sometimes called tissue or paper tissue webs or sheets, find extensive use in modern society. Such items as paper towels, napkins, facial and toilet tissues are staple items of commerce. It has long been recognized that three important physical attributes of these products are their softness; their absorbency, particularly their absorbency for aqueous systems; and their strength, particularly their strength when wet. Research and development efforts have been directed to the improvement of each of these attributes without seriously affecting the others as well as to the improvement of two or three attributes simultaneously.

Softness is the tactile sensation perceived by the consumer as he/she holds a particular product, rubs it across his/her skin, or crumples it within his/her hand. This tactile sensation is provided by a combination of several physical properties. One of the most important



physical properties related to softness is generally considered by those skilled in the art to be the stiffness of the paper web from which the product is made. Stiffness, in turn, is usually considered to be directly dependent on the dry tensile strength of the web and the stiffness of the fibers which make up the web.

Strength is the ability of the product, and its constituent webs, to maintain physical integrity and to resist tearing, bursting, and shredding under use conditions, particularly when wet.

Absorbency is the measure of the ability of a product, and its constituent webs, to absorb quantities of liquid, particularly aqueous solutions or dispersions. Overall absorbency as perceived by the consumer is generally considered to be a combination of the total quantity of liquid a given mass of tissue paper will absorb at saturation as well as the rate at which the mass absorbs the liquid.

The use of wet strength resins to enhance the strength of a paper web is widely known. For example, Westfelt described a number of such materials and discussed their chemistry in *Cellulose Chemistry and Technology*, Volume 13, at pages 813-825 (1979). Freimark et al. in U.S. Pat. No. 3,755,220 issued August 28, 1973 mention that certain chemical additives known as debonding agents interfere with the natural fiber-to-fiber bonding that occurs during sheet formation in papermaking processes. This reduction in bonding leads to a softer, or less harsh, sheet of paper. Freimark et al. go on to teach the use of wet strength resins in conjunction with the use of debonding agents to offset the undesirable effects of the debonding agents. These debonding agents do reduce both dry tensile strength and wet tensile strength.

Shaw, in U.S. Pat. No. 3,821,068, issued June 28, 1974, also teaches that chemical debonders can be used to reduce the stiffness, and thus enhance the softness, of a tissue paper web.

Chemical debonding agents have been disclosed in various references such as U.S. Pat. No. 3,554,862, issued to Hervey et al. on January 12, 1971. These materials include quaternary ammonium salts such as cocotrimethylammonium chloride, oleyltrimethylammonium chloride, di(hydrogenated)tallow dimethyl ammonium chloride and stearyltrimethyl ammonium chloride.

Emanuelsson et al., in U.S. Pat. No. 4,144,122, issued March 13, 1979, teach the use of complex quaternary ammonium compounds

26 AUG 1976

such as bis(alkoxy(2-hydroxy)propylene) quaternary ammonium chlorides to soften webs. These authors also attempt to overcome any decrease in absorbency caused by the debonders through the use of nonionic surfactants such as ethylene oxide and propylene oxide adducts of fatty alcohols.

Armak Company, of Chicago, Illinois, in their bulletin 76-17 (1977) disclose the use of dimethyl di(hydrogenated)tallow ammonium chloride in combination with fatty acid esters of polyoxyethylene glycols to impart both softness and absorbency to tissue paper webs.

One exemplary result of research directed toward improved paper webs is described in U.S. Pat. No. 3,301,746, issued to Sanford and Sisson on January 31, 1967. Despite the high quality of paper webs made by the process described in this patent, and despite the commercial success of products formed from these webs, research efforts directed to finding improved products have continued.

For example, Becker et al. in U.S. Pat. No. 4,158,594, issued January 19, 1979, describe a method they contend will form a strong, soft, fibrous sheet. More specifically, they teach that the strength of a tissue paper web (which may have been softened by the addition of chemical debonding agents) can be enhanced by adhering, during processing, one surface of the web to a creping surface in a fine patterned arrangement by a bonding material (such as an acrylic latex rubber emulsion, a water soluble resin, or an elastomeric bonding material) which has been adhered to one surface of the web and to the creping surface in the fine patterned arrangement, and creping the web from the creping surface to form a sheet material.

Conventional quaternary ammonium compounds such as the well known dialkyl dimethyl ammonium salts (e.g. ditallow dimethyl ammonium chloride, ditallow dimethyl ammonium methyl sulfate, di(hydrogenated)tallow dimethyl ammonium chloride etc ...) are effective chemical debonding agents. Unfortunately, these quaternary ammonium compounds are not hydrophilic. Applicants have discovered that the chemical softening compositions of the present invention enhance both softness and absorbency rate of fibrous cellulose materials.

Furthermore, providing chemical softening compositions containing these softener compounds in substantially waterless forms,

26 AUG 1996

results in cost saving on shipping the product (less weight), cost savings on packaging material, and cost savings on machinery required for processing the chemical softening compositions (less equipment needed to make-up the aqueous dispersions). In addition, the present invention also provides environmental safety advantages because of the elimination of the organic solvents, especially volatile organic solvents typically used in the preparation of concentrated softening compositions.

It is an object of this invention to provide a substantially waterless self-emulsifiable chemical softening composition useful for treating fibrous cellulose materials.

It is a further object of this invention to provide soft, absorbent tissue paper products.

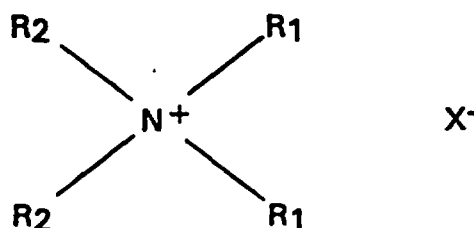
It is also a further object of this invention to provide a process for making soft, absorbent tissue paper products.

These and other objects are obtained using the present invention, as will become readily apparent from a reading of the following disclosure.

SUMMARY OF THE INVENTION

The present invention provides a substantially waterless self-emulsifiable chemical softening composition useful for treating fibrous cellulose materials. Briefly, the waterless self-emulsifiable chemical softening composition comprises a mixture of :

- (a) a quaternary ammonium compound having the formula



26 AUG 1996

wherein each R₂ substituent is a C₁ - C₆ alkyl or hydroxyalkyl group, or mixture thereof; each R₁ substituent is a C₁₄ - C₂₂ hydrocarbyl group, or mixture thereof; and X⁻ is a suitable anion; and

- (b) a polyhydroxy compound selected from the group consisting of glycerol, polyglycerols having a weight average molecular weight of from about 150 to about 800 and polyoxyethylene glycols and polyoxypropylene glycols having a weight average molecular weight from about 200 to 4000;

wherein the weight ratio of the quaternary ammonium compound to the polyhydroxy compound ranges from about 1 : 0.1 to 0.1 : 1; and wherein said polyhydroxy compound is miscible with the quaternary ammonium compound at a temperature of at least 40°C . The chemical softening composition of the present invention is a stable, homogenous, solid or viscous fluid at a temperature greater than or about 20°C . The fluid may have either a liquid or a liquid crystal phase structure. The moisture content of the substantially self-emulsifiable chemical softening composition is less than about 20 % by weight, preferably the moisture content of the chemical softening composition is less than about 10 % by weight and more preferably the moisture content of the chemical softening composition is less than 5 % by weight.

Examples of quaternary ammonium compounds suitable for use in the present invention include the well-known dialkyldimethylammonium salts such as DiTallow DiMethyl Ammonium Chloride (DTDMAC), DiTallow DiMethyl Ammonium Methyl Sulfate (DTDMAMS), Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate (DHTDMAMS), Di(Hydrogenated)Tallow DiMethyl Ammonium Chloride (DHTDMAC).

Examples of polyhydroxy compounds useful in the present invention include glycerol, polyglycerols having a weight average molecular weight of from about 150 to about 800 and polyoxyethylene glycols having a weight average molecular weight of from about 200 to about 4000, with polyoxyethylene glycols having a weight average molecular weight of from about 200 to about 600 being preferred.

20 AUG 1996

Briefly, the process for making the tissue webs of the present invention comprises the steps of formation of a papermaking furnish from the aforementioned components, deposition of the papermaking furnish onto a foraminous surface such as a Fourdrinier wire, and removal of the water from the deposited furnish.

All percentages, ratios and proportions herein are by weight unless otherwise specified.

BRIEF DESCRIPTION OF THE DRAWINGS

While the Specification concludes with claims particularly pointing out and distinctly claiming the present invention, it is believed the invention is better understood from the following description taken in conjunction with the associated drawings, in which :

Figure 1 are the phase diagrams of DiOctadecyl DiMethyl Ammonium Methyl Sulfate (DODMAMS) and of DHTDMAMS.

Figure 2 is a phase diagram of the DODMAMS / PEG-400 system.

Figure 3 is a cryo-transmission photo-micrograph taken at X 63,000 of the 2% dispersion formed by diluting a solid premix of a 1 : 1 by weight ratio of a DHTDMAMS and PEG-400 system.

Figure 4 is a cryo-transmission photo-micrograph taken at X 63,000 of the 2% dispersion formed by diluting a liquid premix of a 1 : 1 by weight ratio of a DHTDMAMS and PEG-400 system.

Figure 5 is a cryo-transmission photo-micrograph taken at X 63,000 of the 2% dispersion formed by diluting a liquid premix of a 1 : 1 by weight ratio of a DHTDMAC and a mixture of glycerol and PEG-400 system.

The present invention is described in more detail below.

DETAILED DESCRIPTION OF THE INVENTION

While this specification concludes with claims particularly pointing out and distinctly claiming the subject matter regarded as the invention, it is believed that the invention can be better understood from a reading of the following detailed description and of the appended examples.

28 AUG 1996

As used herein, the term "viscous fluid" refers to a fluid having a viscosity greater than or equal to 10,000 centipoise at 20°C.

As used herein, the term "homogenous mixture" refers to compositions wherein the quaternary ammonium and polyhydroxy compounds are dissolved or dispersed in each other.

As used herein, the term "self-emulsifiable" refers to compositions that will form a uniform colloidal dispersion with a minimum of shear, heat, dispersing aids, etc. ... when added to a liquid carrier such as water.

As used herein, the terms "tissue paper web, paper web, web, paper sheet and paper product" all refer to sheets of paper made by a process comprising the steps of forming an aqueous papermaking furnish, depositing this furnish on a foraminous surface, such as a Fourdrinier wire, and removing the water from the furnish as by gravity or vacuum-assisted drainage, with or without pressing, and by evaporation.

As used herein, an "aqueous papermaking furnish" is an aqueous slurry of papermaking fibers and the chemicals described hereinafter.

The first step in the process of this invention is the forming of an aqueous papermaking furnish. The furnish comprises papermaking fibers (hereinafter sometimes referred to as wood pulp), and a mixture of at least one quaternary ammonium compound and at least one polyhydroxy compound, all of which will be hereinafter described.

It is anticipated that wood pulp in all its varieties will normally comprise the papermaking fibers used in this invention. However, other cellulose fibrous pulps, such as cotton liners, bagasse, rayon, etc., can be used and none are disclaimed. Wood pulps useful herein include chemical pulps such as Kraft, sulfite and sulfate pulps as well as mechanical pulps including for example, ground wood, thermomechanical pulps and chemically modified thermomechanical pulp (CTMP). Pulps derived from both deciduous and coniferous trees can be used. Also applicable to the present invention are fibers derived from recycled paper, which may contain any or all of the above categories as well as other non-fibrous materials such as fillers and adhesives used to facilitate the original papermaking. Preferably, the papermaking fibers used in this invention comprise Kraft pulp derived from northern softwoods.

