United States Patent

[11] 3,617,439

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[54] **PROCESS FOR IMPROVING COMMINUTION PULP SHEETS AND RESULTING AIR-LAID ABSORBENT PRODUCTS**
9 Claims, No Drawings

[52] **U.S. Cl.** **162/158,** 128/284, 162/179, 252/DIG. 7, 260/404, 260/501.15, 264/121
[51] **Int. Cl.** **D21d 3/00**
[50] **Field of Search** 260/501.15, 404, 501.13, 248.5; 162/158, 179; 128/284; 252/DIG. 7

[56] **References Cited**

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Schwarty and Perry, Surface Active Agents, 1949 p. 172.

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ABSTRACT: A method for producing comminution pulp sheets from cellulosic fibers and the products resulting therefrom as pulp sheets and air-laid absorbent batts, which method comprises impregnating the fibers of the comminution pulp sheets with about 0.1 to 2 percent of a selected zwitterionic surfactant, such as N-octadecyl -N, N- dimethylammonio-12-dodecanoate either in slurry prior to or during comminution pulp sheet formation and prior to pulp sheet drying. The resulting comminution pulp sheet is easily and effectively fiberized or comminuted to yield fibers from which air-laid absorbent products are prepared, and the air-laid absorbent products are characterized by improved bulk, resiliency and absorbency characteristics.

PROCESS FOR IMPROVING COMMINUTION PULP SHEETS AND RESULTING AIR-LAID ABSORBENT PRODUCTS

BACKGROUND OF THE INVENTION

This invention relates to processes for the manufacture of comminution pulp sheets comprised of cellulosic fibers and intended for subsequent comminution and air laying to form absorbent fibrous batts, pads, or sheets. The absorbent fibrous batts, pads, or sheets are used in the structures of bandages, diapers, sanitary napkins, tampons and like articles. More particularly, the invention relates to the fibrous impregnation of such comminution pulp sheets with selected zwitterionic surfactants whereby the pulp sheets are rendered easily comminutable into predominantly whole fibers. The air-laid batts formed therefrom substantially retain the absorbency characteristics of conventional unimpregnated pulp sheets and by meaningful use tests exceed the fluid inhibition and resiliency of such air-laid batts prepared from fibers derived from unimpregnated comminution pulp sheets. The fibrous impregnation in the present invention is effected prior to final dewatering of the pulp sheet in sheet formation.

Specifically, the present invention consists of a method for impregnating the fibers of a comminution pulp sheet comprised of wood fibers or other cellulosic fibers with effective amounts of nitrogen containing zwitterionic surfactants more fully described below by means of structure and chemical nomenclature specification.

Air laying, or the process consisting of comminuting or fiberizing pulp sheets to form a mass of individual fibers dispersed in air and subsequent deposition of fibers on a foraminous screen to form a batt, pad, or sheet has long been practiced with varying degrees of success. The air-laid batts, pads, or sheets have been accorded cohesiveness by various means including cohesive pressing, soluble glue spraying, latex dipping and thermal setting, where thermoplastic fibers were involved.

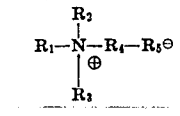
In particular, such air-laid products, because of the economies involved in the relatively simple process of fiberizing and reconstituting pulp sheets to form absorbent batts or pads by the air lay method, have been widely used in absorbent products of a disposable nature as set forth above. The comminution of cellulosic fiber pulp sheets, and in particular wood pulp sheets, has in practice been troublesome in the respect of requiring large amounts of power, producing high noise levels and resulting in large amounts of broken fibers and fines rather than the desired long whole fibers.