26 AUG 1996

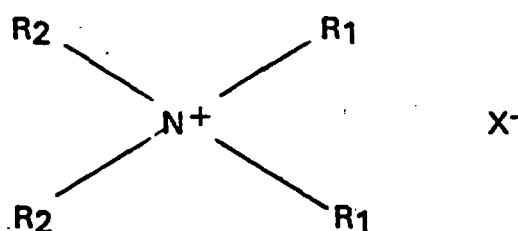
Waterless Self-emulsifiable Chemical Softener Compositions

The present invention contains as an essential component a mixture of a quaternary ammonium compound and a polyhydroxy compound. The ratio of the quaternary ammonium compound to the polyhydroxy compound ranges from about 1 : 0.1 to 0.1 : 1; preferably, the weight ratio of the quaternary ammonium compound to the polyhydroxy compound is about 1 : 0.3 to 0.3 : 1; more preferably, the weight ratio of the quaternary ammonium compound to the polyhydroxy compound is about 1 : 0.7 to 0.7 : 1, although this ratio will vary depending upon the molecular weight of the particular polyhydroxy compound and/or quaternary ammonium compound used.

Each of these types of compounds will be described in detail below.

A. Quaternary Ammonium Compound

The substantially waterless self-emulsifiable chemical softening composition contains as an essential component a quaternary ammonium compound having the formula :



In the structure named above each R₁ is C₁₄-C₂₂ hydrocarbon group, preferably tallow, R₂ is a C₁ - C₆ alkyl or hydroxyalkyl group, preferably C₁-C₃ alkyl, X⁻ is a suitable anion, such as an halide (e.g. chloride or bromide) or methyl sulfate. As discussed in Swern, Ed. in Bailey's Industrial Oil and Fat Products, Third Edition, John Wiley and Sons (New York 1964), tallow is a naturally occurring material having a variable composition. Table 6.13 in the above-identified reference edited by Swern indicates that typically 78% or more of the fatty acids of tallow contain 16 or 18 carbon atoms. Typically, half of the fatty acids present in tallow are unsaturated, primarily in the form of oleic acid. Synthetic as well as natural "tallows" fall within the scope of the present invention. Preferably, each R₁ is C₁₆-C₁₈ alkyl, most preferably each R₁ is straight-chain C₁₈ alkyl. Preferably, each R₂ is methyl and X⁻ is chloride or methyl sulfate.

26 AUG 1996

Examples of quaternary ammonium compounds suitable for use in the present invention include the well-known dialkyldimethylammonium salts such as ditallow dimethyl ammonium chloride, ditallow dimethylammonium methyl sulfate, di(hydrogenated)tallow dimethyl ammonium chloride; with di(hydrogenated)tallow dimethyl ammonium methyl sulfate being preferred. This particular material is available commercially from Sherex Chemical Company Inc. of Dublin, Ohio under the tradename "Varisoft® 137".

B. Polyhydroxy Compound

The chemical softening composition contains as an essential component a polyhydroxy compound.

Examples of polyhydroxy compounds useful in the present invention include glycerol, polyglycerols having a weight average molecular weight of from about 150 to about 800 and polyoxyethylene glycols and polyoxypropylene glycols having a weight average molecular weight of from about 200 to about 4000, preferably from about 200 to about 1000, most preferably from about 200 to about 600. Poxoxyethylene glycols having an weight average molecular weight of from about 200 to about 600 are especially preferred. Mixtures of the above-described polyhydroxy compounds may also be used. For example, mixtures of glycerol and polyoxyethylene glycols having a weight average molecular weight from about 200 to 1000, more preferably from about 200 to 600 are useful in the present invention. Preferably, the weight ratio of glycerol to polyoxyethylene glycol ranges from about 10 : 1 to 1 : 10.

A particularly preferred polyhydroxy compound is polyoxyethylene glycol having an weight average molecular weight of about 400. This material is available commercially from the Union Carbide Company of Danbury, Connecticut under the tradename "PEG-400".

The waterless self-emulsifiable chemical softening composition described above i.e. mixture of a quaternary ammonium compounds and a polyhydroxy compound are preferably diluted to a desired concentration to form a dispersion of the quat and polyhydroxy compounds before being added to the aqueous slurry of papermaking fibers, or furnish, in the wet end of the papermaking machine at some suitable point ahead of the Fourdrinier wire or sheet forming stage.

26 AUG 1986

However, applications of the above described chemical softening composition subsequent to formation of a wet tissue web and prior to drying of the web to completion will also provide significant softness, absorbency, and wet strength benefits and are expressly included within the scope of the present invention.

It has been discovered that the chemical softening composition is more effective when the quaternary ammonium compound and the polyhydroxy compound are first pre-mixed together before being added to the papermaking furnish. A preferred method, as will be described in greater detail hereinafter in Example 1, consists of first heating the polyhydroxy compound to a temperature of about 66°C (150°F), and then adding the quaternary ammonium compound to the hot polyhydroxy compound to form a homogenous fluid. The weight ratio of the quaternary ammonium compound to the polyhydroxy compound ranges from about 1 : 0.1 to 0.1 : 1; preferably, the weight ratio of the quaternary ammonium compound to the compound is about 1 : 0.3 to 0.3 : 1; more preferably, the weight ratio of the quaternary ammonium compound to the compound is about 1 : 0.7 to 0.7 : 1, although this ratio will vary depending upon the molecular weight of the particular compound and/or quaternary ammonium compound used. The moisture content of the chemical softening composition is less than about 20 % by weight, preferably the moisture content of the chemical softening composition is less than about 10 % by weight and more preferably the moisture content of the chemical softening composition is less than 5 % by weight. Importantly, the chemical softening composition is a stable, homogenous, solid or viscous fluid at a temperature greater than or about 20°C .

The substantially waterless self-emulsifiable chemical softener composition can be pre-mixed at the chemical supplier (e.g. Sherex company of Dublin, Ohio). Providing chemical softening compositions containing these softener compounds in substantially waterless forms results in cost saving on shipping the product (less weight), cost savings on packaging material and cost savings on machinery for processing the chemical softening compositions (less equipment needed to make-up the aqueous dispersion). In addition, the present invention also provides environmental safety advantages because of the elimination of the organic solvents, especially volatile organic solvents.

25 AUG 1996

The ultimate users of the chemical softening composition simply dilute the mixture with a liquid carrier (i.e., water) to form an aqueous dispersion of the quaternary ammonium compound / polyhydroxy compound mixture, which is then added to the papermaking furnish. The homogenous mixture of the quaternary ammonium compound and the polyhydroxy compound can exist either in a solid state or in a fluid state before being dispersed in the aqueous media. Preferably, the mixture of the quaternary ammonium compound and polyhydroxy compound is diluted with a liquid carrier such as water to a concentration of from about 0.01% to about 25% by weight of the softening composition before being added to the papermaking furnish. The temperature of the liquid carrier preferably ranges from about 20°C to about 80°C. After mixing, the quaternary ammonium compound and the polyhydroxy compound are present as particles dispersed in the liquid carrier. The average particle size preferably ranges from about 0.01 to 10 microns, most preferably from about 0.1 to about 1.0 micron. As shown in Figures 3 - 5, the dispersed particles are in the form of either closed vesicles or open particles.

It has unexpectedly been found that the adsorption of the polyhydroxy compound onto paper is significantly enhanced when it is premixed with the quaternary ammonium compound and added to the paper by the above described process. In fact, at least 20% of the polyhydroxy compound and the quaternary ammonium compound added to the fibrous cellulose are retained; preferably, the retention level of quaternary ammonium compound and the polyhydroxy compound is from about 50% to about 90% of the added levels.

Importantly, adsorption occurs at a concentration and within a time frame that are practical for use during paper making. In an effort to better understand the surprisingly high retention rate of polyhydroxy compound onto the paper, the physical science of the melted solution and the aqueous dispersion of a Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate (DHTDMAMS), and polyoxyethylene glycol 400 were studied.

Without wishing to be bound by theory, or to otherwise limit the present invention, the following discussion is offered for explaining how the quaternary ammonium compound promotes the adsorption of the polyhydroxy compound onto paper.

25 AUG 1996

Information on the physical state of DHTDMAMS, Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate, $R_2N^+(CH_3)_2, CH_3OSO_3^-$ and on DODMAMS is provided by X-ray and NMR (Nuclear Magnetic Resonance) data on the commercial mixture. DODMAMS (DiOctadecyl DiMethyl Ammonium Methyl Sulfate, $(C_{18}H_{37})_2N^+(CH_3)_2, CH_3OSO_3^-$) is a major component of DHTDMAMS, and serves as a model compound for the commercial mixture. It is useful to consider first the simpler DODMAMS system, and then the more complex commercial DHTDMAMS mixture.

Depending on the temperature, DODMAMS may exist in any of four phase states (Figure 1): two polymorphic crystals (X^β and X^α), a lamellar (Lam) liquid crystal, or a liquid phase. The X^β crystal exists from below room temperature to 47°C. At this temperature it is transformed into the polymorphic X^α crystal, which at 72°C is transformed into the Lam liquid crystal phase. This phase, in turn, is transformed into an isotropic liquid at 150°C. DHTDMAMS is expected to resemble DODMAMS in its physical behavior, except that the temperatures of the phase transitions will be lowered and broadened. For example, the transition from the X^β to the X^α crystal occurs at 27°C in DHTDMAMS instead of 47°C as in DODMAMS. Also, calorimetric data indicate that several crystal $\leftrightarrow$ Lam phase transitions occur in DHTDMAMS rather than one as in DODMAMS. The onset temperature of the highest of these transitions is 56°C, in good agreement with the X-ray data.

DODMAC (DiOctadecyl DiMethyl Ammonium Chloride) displays qualitatively different behavior from DODMAMS in that the Lam liquid crystal phase does not exist in this compound (Laughlin et al., Journal of Physical Chemistry, Physical Science of the Dioctadecyldimethylammonium Chloride-Water System. 1. Equilibrium Phase Behavior, 1990, volume 94, pages 2546-2552, incorporated herein by reference). This difference, however, is believed not to be important to the use of this compound (or its commercial analog DHTDMAC) in the treatment of paper.

Mixtures of DHTDMAMS with PEG-400.

A 1:1 weight ratio mixture of these two materials is studied, and a plausible model for the phase behavior of this system is suggested in Figure 2. In this diagram DODMAMS and PEG are shown to be

26 AUG 1996

immiscible at high temperatures, where they coexist as two liquid phases. As mixtures of the two liquids within this region are cooled, a Lam phase separates from the mixture. This study therefore shows that these two materials, while immiscible at high temperatures do become miscible at lower temperatures within the Lam liquid crystal phase. At still lower temperatures crystal phases are expected to separate from the Lam phase, and the compounds are again immiscible.

These studies therefore suggest that in order to form good dispersions of DHTDMAMS and PEG-400 in water, the premix that is diluted with water should be held within the intermediate temperature range where the two compounds are miscible.

Mixtures of DHTDMAC with PEG-400.

Phase studies of these two materials using the step-wise dilution method demonstrate that their physical behavior is considerably different from that of DHTDMAMS. No liquid crystal phases are found. These compounds are miscible as liquid solution over a wide range of temperatures, which indicates that dispersions may be prepared from these mixtures over a comparable range of temperatures. In particular no upper temperature limit of miscibility exists.

Preparation of dispersions.

Dispersions of either of these materials may be prepared by diluting a premix, that is held at a temperature at which the polyhydroxy compound and the quaternary ammonium salt are miscible, with water. It does not matter greatly whether they are miscible as a liquid crystalline phase (as in the case of DHTDMAMS), or as a liquid phase (as in the case of DHTDMAC). Neither DHTDMAMS nor DHTDMAC are soluble in water, so that dilution of either dry phase with water will precipitate the quaternary ammonium compound as small particles. Both quaternary ammonium compounds will precipitate at elevated temperatures as a liquid-crystal phase in dilute aqueous solutions, regardless of whether the dry solution was liquid or liquid crystalline. The polyhydroxy compound is soluble with water in all proportions, so is not precipitated.

Cryoelectron microscopy demonstrates that the particles present in the dispersion are about 0.1 to 1.0 micrometers in size, and highly varied in structure. Some are sheets (curved or flat), while others are closed vesicles. The membranes of all these particles are bilayers of

26 AUG 1996

molecular dimensions in which the head groups are exposed to water, the tails are together. The PEG is presumed to be associated with these particles. The application of dispersions prepared in this manner to paper results in attachment of the quaternary ammonium ion to the paper, strongly promotes the adsorption of the polyhydroxy compound onto paper, and produces the desired enhancement of softness with retention of wettability.

State of the dispersions.

When the above described dispersions are cooled, the partial crystallization of the material within the colloidal particles may occur. However, it is likely that the attainment of the equilibrium state will require a long time (perhaps months), so that the membranes within those particles that interact with paper are in a disordered state.

It is believed that the vesicles containing DHTDMAMS and PEG break apart upon drying of the fibrous cellulosic material. Once the vesicle is broken, the majority of the PEG component may penetrate into the interior of the cellulose fibers where it enhances the fiber flexibility. Importantly, some of the PEG is retained on the surface of the fiber where it acts to enhance the absorbency rate of the cellulose fibers. Due to ionic interactions, the majority of the DHTDMAMS component stays on the surface of the cellulose fiber, where it enhances the surface feel and softness of the paper product.

The second step in the process of this invention is the depositing of the papermaking furnish using the above described chemical softener composition as an additive on a foraminous surface and the third step is the removing of the water from the furnish so deposited. Techniques and equipment which can be used to accomplish these two processing steps will be readily apparent to those skilled in the papermaking art. Preferred tissue paper embodiments of the present invention contain from about 0.005% to about 5.0%, more preferably from about 0.03% to 0.5% by weight, on a dry fiber basis of the chemical softening composition described herein.

The present invention is applicable to tissue paper in general, including but not limited to conventionally felt-pressed tissue paper; high bulk pattern densified tissue paper; and high bulk, uncompacted tissue paper. The tissue paper may be of a homogenous or multilayered

20 AUG 1996

construction; and tissue paper products made therefrom may be of a single-ply or multi-ply construction. Tissue structures formed from layered paper webs are described in U.S. Patent 3,994,771, Morgan, Jr. et al. issued November 30, 1976, and incorporated herein by reference. In general, a wet-laid composite, soft, bulky and absorbent paper structure is prepared from two or more layers of furnish which are preferably comprised of different fiber types. The layers are preferably formed from the deposition of separate streams of dilute fiber slurries, the fibers typically being relatively long softwood and relatively short hardwood fibers as used in tissue papermaking, upon one or more endless foraminous screens. The layers are subsequently combined to form a layered composite web. The layered web is subsequently caused to conform to the surface of an open mesh drying/imprinting fabric by the application of a fluid force to the web and thereafter thermally predried on said fabric as part of a low density papermaking process. The layered web may be stratified with respect to fiber type or the fiber content of the respective layers may be essentially the same. The tissue paper preferably has a basis weight of between 10 g/m² and about 65 g/m², and density of about 0.60 g/cm³ or less. Preferably, basis weight will be below about 35 g/m² or less; and density will be about 0.30 g/cm³ or less. Most preferably, density will be between 0.04 g/cm³ and about 0.20 g/cm³.

Conventionally pressed tissue paper and methods for making such paper are known in the art. Such paper is typically made by depositing papermaking furnish on a foraminous forming wire. This forming wire is often referred to in the art as a Fourdrinier wire. Once the furnish is deposited on the forming wire, it is referred to as a web. The web is dewatered by transferring to a dewatering felt, pressing the web and drying at elevated temperature. The particular techniques and typical equipment for making webs according to the process just described are well known to those skilled in the art. In a typical process, a low consistency pulp furnish is provided in a pressurized headbox. The headbox has an opening for delivering a thin deposit of pulp furnish onto the Fourdrinier wire to form a wet web. The web is then typically dewatered to a fiber consistency of between about 7% and about 25% (total web weight basis) by vacuum dewatering and further dewatered by pressing operations wherein the web is subjected

23 AUG 1996

to pressure developed by opposing mechanical members, for example, cylindrical rolls.

The dewatered web is then further pressed during transfer and being dried by a stream drum apparatus known in the art as a Yankee dryer. Pressure can be developed at the Yankee dryer by mechanical means such as an opposing cylindrical drum pressing against the web. Vacuum may also be applied to the web as it is pressed against the Yankee surface. Multiple Yankee dryer drums may be employed, whereby additional pressing is optionally incurred between the drums. The tissue paper structures which are formed are referred to hereinafter as conventional, pressed, tissue paper structures. Such sheets are considered to be compacted since the web is subjected to substantial mechanical compression forces while the fibers are moist and are then dried while in a compressed state.

Pattern densified tissue paper is characterized by having a relatively high bulk field of relatively low fiber density and an array of densified zones of relatively high fiber density. The high bulk field is alternatively characterized as a field of pillow regions. The densified zones are alternatively referred to as knuckle regions. The densified zones may be discretely spaced within the high bulk field or may be interconnected, either fully or partially, within the high bulk field. Preferred processes for making pattern densified tissue webs are disclosed in U.S. Patent No. 3,301,746, issued to Sanford and Sisson on January 31, 1967, U.S. Patent No. 3,974,025, issued to Peter G. Ayers on August 10, 1976, and U.S. Patent No. 4,191,609, issued to Paul D. Trokhan on March 4, 1980, and U.S. Patent 4,637,859, issued to Paul D. Trokhan on January 20, 1987; all of which are incorporated herein by reference.

In general, pattern densified webs are preferably prepared by depositing a papermaking furnish on a foraminous forming wire such as a Fourdrinier wire to form a wet web and then juxtaposing the web against an array of supports. The web is pressed against the array of supports, thereby resulting in densified zones in the web at the locations geographically corresponding to the points of contact between the array of supports and the wet web. The remainder of the web not compressed during this operation is referred to as the high bulk field. This high bulk field can be further dedensified by application of fluid

25 AUG 1996

pressure, such as with a vacuum type device or a blow-through dryer. The web is dewatered, and optionally predried, in such a manner so as to substantially avoid compression of the high bulk field. This is preferably accomplished by fluid pressure, such as with a vacuum type device or blow-through dryer, or alternately by mechanically pressing the web against an array of supports wherein the high bulk field is not compressed. The operations of dewatering, optional predrying and formation of the densified zones may be integrated or partially integrated to reduce the total number of processing steps performed. Subsequent to formation of the densified zones, dewatering, and optional predrying, the web is dried to completion, preferably still avoiding mechanical pressing. Preferably, from about 8% to about 55% of the tissue paper surface comprises densified knuckles having a relative density of at least 125% of the density of the high bulk field.

The array of supports is preferably an imprinting carrier fabric having a patterned displacement of knuckles which operate as the array of supports which facilitate the formation of the densified zones upon application of pressure. The pattern of knuckles constitutes the array of supports previously referred to. Imprinting carrier fabrics are disclosed in U.S. Patent No. 3,301,746, Sanford and Sisson, issued January 31, 1967, U.S. Patent No. 3,821,068, Salvucci, Jr. et al., issued May 21, 1974, U.S. Patent No. 3,974,025, Ayers, issued August 10, 1976, U.S. Patent No. 3,573,164, Friedberg et al., issued March 30, 1971, U.S. Patent No. 3,473,576, Amneus, issued October 21, 1969, U.S. Patent No. 4,239,065, Trokhan, issued December 16, 1980, and U.S. Patent No. 4,528,239, Trokhan, issued July 9, 1985, all of which are incorporated herein by reference.

Preferably, the furnish is first formed into a wet web on a foraminous forming carrier, such as a Fourdrinier wire. The web is dewatered and transferred to an imprinting fabric. The furnish may alternately be initially deposited on a foraminous supporting carrier which also operates as an imprinting fabric. Once formed, the wet web is dewatered and, preferably, thermally predried to a selected fiber consistency of between about 40% and about 80%. Dewatering can be performed with suction boxes or other vacuum devices or with blow-through dryers. The knuckle imprint of the imprinting fabric is impressed in the web as discussed above, prior to drying the web to completion.

20 AUG 1976

One method for accomplishing this is through application of mechanical pressure. This can be done, for example, by pressing a nip roll which supports the imprinting fabric against the face of a drying drum, such as a Yankee dryer, wherein the web is disposed between the nip roll and drying drum. Also, preferably, the web is molded against the imprinting fabric prior to completion of drying by application of fluid pressure with a vacuum device such as a suction box, or with a blow-through dryer. Fluid pressure may be applied to induce impression of densified zones during initial dewatering, in a separate, subsequent process stage, or a combination thereof.

Uncompacted, nonpattern-densified tissue paper structures are described in U.S. Patent No. 3,812,000 issued to Joseph L. Salvucci, Jr. and Peter N. Yiannos on May 21, 1974 and U.S. Patent No. 4,208,459, issued to Henry E. Becker, Albert L. McConnell, and Richard Schutte on June 17, 1980, both of which are incorporated herein by reference. In general, uncompacted, non pattern densified tissue paper structures are prepared by depositing a papermaking furnish on a foraminous forming wire such as a Fourdrinier wire to form a wet web, draining the web and removing additional water without mechanical compression until the web has a fiber consistency of at least 80%, and creping the web. Water is removed from the web by vacuum dewatering and thermal drying. The resulting structure is a soft but weak high bulk sheet of relatively uncompacted fibers. Bonding material is preferably applied to portions of the web prior to creping.

The tissue paper web of this invention can be used in any application where soft, absorbent tissue paper webs are required. Particularly advantageous uses of the tissue paper web of this invention are in paper towel, toilet tissue and facial tissue products. For example, two tissue paper webs of this invention can be embossed and adhesively secured together in face to face relation as taught by U.S. Pat. No. 3,414,459, which issued to Wells on December 3, 1968 and which is incorporated herein by reference, to form 2-ply paper towels.

Molecular Weight Determination

A. Introduction

The essential distinguishing characteristic of polymeric materials is their molecular size. The properties which have enabled polymers to

28 AUG 1976

be used in a diversity of applications derive almost entirely from their macro-molecular nature. In order to characterize fully these materials it is essential to have some means of defining and determining their molecular weights and molecular weight distributions. It is more correct to use the term relative molecular mass rather the molecular weight, but the latter is used more generally in polymer technology. It is not always practical to determine molecular weight distributions. However, this is becoming more common practice using chromatographic techniques. Rather, recourse is made to expressing molecular size in terms of molecular weight averages.

B. Molecular weight averages

If we consider a simple molecular weight distribution which represents the weight fraction (w_i) of molecules having relative molecular mass (M_i), it is possible to define several useful average values. Averaging carried out on the basis of the number of molecules (N_i) of a particular size (M_i) gives the Number Average Molecular Weight

$$\bar{n} = \frac{\sum N_i M_i}{\sum N_i}$$

An important consequence of this definition is that the Number Average Molecular Weight in grams contains Avogadro's Number of molecules. This definition of molecular weight is consistent with that of monodisperse molecular species, i.e. molecules having the same molecular weight. Of more significance is the recognition that if the number of molecules in a given mass of a polydisperse polymer can be determined in some way then $\bar{n}$, can be calculated readily. This is the basis of colligative property measurements.

Averaging on the basis of the weight fractions (W_i) of molecules of a given mass (M_i) leads to the definition of Weight Average Molecular Weights

$$\bar{w} = \frac{\sum W_i N_i}{\sum W_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

23 AUG 1976

w is a more useful means for expressing polymer molecular weights than n since it reflects more accurately such properties as melt viscosity and mechanical properties of polymers and is therefor used in the present invention.

Analytical and Testing Procedures

Analysis of the amount of treatment chemicals used herein or retained on tissue paper webs can be performed by any method accepted in the applicable art.