One solution to the foregoing problems is found in U.S. Pat. No. 3,395,708, issued to Laurence R. B. Hervey and Donald K. George on Aug. 6, 1968, which patent discloses and claims the use of a specific class of cationic debonding agents to result in a comminution-prone woodpulp sheet. While it is true that certain benefits in ease of comminution and in resultant air-laid product characteristics result from use of the cationic debonding agents disclosed and claimed by the aforementioned patent, applicant has found that the cationic debonding agents, for example dimethyl dihydrogenated tallow quaternary ammonium chloride, achieve comminution ease in a woodpulp sheet at a considerable disadvantage to both absorbent rate and total absorbent capacity in subsequent air-laid products. In fact, and although a woodpulp sheet without surfactant impregnation is difficult to comminute or fiberize in the preparation of air-carried fibrous masses to be deposited on foraminous media in the air-laid process, the characteristics of both absorbent rate and absorbent capacity of an air-laid pad prepared from such material is in fact superior to that prepared from woodpulp sheets impregnated with a cationic debonding agent.

Most assuredly the comminution-promoting effect of the cationic debonding agents disclosed in the aforementioned patent and in the paper literature constitutes an improvement over the use of unimpregnated woodpulp sheets. However, applicant has discovered that the impregnation of woodpulp and other cellulosic sheets with zwitterionic surfactants having particular structures imparts comminution ease to wood pulp sheets, which comminution ease is essentially equivalent to that imparted by the cationic debonding agents, while substantially retaining and improving in several respects the absorbent product characteristics of unimpregnated woodpulp sheets.

SUMMARY OF THE INVENTION

Inasmuch as pulp sheets having a predilection toward easy comminution into whole fibers were desired for use in the manufacture of various types of absorbent air-laid batts, pads, and sheets, applicant investigated his initial discovery that certain zwitterionic surfactants when used as impregnants for woodpulp sheets did improve the ease and completeness of comminution or fiberization to a surprisingly high degree without engendering an attentant prohibitive loss in subsequent air-laid pad absorbency. Applicant discovered that the desired ease of comminution, with attendant and subsequent air-laid pad absorbency can be achieved by impregnating woodpulp sheets prior to final dewatering in the formation process with a zwitterionic surfactant having the general structure:



wherein R_1 is an alkyl or alkenyl group containing about 16 to about 22 carbon atoms, R_2 and R_3 are selected from the group consisting of hydrogen and alkyl groups containing one to two carbon atoms, R_4 is an alkylene group containing one to about 11 carbon atoms, which alkylene group can have one or more hydroxyl groups attached to carbon atoms, and R_5 is selected from the group consisting of $-COO^1$, $-SO_3^1$, and $-OSO_3^1$.

In air-laid absorbent pads, applicant was surprised to discover that the use of the aforementioned zwitterionic surfactants as impregnants for woodpulp and other cellulosic fiber sheets resulted in improving their comminution characteristics while providing excellent power requirement and total absorptive capacity characteristics with regard to both cationic impregnated woodpulp sheets and woodpulp sheets devoid of any surfactant. The use of zwitterionic surfactants is also enhanced, particularly in instances where batt or pad clarity or color is a desirable feature, by the fact that the present zwitterionic surfactants form clear or water-white solutions for sheet impregnation. While the present process and resultant products are primarily described in terms of wood fiber absorbent pads, it is specifically noted that the attendant benefits will accrue to comminution pulp sheets prepared from other cellulosic fibers or admixtures of other cellulosic fibers with wood fibers. Additionally, the ease of comminution effects of the present invention are applicable to processes other than the preparation of air-laid absorbent structures wherein pulp sheets are comminuted, for example in the preparation of viscose rayon by the slurry process, the preparation of the cellulose nitrate, the preparation of cellulose acetate and other cellulose derivatives.

Applicant was further surprised to find that the use of the disclosed zwitterionic surfactants can be carried out, not only by their introduction into fiber slurries prior to sheet formation, but by displacement of the water contained in a sheet of pulp as first formed with a displacement wash or shower on the forming wire. The displacement shower is comprised of an aqueous solution of the selected zwitterionic surfactant. The displacement shower system of sheet impregnation offers desirable advantages in that it effects economy in surfactant use, since only the displacement shower water system and not the entire white water or slurry water systems of a paper machine must be loaded with surfactant. Further advantages

accrue from displacement showering in that changes to nonimpregnated woodpulp sheets are easily effected because the entire white water system of the paper machine is not surfactant loaded.

A principal object of this invention is, accordingly, to provide woodpulp sheets for comminution and later formation into air-laid absorbent pads of various types and methods for their production, which cellulose sheets are impregnated with the zwitterionic surfactants disclosed herein.