A. Quantitative analysis for quaternary ammonium and polyhydroxy compounds

For example, the level of the quaternary ammonium compound, such as Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate (DHTDMAMS) retained by the tissue paper can be determined by solvent extraction of the DHTDMAMS by an organic solvent followed by an anionic/cationic titration using Dimidium Bromide as indicator; the level of the polyhydroxy compound, such as PEG-400, can be determined by extraction in an aqueous solvent such as water followed by gas chromatography or colorimetry techniques to determine the level of PEG-400 in the extract. These methods are exemplary, and are not meant to exclude other methods which may be useful for determining levels of particular components retained by the tissue paper.

B. Hydrophilicity (absorbency)

Hydrophilicity of tissue paper refers, in general, to the propensity of the tissue paper to be wetted with water. Hydrophilicity of tissue paper may be somewhat quantified by determining the period of time required for dry tissue paper to become completely wetted with water. This period of time is referred to as "wetting time". In order to provide a consistent and repeatable test for wetting time, the following procedure may be used for wetting time determinations: first, a conditioned sample unit sheet (the environmental conditions for testing of paper samples are $23 \pm 1^\circ\text{C}$ and $50 \pm 2\%$ R.H. as specified in TAPPI Method T 402), approximately 4-3/8 inch x 4-3/4 inch (about 11.1 cm x 12 cm) of tissue paper structure is provided; second, the sheet is folded into four (4) juxtaposed quarters, and then crumpled into a ball approximately 0.75 inches (about 1.9 cm) to about 1 inch (about 2.5

20 AUG 1996

cm) in diameter; third, the balled sheet is placed on the surface of a body of distilled water at $23 \pm 1^\circ\text{C}$ and a timer is simultaneously started; fourth, the timer is stopped and read when wetting of the balled sheet is completed. Complete wetting is observed visually.

Hydrophilicity characters of tissue paper embodiments of the present invention may, of course, be determined immediately after manufacture. However, substantial increases in hydrophobicity may occur during the first two weeks after the tissue paper is made: i.e., after the paper has aged two (2) weeks following its manufacture. Thus, the wetting times are preferably measured at the end of such two week period. Accordingly, wetting times measured at the end of a two week aging period at room temperature are referred to as "two week wetting times."

C. Density

The density of tissue paper, as that term is used herein, is the average density calculated as the basis weight of that paper divided by the caliper, with the appropriate unit conversions incorporated therein. Caliper of the tissue paper, as used herein, is the thickness of the paper when subjected to a compressive load of 95 g/in^2 (15.5 g/cm^2).

Optional Ingredients

Other chemicals commonly used in papermaking can be added to the substantially waterless self-emulsifiable chemical softening composition described herein, or to the papermaking furnish so long as they do not significantly and adversely affect the softening, absorbency of the fibrous material, and enhancing actions of the chemical softening composition.

For example, surfactants may be used to treat the tissue paper webs of the present invention. The level of surfactant, if used, is preferably from about 0.01% to about 2.0% by weight, based on the dry fiber weight of the tissue paper. The surfactants preferably have alkyl chains with eight or more carbon atoms. Exemplary anionic surfactants are linear alkyl sulfonates, and alkylbenzene sulfonates. Exemplary nonionic surfactants are alkylglycosides including alkylglycoside esters such as Crodesta SL-40 which is available from Croda, Inc. (New York, NY); alkylglycoside ethers as described in U.S.

26 AUG 1996

Patent 4,011,389, issued to W. K. Langdon, et al. on March 8, 1977; and alkylpolyethoxylated esters such as Pegosperse 200 ML available from Glyco Chemicals, Inc. (Greenwich, CT) and IGEPAL RC-520 available from Rhone Poulenc Corporation (Cranbury, N.J.).

Other types of chemicals which may be added, include dry strength additives to increase the tensile strength of the tissue webs. Examples of dry strength additives include carboxymethyl cellulose, and cationic polymers from the Acco chemical family such as Acco 711 and Acco 514, with the Acco chemical family being preferred. These materials are available commercially from the American Cyanamid Company of Wayne, New Jersey. The level of dry strength additive, if used, is preferably from about 0.01% to about 1.0%, by weight, based on the dry fiber weight of the tissue paper.

Other types of chemicals which may be added, include wet strength additives to increase the wet burst of the tissue webs. The present invention may contain as an optional component from about 0.01% to about 3.0%, more preferably from about 0.3% to about 1.5% by weight, on a dry fiber weight basis, of a water-soluble permanent wet strength resin.

Permanent wet strength resins useful herein can be of several types. Generally, those resins which have previously found and which will hereafter find utility in the papermaking art are useful herein. Numerous examples are shown in the aforementioned paper by Westfelt, incorporated herein by reference.

In the usual case, the wet strength resins are water-soluble, cationic materials. That is to say, the resins are water-soluble at the time they are added to the papermaking furnish. It is quite possible, and even to be expected, that subsequent events such as cross-linking will render the resins insoluble in water. Further, some resins are soluble only under specific conditions, such as over a limited pH range.

Wet strength resins are generally believed to undergo a cross-linking or other curing reactions after they have been deposited on, within, or among the papermaking fibers. Cross-linking or curing does not normally occur so long as substantial amounts of water are present.

Of particular utility are the various polyamide-epichlorohydrin resins. These materials are low molecular weight polymers provided with reactive functional groups such as amino, epoxy, and azetidinium

25 AUG 1996

groups. The patent literature is replete with descriptions of processes for making such materials. U.S. Pat. No. 3,700,623, issued to Keim on October 24, 1972 and U.S. Pat. No. 3,772,076, issued to Keim on November 13, 1973 are examples of such patents and both are incorporated herein by reference.

Polyamide-epichlorohydrin resins sold under the trademarks Kymene[®] 557H and Kymene[®] 2064 by Hercules Incorporated of Wilmington, Delaware, are particularly useful in this invention. These resins are generally described in the aforementioned patents to Keim.

Base-activated polyamide-epichlorohydrin resins useful in the present invention are sold under the Santo Res trademark, such as Santo Res 31, by Monsanto Company of St. Louis, Missouri. These types of materials are generally described in U.S. Pat. Nos. 3,855,158 issued to Petrovich on December 17, 1974; 3,899,388 issued to Petrovich on August 12, 1975; 4,129,528 issued to Petrovich on December 12, 1978; 4,147,586 issued to Petrovich on April 3, 1979; and 4,222,921 issued to Van Eenam on September 16, 1980, all incorporated herein by reference.

Other water-soluble cationic resins useful herein are the polyacrylamide resins such as those sold under the Parex trademark, such as Parex 631NC, by American Cyanamid Company of Stamford, Connecticut. These materials are generally described in U.S. Pat. Nos. 3,556,932 issued to Coscia et al. on January 19, 1971; and 3,556,933 issued to Williams et al. on January 19, 1971, all incorporated herein by reference.

Other types of water-soluble resins useful in the present invention include acrylic emulsions and anionic styrene-butadiene latexes. Numerous examples of these types of resins are provided in U.S. Patent 3,844,880, Meisel, Jr. et al., issued October 29, 1974, incorporated herein by reference.

Still other water-soluble cationic resins finding utility in this invention are the urea formaldehyde and melamine formaldehyde resins. These polyfunctional, reactive polymers have molecular weights on the order of a few thousand. The more common functional groups include nitrogen containing groups such as amino groups and methylol groups attached to nitrogen.

25 AUG 1996

Although less preferred, polyethylenimine type resins find utility in the present invention.

More complete descriptions of the aforementioned water-soluble resins, including their manufacture, can be found in TAPPI Monograph Series No. 29, **Wet Strength In Paper and Paperboard**, Technical Association of the Pulp and Paper Industry (New York; 1965), incorporated herein by reference. As used herein, the term "permanent wet strength resin" refers to a resin which allows the paper sheet, when placed in an aqueous medium, to keep a majority of its initial wet strength for a period of time greater than at least two minutes.

The above-mentioned wet strength additives typically result in paper products with permanent wet strength, i.e., paper which when placed in an aqueous medium retains a substantial portion of its initial wet strength over time. However, permanent wet strength in some types of paper products can be an unnecessary and undesirable property. Paper products such as toilet tissues, etc., are generally disposed of after brief periods of use into septic systems and the like. Clogging of these systems can result if the paper product permanently retains its hydrolysis-resistant strength properties. More recently, manufacturers have added temporary wet strength additives to paper products for which wet strength is sufficient for the intended use, but which then decays upon soaking in water. Decay of the wet strength facilitates flow of the paper product through septic systems.

Examples of suitable temporary wet strength resins include modified starch temporary wet strength agents, such as National Starch 78-0080, marketed by the National Starch and Chemical Corporation (New York, New York). This type of wet strength agent can be made by reacting dimethoxyethyl-N-methyl-chloroacetamide with cationic starch polymers. Modified starch temporary wet strength agents are also described in U.S. Pat. No. 4,675,394, Solarek, et al., issued June 23, 1987, and incorporated herein by reference. Preferred temporary wet strength resins include those described in U.S. Pat. No. 4,981,557, Bjorkquist, issued January 1, 1991, and incorporated herein by reference.

With respect to the classes and specific examples of both permanent and temporary wet strength resins listed above, it should be

26 AUG 1996

understood that the resins listed are exemplary in nature and are not meant to limit the scope of this invention.

Mixtures of compatible wet strength resins can also be used in the practice of this invention.

The above listings of optional chemical additives is intended to be merely exemplary in nature, and are not meant to limit the scope of the invention.

The following examples illustrate the practice of the present invention but are not intended to be limiting thereof.

EXAMPLE 1

The purpose of this example is to illustrate a method that can be used to make-up a substantially waterless self-emulsifiable chemical softener composition comprising a mixture of Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate (DHTDMAMS) and Polyoxyethylene Glycol 400 (PEG-400).

A waterless self-emulsifiable chemical softener composition is prepared according to the following procedure : 1. An equivalent weight of DHTDMAMS and PEG-400 is weighed separately; 2. PEG is heated up to about 66°C (150°F); 3. DHTDMAMS is dissolved in the PEG to form a melted solution at 66°C (150°F); 4. Adequate mixing is provided to form a homogenous mixture of DHTDMAMS in PEG; 5. The homogenous mixture of (4) is cooled down to a solid form at room temperature.

The substantially waterless self-emulsifiable chemical softener composition of (5) can be pre-mixed (steps 1-5 above) at the chemical supplier (e.g. Sherex company of Dublin, Ohio) and then economically shipped to the ultimate users of the chemical softening composition where it can then be diluted to the desired concentration.

EXAMPLE 2

The purpose of this example is to illustrate a method that can be used to make-up a substantially waterless self-emulsifiable chemical

26 AUG 1996

softener composition which comprises a mixture of Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate (DHTDMAMS) and a mixture of Glycerol and PEG-400.

A substantially waterless self-emulsifiable chemical softener composition is prepared according to the following procedure : 1. A mixture of Glycerol and PEG-400 is blended at 75 : 25 by weight ratio; 2. Equivalent weights of DHTDMAMS and the mixture of (1) are weighted separately; 3. The mixture of (1) is heated up to about 66°C (150°F); 4. DHTDMAMS is dissolved in (3) to form a melted solution at 66°C (150°F); 5. Adequate mixing is provided to form a homogenous mixture of DHTDMAMS in (3); 6. The homogenous mixture of (5) is cooled down to a solid form at room temperature.

The substantially waterless self-emulsifiable chemical softener composition of (6) can be pre-mixed (steps 1-6 above) at the chemical supplier (e.g. Sherex company of Dublin, Ohio) and then economically shipped to the ultimate users of the chemical softening composition where it can then be diluted to the desired concentration.

EXAMPLE 3

The purpose of this example is to illustrate a method using a blow through drying papermaking technique to make soft and absorbent paper towel sheets treated with a substantially waterless self-emulsifiable chemical softener composition comprising a premix of Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate (DHTDMAMS) and a Polyoxyethylene Glycol 400 (PEG-400) in solid state, and a permanent wet strength resin .

A pilot scale Fourdrinier papermaking machine is used in the practice of the present invention. First, the substantially waterless self-emulsifiable chemical softener composition is prepared according to the procedure in Example 1 wherein the homogenous pre-mixed of DHTDMAMS and PEG-400 in solid state is dispersed in a conditioned water tank (Temperature ~ 66°C) to form a sub-micron vesicle dispersion. The particle size of the vesicle dispersion is determined using an optical microscopic technique. The particle size range is from about 0.1 to 1.0 micron. Figure 3 illustrates a cryo-transmission micro-

26 AUG 1996

photograph taken at X 63,000 of a vesicle dispersion of a 1 : 1 by weight ratio of a DHTDMAMS and PEG-400 system. Figure 3 indicates that the particles have membranes one or two bilayers thick, whose geometry ranges from closed/open vesicles; to disc-like structures and sheets.

Second, a 3% by weight aqueous slurry of NSK is made up in a conventional re-pulper. The NSK slurry is refined gently and a 2% solution of a permanent wet strength resin (i.e. Kymene® 557H marketed by Hercules Incorporated of Wilmington, DE) is added to the NSK stock pipe at a rate of 1% by weight of the dry fibers. The adsorption of Kymene® 557H to NSK is enhanced by an in-line mixer. A 1% solution of Carboxy Methyl Cellulose (CMC) is added after the in-line mixer at a rate of 0.2% by weight of the dry fibers to enhance the dry strength of the fibrous substrate. The adsorption of CMC to NSK can be enhanced by an in-line mixer. Then, a 1% solution of the chemical softener mixture (DHTDMAMS/ PEG) is added to the NSK slurry at a rate of 0.1% by weight of the dry fibers. The adsorption of the chemical softener mixture to NSK can also be enhanced via an in-line mixer. The NSK slurry is diluted to 0.2% by the fan pump.

Third, a 3% by weight aqueous slurry of CTMP is made up in a conventional re-pulper. A non-ionic surfactant (Pegospense) is added to the re-pulper at a rate of 0.2% by weight of dry fibers. A 1% solution of the chemical softener mixture is added to the CTMP stock pipe before the stock pump at a rate of 0.1% by weight of the dry fibers. The adsorption of the chemical softener mixture to CTMP can be enhanced by an in-line mixer. The CTMP slurry is diluted to 0.2% by the fan pump. The treated furnish mixture (NSK / CTMP) is blended in the head box and deposited onto a Fourdrinier wire to form an embryonic web. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and vacuum boxes. The Fourdrinier wire is of a 5-shed, satin weave configuration having 84 machine-direction and 76 cross-machine-direction monofilaments per inch, respectively. The embryonic wet web is transferred from the Fourdrinier wire, at a fiber consistency of about 22% at the point of transfer, to a photo-polymer fabric having 240 linear Idaho cells per square inch, 34 percent knuckle areas and 14 mils of photo-polymer depth. The name "linear Idaho" is based on the fact that the cross-section of conduits from which this

26 AUG 1996

pattern was derived, originally resembled the shape of a potato. The walls of the conduits on four sides, however, are formed by generally straight lines, thus the pattern is referred to as being a "linear" Idaho rather than simply as an Idaho pattern. Further de-watering is accomplished by vacuum assisted drainage until the web has a fiber consistency of about 28%. The patterned web is pre-dried by air blow-through to a fiber consistency of about 65% by weight. The web is then adhered to the surface of a Yankee dryer with a sprayed creping adhesive comprising 0.25% aqueous solution of Polyvinyl Alcohol (PVA). The fiber consistency is increased to an estimated 96% before the dry creping the web with a doctor blade. The doctor blade has a bevel angle of about 25 degrees and is positioned with respect to the Yankee dryer to provide an impact angle of about 81 degrees; the Yankee dryer is operated at about 800 fpm (feet per minute) (about 244 meters per minute). The dry web is formed into roll at a speed of 700 fpm (214 meters per minutes).

Two plies of the web are formed into paper towel products by embossing and laminating them together using PVA adhesive. The paper towel has about 26 #/3M Sq Ft basis weight, contains about 0.2% of the substantially waterless self-emulsifiable chemical softener mixture and about 1.0% of the permanent wet strength resin. The resulting paper towel is soft, absorbent, and very strong when wetted.

EXAMPLE 4

The purpose of this example is to illustrate a method using a blow through drying and layered papermaking techniques to make soft and absorbent toilet tissue paper treated with a substantially waterless self-emulsifiable chemical softener composition comprising a premix of Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate (DHTDMAMS) and a Polyoxyethylene Glycol 400 (PEG-400) in liquid state and a temporary wet strength resin.

A pilot scale Fourdrinier papermaking machine is used in the practice of the present invention. First, the substantially waterless self-emulsifiable chemical softener composition is prepared according to the procedure in Example 1 wherein the homogenous premix of DHTDMAMS and polyhydroxy compounds in solid state is re-melted at a

28 AUG 1996

temperature of about 66°C (150°F). The melted mixture is then dispersed in a conditioned water tank (Temperature = 66°C) to form a sub-micron vesicle dispersion. The particle size of the vesicle dispersion is determined using an optical microscopic technique. The particle size range is from about 0.1 to 1.0 micron. Figure 4 illustrates a cryo-transmission micro-photograph taken at X 63,000 of a vesicle dispersion of a 1 : 1 by weight ratio of a DHTDMAMS and polyhydroxy compounds system. Figure 4 indicates that the particles have membranes one or two bilayers thick, whose geometry ranges from closed/open vesicles, to disc-like structures and sheets.

Second, a 3% by weight aqueous slurry of NSK is made up in a conventional re-pulper. The NSK slurry is refined gently and a 2% solution of the temporary wet strength resin (i.e. National starch 78-0080 marketed by National Starch and Chemical corporation of New-York, NY) is added to the NSK stock pipe at a rate of 0.75% by weight of the dry fibers. The adsorption of the temporary wet strength resin onto NSK fibers is enhanced by an in-line mixer. The NSK slurry is diluted to about 0.2% consistency at the fan pump. Third, a 3% by weight aqueous slurry of Eucalyptus fibers is made up in a conventional re-pulper. A 1% solution of the chemical softener mixture is added to the Eucalyptus stock pipe before the stock pump at a rate of 0.2% by weight of the dry fibers. The adsorption of the substantially waterless self-emulsifiable chemical softener mixture to Eucalyptus fibers can be enhanced by an in-line mixer. The Eucalyptus slurry is diluted to about 0.2% consistency at the fan pump.

The treated furnish mixture (30% of NSK / 70% of Eucalyptus) is blended in the head box and deposited onto a Fourdrinier wire to form an embryonic web. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and vacuum boxes. The Fourdrinier wire is of a 5-shed, satin weave configuration having 84 machine-direction and 76 cross-machine-direction monofilaments per inch, respectively. The embryonic wet web is transferred from the photo-polymer wire, at a fiber consistency of about 15% at the point of transfer, to a photo-polymer fabric having 562 Linear Idaho cells per square inch, 40 percent knuckle area and 9 mils of photo-polymer depth. Further dewatering is accomplished by vacuum assisted drainage until the web has a fiber consistency of about 28%. The patterned web is pre-dried

26 AUG 1996

by air blow-through to a fiber consistency of about 65% by weight. The web is then adhered to the surface of a Yankee dryer with a sprayed creping adhesive comprising 0.25% aqueous solution of Polyvinyl Alcohol (PVA). The fiber consistency is increased to an estimated 96% before the dry creping the web with a doctor blade. The doctor blade has a bevel angle of about 25 degrees and is positioned with respect to the Yankee dryer to provide an impact angle of about 81 degrees; the Yankee dryer is operated at about 800 fpm (feet per minute) (about 244 meters per minute). The dry web is formed into roll at a speed of 700 fpm (214 meters per minutes).

The web is converted into a one ply tissue paper product. The tissue paper has about 18 #/3M Sq Ft basis weight, contains about 0.1% of the chemical softener mixture and about 0.2% of the temporary wet strength resin. Importantly, the resulting tissue paper is soft, absorbent and is suitable for use as facial and/or toilet tissues.

EXAMPLE 5

The purpose of this example is to illustrate a method using a-blow through drying papermaking technique to make soft and absorbent toilet tissue paper treated with a substantially waterless self-emulsifiable chemical softener composition comprising a premix of Di(Hydrogenated)Tallow DiMethyl Ammonium Chloride (DHTDMAC) and a mixture of polyhydroxy compound (Glycerol / PEG-400) in liquid state and a dry strength additive resin.

A pilot scale Fourdrinier papermaking machine is used in the practice of the present invention. First, the substantially waterless self-emulsifiable chemical softener composition is prepared according to the procedure in Example 2 wherein the homogenous premix of DHTDMAC and polyhydroxy compounds in solid state is re-melted at a temperature of about 66°C (150°F). The melted mixture is then dispersed in a conditioned water tank (Temperature ~ 66°C) to form a sub-micron vesicle dispersion. The particle size of the vesicle dispersion is determined using an optical microscopic technique. The particle size range is from about 0.1 to 1.0 micron. Figure 5 illustrates a cryo-transmission micro-photograph taken at X 63,000 of a vesicle dispersion of a 1 : 1 by weight ratio of a DHTDMAC and polyhydroxy

26 AUG 1996

compounds system. Figure 5 indicates that the particles have membranes one or two bilayers thick, whose geometry ranges from closed/open vesicles, to disc-like structures and sheets.

Second, a 3% by weight aqueous slurry of NSK is made up in a conventional re-pulper. The NSK slurry is refined gently and a 2% solution of the dry strength resin (i.e. Acco 514, Acco 711 marketed by American Cyanamid company of Fairfield, OH) is added to the NSK stock pipe at a rate of 0.2% by weight of the dry fibers. The adsorption of the dry strength resin onto NSK fibers is enhanced by an in-line mixer. The NSK slurry is diluted to about 0.2% consistency at the fan pump. Third, a 3% by weight aqueous slurry of Eucalyptus fibers is made up in a conventional re-pulper. A 1% solution of the chemical softener mixture is added to the Eucalyptus stock pipe before the stock pump at a rate of 0.2% by weight of the dry fibers. The adsorption of the substantially waterless self-emulsifiable chemical softener mixture to Eucalyptus fibers can be enhanced by an in-line mixer. The Eucalyptus slurry is diluted to about 0.2% consistency at the fan pump.

The treated furnish mixture (30% of NSK / 70% of Eucalyptus) is blended in the head box and deposited onto a Fourdrinier wire to form an embryonic web. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and vacuum boxes. The Fourdrinier wire is of a 5-shed, satin weave configuration having 84 machine-direction and 76 cross-machine-direction monofilaments per inch, respectively. The embryonic wet web is transferred from the photo-polymer wire, at a fiber consistency of about 15% at the point of transfer, to a photo-polymer fabric having 562 Linear Idaho cells per square inch, 40 percent knuckle area and 9 mils of photo-polymer depth. Further dewatering is accomplished by vacuum assisted drainage until the web has a fiber consistency of about 28%. The patterned web is pre-dried by air blow-through to a fiber consistency of about 65% by weight. The web is then adhered to the surface of a Yankee dryer with a sprayed creping adhesive comprising 0.25% aqueous solution of Polyvinyl Alcohol (PVA). The fiber consistency is increased to an estimated 96% before the dry creping the web with a doctor blade. The doctor blade has a bevel angle of about 25 degrees and is positioned with respect to the Yankee dryer to provide an impact angle

26 AUG 1996

of about 81 degrees; the Yankee dryer is operated at about 800 fpm (feet per minute) (about 244 meters per minute). The dry web is formed into roll at a speed of 700 fpm (214 meters per minutes).