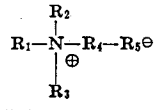
A further objective of the present invention is to provide zwitterionic surfactant impregnated woodpulp sheets for comminution and later deposition to form air-laid absorbent pads, which woodpulp sheets exhibit a surprising ease of comminution to form fibers for deposition into air-laid absorbent pads having improved absorbent characteristics.

Another object of this invention is to provided improved air-laid batts, pads, and sheets, for catamenial tampons, sanitary napkins, surgical dressings, disposable diapers and other absorbent pads and fibrous structures, prepared from woodpulp sheets impregnated with the herein disclosed zwitterionic surfactants.

Yet another object of the invention is to provide comminution pulp sheets which are easily reduced to individual fibers for use in the production of cellulose chemicals and cellulose derivatives.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In general, applicant has found that the foregoing objectives can be met, as before stated, by impregnating an otherwise suitable woodpulp sheet prior to substantial water removal or drying with zwitterionic surfactants having the general structure:



wherein R_1 is an alkyl or alkenyl group containing about 16 to about 22 carbon atoms, R_2 and R_3 are selected from the group consisting of hydrogen and alkyl groups containing one to two carbon atoms, R_4 is an alkylene group containing one to about 11 carbon atoms, which alkylene group can have one or more hydroxyl groups attached to carbon atoms, and R_5 is selected from the group consisting of $-COO^1$, $-SO_3^1$, and $-OSO_3^1$.

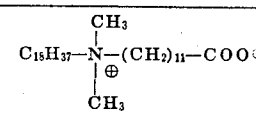
As stated and inferred hereinbefore, impregnation of the woodpulp sheets in the present sense envisions the introduction of effectively distributed amounts of the herein disclosed zwitterionic surfactants to the fibers of a woodpulp sheet during sheet formation and prior to substantial water removal and drying. It is noted that comminution pulp sheets in general have a fairly high basis weight and thickness, for example a comminution pulp sheet can have a basis weight of about 200 lbs. per ream of 500 sheets measuring 19 inches by 24 inches, and a thickness of about 0.050 inches, although the present fiberization and absorbency effects will be noted in comminution pulp sheets of other basis weights and thicknesses. Impregnation can be accomplished by adding the requisite amounts of zwitterionic surfactant to holding tanks or head boxes prior to sheet formation, however, this method of addition is considered wasteful of the relatively high-priced surfactants and is detrimental to continued paper formation in that the entire white water system of the paper machine is inevitably contaminated with surfactant. Applicant has found that one excellent means of addition is that of adding the zwitterionic surfactants of this invention by showering an aqueous solution of the selected zwitterionic surfactant, using about 2 lbs. to about 6 lbs. of solution per lb. of pulp (the solution containing about 2000 lbs. of water to about 1 lb. active surfactant) onto a comminution pulp sheet traveling on the forming wire of a paper machine prior to substantial dewatering in the formation process. A preferred method of spray addition, in order to effect good surfactant distribution, is to direct a distributed system of flooding nozzles to impinge the surfactant solution upon the head box side of a dandy roll mounted in operative position above the forming wire. An alternate system is to use a well-distributed system of nonwashing sprays to accomplish surfactant addition.

This is to say that the zwitterionic surfactant addition point can be prior to, over, or following an initial formation vacuum box or dewatering device and can be prior to or within a dandy roll which is positioned prior to subsequent vacuum boxes. These methods of zwitterionic surfactant addition are preferred in order to achieve a uniform distribution of the zwitterionic surfactant across and through the formed sheet and allow, as an additional benefit, adequate displacement of the initial water associated with the formed sheet by the zwitterionic surfactant solution. Other systems for application of the zwitterionic surfactants to comminution pulp sheets will also be effective, if good distribution is achieved.