Two plies of the web are formed into tissue paper products and laminating them together using ply bonded technique. The tissue paper has about 23 #/3M Sq Ft basis weight, contains about 0.1% of the substantially waterless self-emulsifiable chemical softener mixture and about 0.1% of the dry strength resin. Importantly, the resulting tissue paper is soft, absorbent and is suitable for use as facial and/or toilet tissues.

EXAMPLE 6

The purpose of this example is to illustrate a method using a conventional drying papermaking technique to make soft and absorbent toilet tissue paper treated with a substantially waterless self-emulsifiable chemical softener composition comprising a premix of Di(Hydrogenated)Tallow DiMethyl Ammonium Methyl Sulfate (DHTDMAMS) and a Polyoxyethylene Glycol 400 (PEG-400) in solid state and a dry strength additive resin .

A pilot scale Fourdrinier papermaking machine is used in the practice of the present invention. First, the substantially waterless self-emulsifiable chemical softener composition is prepared according to the procedure in Example 1 wherein the homogenous premix of DHTDMAMS and PEG-400 in solid state is dispersed in a conditioned water tank (Temperature ~ 66°C) to form a sub-micron vesicle dispersion. The particle size of the vesicle dispersion is determined using an optical microscopic technique. The particle size range is from about 0.1 to 1.0 micron. Figure 3 illustrates a cryo-transmission microphotograph taken at X 63,000 of a vesicle dispersion of a 1 : 1 by weight ratio of a DHTDMAMS and PEG-400 system. Figure 3 indicates that the particles have membranes one or two bilayers thick, whose geometry ranges from closed/open vesicles, to disc-like structures and sheets.

Second, a 3% by weight aqueous slurry of NSK is made up in a conventional re-pulper. The NSK slurry is refined gently and a 2% solution of the dry strength resin (i.e. Acco 514, Acco 711 marketed by

23 AUG 1996

American Cyanamid company of Wayne, New Jersey) is added to the NSK stock pipe at a rate of 0.2% by weight of the dry fibers. The adsorption of the dry strength resin onto NSK fibers is enhanced by an in-line mixer. The NSK slurry is diluted to about 0.2% consistency at the fan pump. Third, a 3% by weight aqueous slurry of Eucalyptus fibers is made up in a conventional re-pulper. A 1% solution of the chemical softener mixture is added to the Eucalyptus stock pipe before the stock pump at a rate of 0.2% by weight of the dry fibers. The adsorption of the chemical softener mixture to Eucalyptus fibers can be enhanced by an in-line mixer. The Eucalyptus slurry is diluted to about 0.2% consistency at the fan pump.

The treated furnish mixture (30% of NSK / 70% of Eucalyptus) is blended in the head box and deposited onto a Fourdrinier wire to form an embryonic web. Dewatering occurs through the Fourdrinier wire and is assisted by a deflector and vacuum boxes. The Fourdrinier wire is of a 5-shed, satin weave configuration having 84 machine-direction and 76 cross-machine-direction monofilaments per inch, respectively. The embryonic wet web is transferred from the Fourdrinier wire, at a fiber consistency of about 15% at the point of transfer, to a conventional felt. Further de-watering is accomplished by vacuum assisted drainage until the web has a fiber consistency of about 35%. The web is then adhered to the surface of a Yankee dryer. The fiber consistency is increased to an estimated 96% before the dry creping the web with a doctor blade. The doctor blade has a bevel angle of about 25 degrees and is positioned with respect to the Yankee dryer to provide an impact angle of about 81 degrees; the Yankee dryer is operated at about 800 fpm (feet per minute) (about 244 meters per minute). The dry web is formed into roll at a speed of 700 fpm (214 meters per minutes).

Two plies of the web are formed into tissue paper products and laminating them together using ply bonded technique. The tissue paper has about 23 #/3M Sq. Ft. basis weight, contains about 0.1% of the substantially waterless self-emulsifiable chemical softener mixture and about 0.1% of the dry strength resin. Importantly, the resulting tissue paper is soft, absorbent and is suitable for use as a facial and/or toilet tissues.



THIS SHEET HAS BEEN
REPLACED

REPLACEMENT SHEET

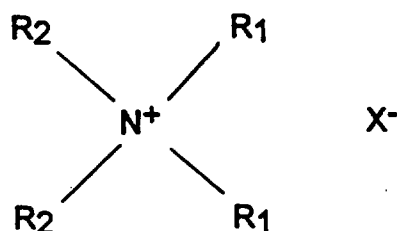
26 AUG 1996

34

What is claimed is:

1. A substantially waterless self-emulsifiable chemical softening composition characterized in that it comprises a mixture of:

(a) a quaternary ammonium compound having the formula



wherein each R₂ substituent is a C1 - C6 alkyl or hydroxyalkyl group, or mixture thereof, preferably C1 - C3 alkyl, most preferably methyl; each R₁ substituent is a C14 - C22 hydrocarbyl group, or mixture thereof, preferably C16 - C18 alkyl; and X⁻ is a suitable anion, preferably chloride or methyl sulfate; and

(b) a polyhydroxy compound selected from glycerol, polyglycerols having a weight average molecular weight of from 150 to 800 and polyoxyethylene glycols and polyoxypropylene glycols having a weight average molecular weight from 200 to 4000, preferably from 200 to 1000, most preferably from 200 to 600;

wherein the weight ratio of the quaternary ammonium compound to the polyhydroxy compound ranges from 1 : 0.1 to 0.1 : 1, preferably from 1:0.3 to 3:1, most preferably from 1:0.7 to 0.7:1, wherein said polyhydroxy compound is mixed with said quaternary ammonium compound at a temperature wherein said quaternary ammonium compound and said polyhydroxy compound are miscible, and wherein the moisture content of said chemical softening composition is less than 20 % by weight.

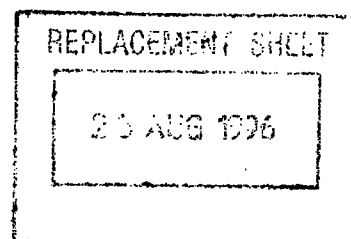
2. The substantially waterless self-emulsifiable chemical softening composition of Claim 1 wherein the chemical softening composition is a stable, homogenous, solid or viscous fluid at a temperature of greater than 20°C.

This Sheet Has Been Replaced





THIS SHEET HAS BEEN
REPLACED



35

3. The substantially waterless self-emulsifiable chemical softening composition of Claim 1 or 2 wherein the quaternary ammonium compound is di(hydrogenated)tallow dimethyl ammonium chloride or di(hydrogenated)tallow dimethyl ammonium methyl sulfate.
4. The substantially waterless self-emulsifiable chemical softening composition of any of Claims 1 - 3 wherein the quaternary ammonium compound is mixed with the polyhydroxy compound at a temperature of at least 40°C, preferably from 56°C to 68°C.
5. The substantially waterless self-emulsifiable chemical softening composition of any of Claims 1 - 4 wherein said quaternary ammonium compound is in a liquid-crystal state or in a liquid state when mixed with said polyhydroxy compound.
6. An aqueous dispersion comprising the substantially waterless self-emulsifiable chemical softening composition of any of Claims 1 - 5 and an aqueous media wherein said homogenous mixture of said quaternary ammonium compound and said polyhydroxy compounds self-disperses in said aqueous media to form a sub-micron vesicle dispersion.
7. The aqueous dispersion of Claim 6 wherein the temperature of the aqueous media is at least 20°C.
8. The aqueous dispersion of Claim 6 or 7 wherein said homogenous mixture of quaternary ammonium and polyhydroxy compounds is in a solid state before being dispersed in said aqueous media.
9. The aqueous dispersion of Claim 6 or 7 wherein said homogenous mixture of quaternary ammonium and polyhydroxy compounds is in a liquid state before being dispersed in said aqueous media.
10. The substantially waterless self-emulsifiable chemical softening composition of any of Claims 1 - 5 wherein the moisture content of said chemical softening is less than 10 % by weight.

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

REPLACEMENT SHEET

26 AUG 1996

36

**WATERLESS SELF-EMULSIFIABLE CHEMICAL
SOFTENING COMPOSITION USEFUL IN FIBROUS
CELLULOSIC MATERIALS**

ABSTRACT

Substantially waterless self-emulsifiable chemical softening compositions are provided comprising a mixture of a quaternary ammonium compound and a polyhydroxy compound. Preferred quaternary ammonium compounds include dialkyl dimethyl ammonium salts such as di(hydrogenated)tallow dimethyl ammonium chloride, di(hydrogenated)tallow dimethyl ammonium methyl sulfate. Preferred polyhydroxy compounds are selected from the group consisting of glycerol, polyglycerols having a weight average molecular weight of from about 150 to about 800 and polyoxyethylene glycols and polyoxypropylene glycols having a weight average molecular weight from about 200 to 4,000. The substantially waterless self-emulsifiable chemical softening compositions are prepared by mixing the quaternary ammonium compound with the polyhydroxy compound at a specific temperature range wherein the polyhydroxy compound is miscible with the quaternary ammonium compound. The resulting stable solid or concentrated fluid mixture can then be economically shipped to the consumer or ultimate user. The ultimate users of the chemical softening composition simply dilute the mixture with a liquid carrier (e.g., water) to form an aqueous dispersion suitable for treating fibrous cellulosic materials. The substantially waterless self-emulsifiable chemical softening compositions disclosed herein are primarily intended for softening disposable paper products such as tissues and towels.