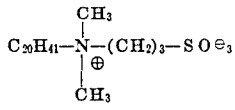
Applicant states that effective amounts of zwitterionic surfactant addition can be about 0.1 percent to about 2.0 percent preferably 0.2 percent, based on the weight of "active" zwitterionic surfactant applied and the weight of bone dry pulp. Additions of less than about 0.1 percent by weight of zwitterionic surfactant to pulp sheets do not fully develop the improvement in comminution. Additions of zwitterionic surfactant of more than about 2.0 percent by weight do not contribute further substantial improvement to fiberization or to the absorbent characteristics of subsequently formed air-laid absorbent pads.

While applicant has not completely explained the mechanism by which the presently disclosed zwitterionic surfactants accomplish their beneficial action and further does not wish to be bound by theory, a general and simplified explanation is that the fibrous surfaces and surfactant are attracted together by electrical forces operating in the aqueous phase of the pulp slurry. The absorption, chemisorption, or substantive reaction which follows such attraction blocks bonding sites which would otherwise result in "hydrogen bonds" in the finally dried pulp sheets. In this manner the zwitterionic surfactant is attracted to the fiber surfaces, and the subsequent sheet strength or fiberization characteristics are an indication of the ability of the surfactant to (1) migrate to the fiber, (2) attach to the fiber, and (3) prevent hydrogen or other bonding mechanisms which normally result in the cohesion of fibers to form the type of fibrous sheets which are referred to collectively as paper. It is likely that the zwitterionic surfactants, due to their structure, provide a larger number of substantive bonds of lesser strength on fibers and provide fibers of lower surface hydrophobicity than do cationic surfactants.

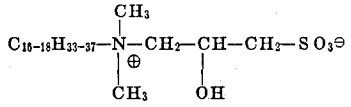
Having stated that the disclosed zwitterionic surfactants give rise to improved ease of comminution in comminution pulp sheets, applicant reemphasizes that incorporation of the zwitterionic surfactants in comminution pulp results in subsequent air-laid absorbent pads having the general characteristics of substantially improved absorbency and loft or bulk properties relative to air-laid absorbent pads prepared from either untreated woodpulp fibers or cationic impregnated wood fibers. Suitable examples of specific zwitterionic surfactants for use in the present invention are:

Chemical name	Structure
(1) N-octadecyl-N,N-dimethylammonio-12-dodecanoate.	

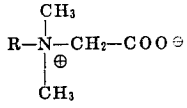
(2) N-eicosyl-N,N-dimethylammonio-3-propane-1-sulfonate.



(3) N-tallowalkyl-N,N-dimethylammonio-2-hydroxy-3-propane-1-sulfonate.

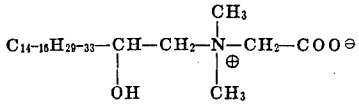


(4) N-C_{16}-C_{18}alkyl (and alkenyl)-N,N-dimethylammonioacetate.

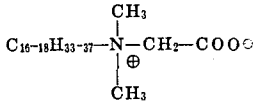


(Where the alkyl and alkenyl R group=60% $C_{18}H_{33}$, 20% $C_{18}H_{35}$, 5% $C_{18}H_{37}$, 15% $C_{16}H_{33}$

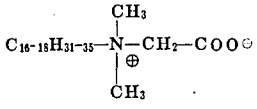
(5) N-(2-hydrozy,C_{16}=C_{18} alkyl)-N,N-dimethylammonioacetate.



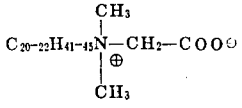
(6) N-tallowalkyl-N,N-dimethylammonioacetate.....



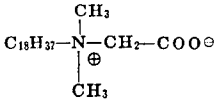
(7) N-soyaalkyl (and alkenyl)-N,N-dimethylammonioacetate.



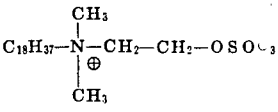
(8) N-eicosyl (and docosyl)-N,N-dimethylammonioacetate.



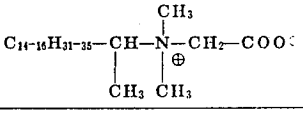
(9) N-octadecyl-N,N-dimethylammonioacetate.....



(10) N-octadecyl-N,N-dimethylammonioethylsulfate.



(11) N-(1-methyl,C_{16}-C_{18}alkyl)-N,N-dimethylammonioacetate.