This Sheet Has Been Replaced



THIS SHEET HAS
BEEN REPLACED

REPLACEMENT SHEET
26 AUG 1955

1/4

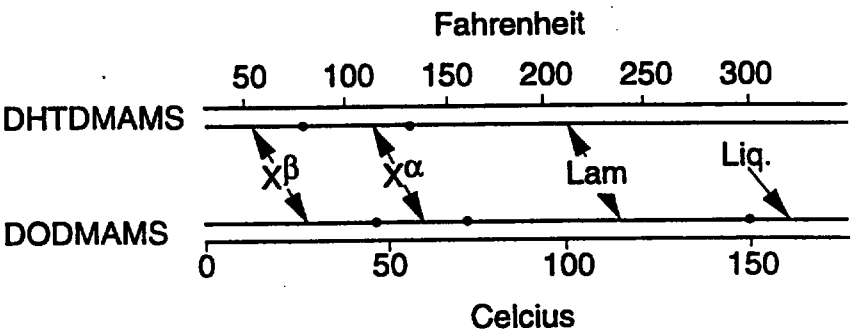


Fig. 1

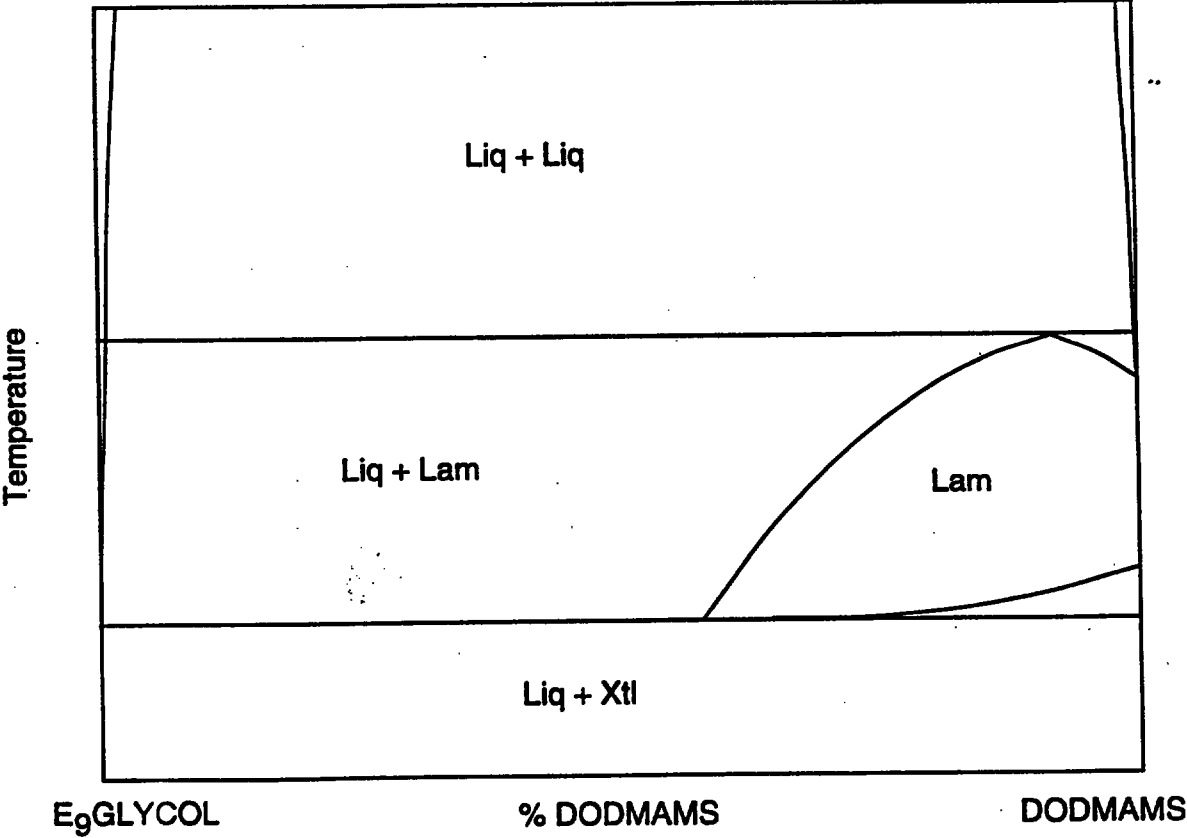


Fig. 2

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

REPLACEMENT SHEET

23 AUG 1996

2/4



Fig. 3

This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

REPLACEMENT SHEET
26 AUG 1996

3/4

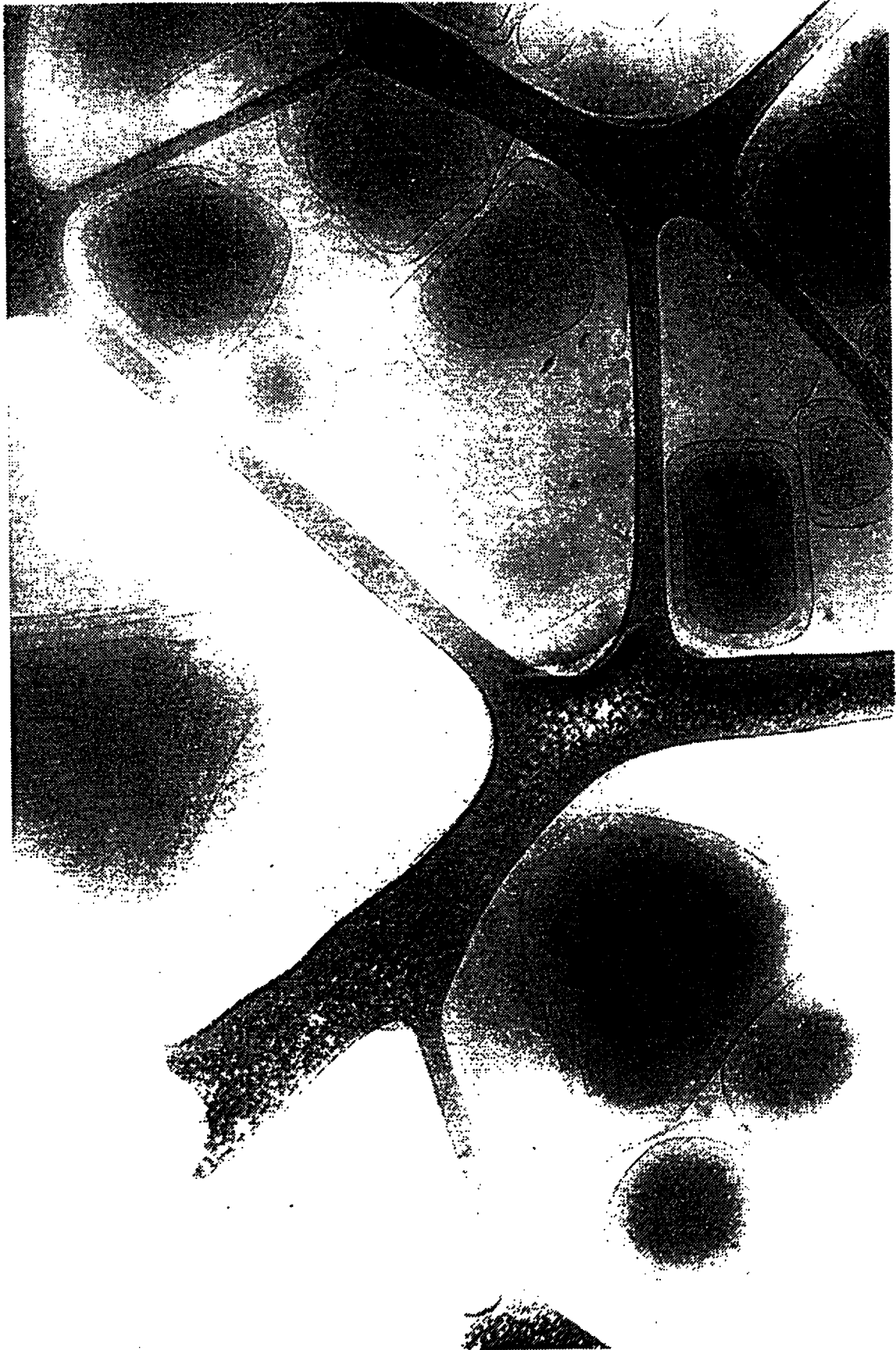


Fig. 4

This Sheet Has Been Replaced



This Sheet Has Been Replaced



THIS SHEET HAS BEEN
REPLACED

REPLACEMENT SHEET

26 AUG 1996

4/4



Fig. 5

3-620000

REPLACEMENT SHEET

16 DEC 1996

1/4

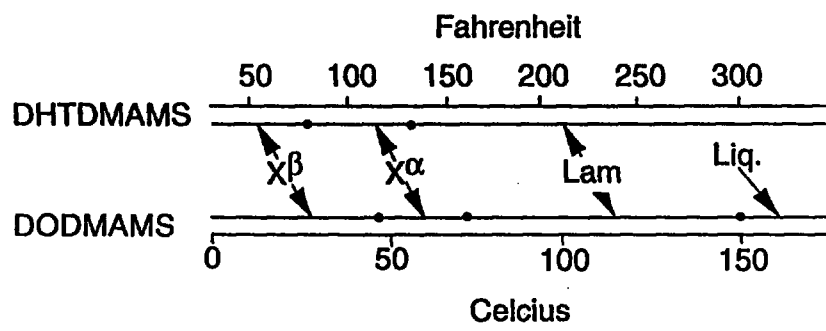


Fig. 1

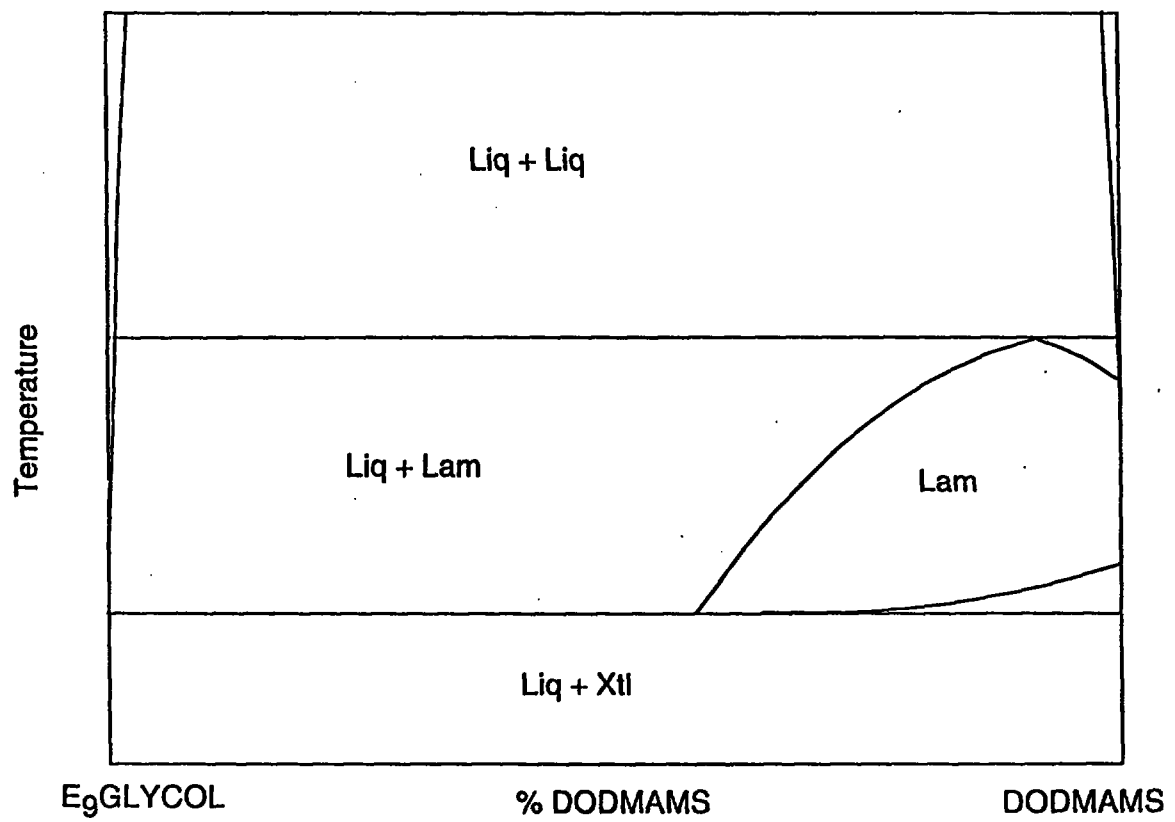


Fig. 2

X-6009-229

16 DEC 1996

2/4



Fig. 3

16 DEC 1996

3/4

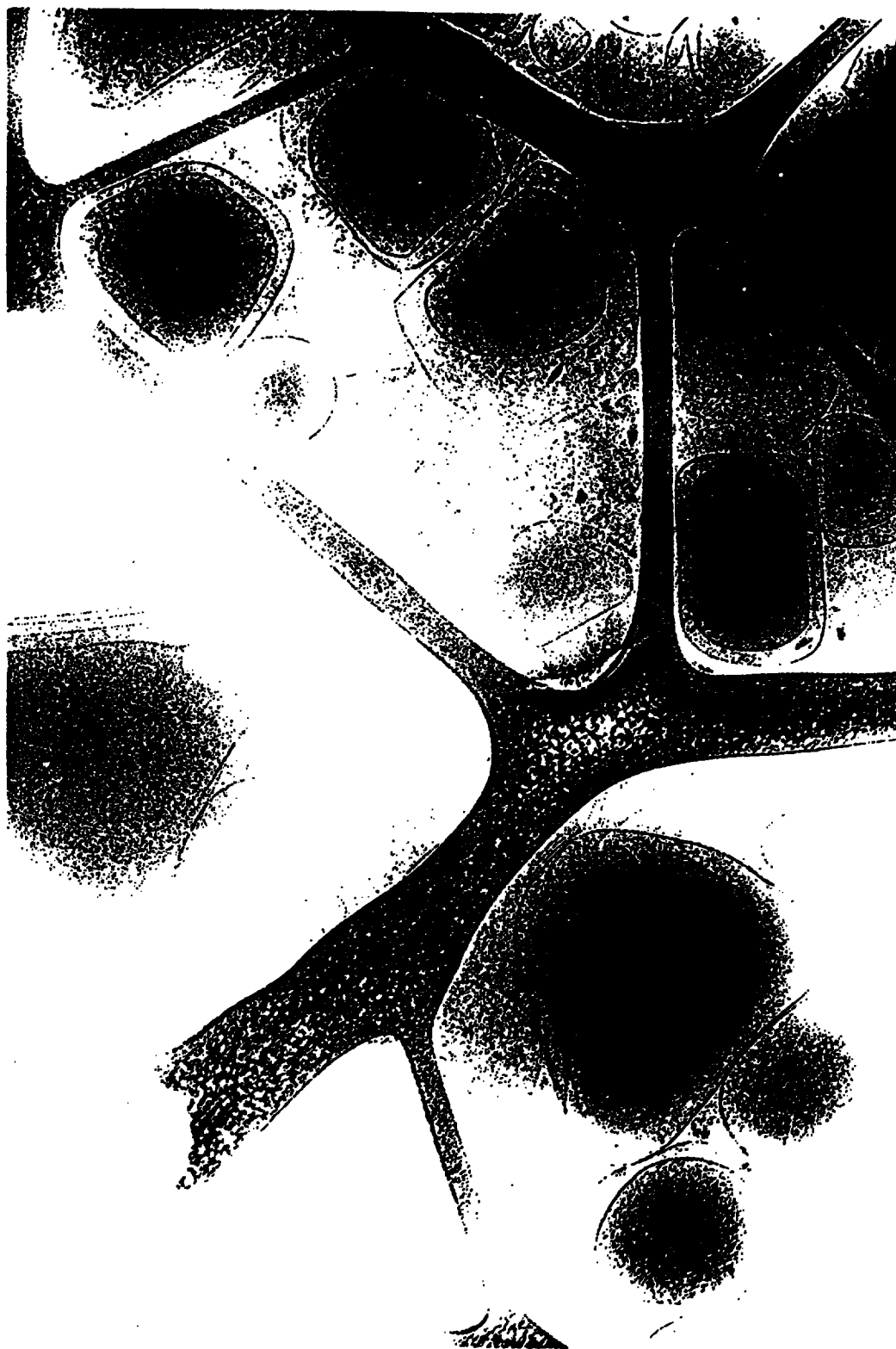


Fig. 4

16 DEC 1996

4/4



Fig. 5

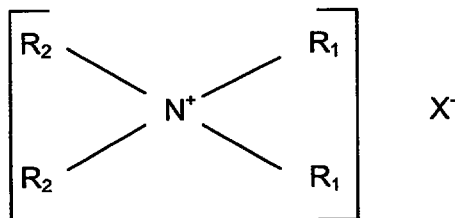


16 NOV 1999

What is claimed is:

1. A substantially waterless self-emulsifiable chemical softening composition for tissue paper webs consisting essentially of a mixture of:

(a) a quaternary ammonium compound having the formula



wherein each R_2 substituent is a C1-C6 alkyl or hydroxyalkyl group, or mixture thereof; each R_1 substituent is a C14-C22 hydrocarbyl group, or mixture thereof; and X^- is a suitable anion; and

- (b) a polyhydroxy compound selected from the group consisting of glycerol, polyglycerols having a weight average molecular weight of from about 150 to about 800 g/mole and polyoxyethylene glycols and polyoxypropylene glycols having a weight average molecular weight from about 200 to 4000 g/mole;

wherein the weight ratio of the quaternary ammonium compound to the polyhydroxy compound ranges from about 1:0.1 to 0.1:1, wherein said polyhydroxy compound is mixed with said quaternary ammonium compound at a temperature wherein said quaternary ammonium compound and said polyhydroxy compound are miscible, and wherein the moisture content of said chemical softening composition is less than about 20% by weight; and wherein the chemical softening composition is a stable, homogenous, solid or viscous fluid and wherein the composition is free of wet strength resins.

2. The substantially waterless self-emulsifiable chemical softening composition of claim 1 wherein each R_2 is selected from C1-C3 alkyl and each R_1 is selected from C16-C18 alkyl.
3. The substantially waterless self-emulsifiable chemical softening composition of claim 2 wherein each R_2 is methyl.



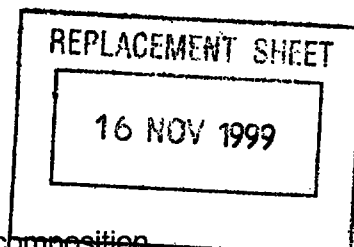
16 NOV 1999

4. The substantially waterless self-emulsifiable chemical softening composition of claim 1 wherein X⁻ is chloride or methyl sulfate.
5. The substantially waterless self-emulsifiable chemical softening composition of claim 3 wherein the quaternary ammonium compound is di(hydrogenated)tallow dimethyl ammonium chloride.
6. The substantially waterless self-emulsifiable chemical softening composition of claim 3 wherein the quaternary ammonium compound is di(hydrogenated)tallow dimethyl ammonium methyl sulfate.
7. The substantially waterless self-emulsifiable chemical softening composition of claim 6 wherein the polyhydroxy compound is miscible with the di(hydrogenated)tallow dimethyl ammonium methyl sulfate in the liquid-crystal phase.
8. The substantially waterless self-emulsifiable chemical softening composition of claim 5 wherein the polyhydroxy compound is miscible with the di(hydrogenated)tallow dimethyl ammonium chloride in the liquid phase.
9. The substantially waterless self-emulsifiable chemical softening composition of claim 1 wherein said polyhydroxy compound is a polyoxyethylene glycol having a weight average molecular weight from about 200 to about 1000 g/mole.
10. The substantially waterless self-emulsifiable chemical softening composition of claim 1 wherein said polyhydroxy compound is a polyoxypropylene glycol having a weight average molecular weight from about 200 to about 1000 g/mole.
11. The substantially waterless self-emulsifiable chemical softening composition of claim 1 wherein said polyhydroxy compound is glycerol.
12. The substantially waterless self-emulsifiable chemical softening composition of claim 1 wherein said polyhydroxy compound is a mixture of glycerol and polyoxyethylene glycol having a weight average molecular weight from about 200 to 1000 g/mole.



16 NOV 1999

13. The substantially waterless self-emulsifiable chemical softening composition of claim 1 wherein the weight ratio of the quaternary ammonium to the polyhydroxy compound ranges from about 1:0.3 to 0.3:1.
14. The substantially waterless self-emulsifiable chemical softening composition of claim 12 wherein the weight ratio of the quaternary ammonium to the polyhydroxy compound ranges from about 1:0.7 to 0.7:1.
15. The substantially waterless self-emulsifiable chemical softening composition of claim 1 wherein the quaternary ammonium compound is mixed with the polyhydroxy compound at a temperature of at least 40° C.
16. The substantially waterless self-emulsifiable chemical softening composition of claim 15 wherein the quaternary ammonium compound is mixed with the polyhydroxy compound at a temperature ranging from about 56° C. to 68° C.
17. The substantially waterless self-emulsifiable chemical softening composition of claim 9 wherein the polyhydroxy compound is polyoxyethylene glycol having a molecular weight of from about 200 to about 600 g/mole.
18. The substantially waterless self-emulsifiable chemical softening composition of claim 10 wherein the polyhydroxy compound is polyoxypropylene glycol having a molecular weight of from about 200 to about 600 g/mole.
19. The substantially waterless self-emulsifiable chemical softening composition of claim 17 wherein the weight ratio of the quaternary ammonium compound to the polyhydroxy compound ranges from about 1:0.7 to 0.7:1.
20. The substantially waterless self-emulsifiable chemical softening composition of claim 18 wherein the weight ratio of the quaternary ammonium compound to the polyhydroxy compound ranges from about 1:0.7 to 0.7:1.
21. The substantially waterless self-emulsifiable chemical softening composition of claim 11 wherein the weight ratio of the quaternary compound to the polyhydroxy compound ranges from 1:0.7 to 0.7:1.



22. The substantially waterless self-emulsifiable chemical softening composition of claim 1 wherein said quaternary ammonium compound is in a liquid-crystal state when mixed with said polyhydroxy compound.
23. The substantially waterless self-emulsifiable chemical softening composition of claim 1 wherein said quaternary ammonium compound is in a liquid state when mixed with said polyhydroxy compound.
24. The substantially waterless self-emulsifiable chemical softening composition of claim 12 wherein the weight ratio of glycerol to polyoxyethylene glycol ranges from about 10:1 to 1:10.
25. The substantially waterless self-emulsifiable chemical softening composition of claim 22 wherein said quaternary ammonium compound forms a homogenous mixture when mixed with said polyhydroxy compound.
26. The substantially waterless self-emulsifiable chemical softening composition of claim 23 wherein said quaternary ammonium compound forms a homogenous mixture when mixed with said polyhydroxy compound.
27. An aqueous dispersion comprising the substantially waterless self-emulsifiable chemical softening composition of claim 22 and an aqueous media wherein said homogenous mixture of said quaternary ammonium compound and said polyhydroxy compounds self-disperses in said aqueous media to form a sub-micron vesicle dispersion.
28. An aqueous dispersion comprising the substantially waterless self-emulsifiable chemical softening composition of claim 23 and an aqueous media wherein said homogenous mixture of said quaternary ammonium compound and said polyhydroxy compounds self-disperses in said aqueous media to form a sub-micron vesicle dispersion.
29. The aqueous dispersion of claim 27 wherein the temperature of the aqueous media is at least about 20° C.
30. The aqueous dispersion of claim 28 wherein the temperature of the aqueous media is at least about 20° C.



REPLACEMENT SHEET

16 NOV 1999

31. The aqueous dispersion of claim 27 wherein said homogenous mixture of quaternary ammonium and polyhydroxy compounds is in a solid state before being dispersed in said aqueous media.
32. The aqueous dispersion of claim 28 wherein said homogenous mixture of quaternary ammonium and polyhydroxy compounds is in a solid state before being dispersed in said aqueous media.
33. The aqueous dispersion of claim 31 wherein said homogenous mixture of quaternary ammonium and polyhydroxy compounds is in a liquid state before being dispersed in said aqueous media.
34. The aqueous dispersion of claim 33 wherein said homogenous mixture of quaternary ammonium and polyhydroxy compounds is in a liquid state before being dispersed in said aqueous media.
35. The substantially waterless self-emulsifiable chemical softening composition of claim 1 wherein the moisture content of said chemical softening is less than about 10% by weight.

16 NOV 1999

**WATERLESS SELF-EMULSIFIABLE CHEMICAL
SOFTENING COMPOSITION USEFUL IN FIBROUS
CELLULOSIC MATERIALS**

ABSTRACT

Substantially waterless self-emulsifiable chemical softening compositions are provided comprising a mixture of a quaternary ammonium compound and a polyhydroxy compound. Preferred quaternary ammonium compounds include dialkyl dimethyl ammonium salts such as di(hydrogenated)tallow dimethyl ammonium chloride, di(hydrogenated)tallow dimethyl ammonium methyl sulfate. Preferred polyhydroxy compounds are selected from the group consisting of glycerol, polyglycerols having a weight average molecular weight of from about 150 to about 800 and polyoxyethylene glycols and polyoxypropylene glycols having a weight average molecular weight from about 200 to 4,000. The substantially waterless self-emulsifiable chemical softening compositions are prepared by mixing the quaternary ammonium compound with the polyhydroxy compound at a specific temperature range wherein the polyhydroxy compound is miscible with the quaternary ammonium compound. The resulting stable solid or concentrated fluid mixture can then be economically shipped to the consumer or ultimate user. The ultimate users of the chemical softening composition simply dilute the mixture with a liquid carrier (e.g., water) to form an aqueous dispersion suitable for treating fibrous cellulosic materials. The substantially waterless self-emulsifiable chemical softening compositions disclosed herein are primarily intended for softening disposable paper products such as tissues and towels.