In testing the comminution pulps prepared according to the process of the present invention, applicant has made use of several definitive testing procedures. These are designated as the Quick Disintegration, Tappi T-233 (Clark Classification), Absorptive Capacity, Cellulose Absorbency (drip method), Bulk Fiber Sink, Wicking (embossed fiber batts) and Loft tests.

In the Quick Disintegration test, pulp sheet samples are conditioned over night at 50 percent relative humidity and 72° F. The conditioned pulp sheet samples are then cut into 1 inch by 1 inch squares. A whole number of squares weighing 10 to 12 grams is weighed and the weight recorded to constitute a sample. The weighed sample of 1 inch by 1 inch squares is placed into a Waring Blender (Model No. CB-5) with dull blades and whizzed at the lowest speed (16,500 r.p.m.) for 15 seconds. The resulting fibers are placed, without densification, on the top of a standard 14-mesh screen placed between two airtight chambers. Compressed air is introduced into the top chamber to violently agitate, but not further comminute the fibers, while the lower chamber is provided with a vacuum system for removing fibers which pass through the screen. The compressed air and vacuum system acting in conjunction provide a 52 mm. Hg differential through the screen, which pressure differential is applied for 2 minutes. The fraction of fiber remaining on the top of the 14-mesh screen and the fraction falling through are then recovered and weighed. The percentage of total fiber weight remaining on the 14-mesh screen is recorded. At least two, and preferably 10, replicate Quick Disintegration tests are made, and their mathematical average is recorded as the test result.

The standard Tappi T-233 test method is a Clark fiber classification. As modified slightly by the applicant, this test is run as set forth in Tappi methods with the exception that a Clark classifier (Catalog No. 218-1, Ser. No. 18572) is employed in classification and the Clark method of classification is followed. The weight percentage of the sample retained on the standard 14-mesh screen is recorded as the test result.

The Absorptive Capacity test employed by applicant determines the absorptive capacity of air-laid pads in the as-formed state and under mild compression stress. The Absorptive Capacity test is carried out on a 5 inch by 5 inch stainless steel plate inclined at an angle of 15 percent with the horizontal. A 4 inch by 4 inch stainless steel cover plate, provided with weights to result in a total loading of 16 lbs., or 1 p.s.i., applied on a 4 inch by 4 inch sample placed between the plates, is also provided. In carrying out the test, applicant prepares eleven 4 inch by 4 inch air-laid pads whose basis weight varies in definite increments of 0.10 grams from 2.00 grams to 3.00 grams with an allowed tolerance in individual air-laid pads of ±0.02 grams. The weight of the individual pads is recorded as

W_1. For convenience in handling during testing, the air-laid pads are formed on a sheet of tissue, covered with a second tissue, and cohesively pressed in a dry state at 0.56 p.s.i. The basis weight and absorptive capacity of the covering tissue under loaded and unloaded test compressive conditions is determined by tissue tests performed on the same equipment. The basis weight and absorptive capacity of the covering tissue is cancelled out of the test results by the method used in test calculation.

In carrying out the Absorptive Capacity test each of the 11 prepared and weighed air-laid pads is open end, single wrapped with a 4 inch by 9 inch piece of 1 mm. thickness polyethylene film secured with pressure-sensitive tape. The wrapped sample is placed on a ⅛-inch thick, 5 inch by 5 inch hard rubber plate, and the weight of the rubber plate together with wrapped sample pad is recorded as W_2. The rubber plate with the wrapped sample thereon is placed on the inclined plate, so that the tape-secured side of the sample is up, and the open ends of the wrapped sample are aligned toward the top and bottom of the inclined plate. Distilled and aerated water from an overhead reservoir is distributed on the rubber plate above, outside of and running down into the top end of the wrapped sample at the rate of 500 ml. per minute for 1 minute. Then, beginning at the top and sides of the rubber plate, all excess water outside the wrapped sample is blotted up with absorbent blotting paper, taking care not to touch the wrapped sample pad on either open end. The rubber plate with wrapped sample thereon is then removed from the inclined plate, and the rubber plate is carefully wiped dry in a horizontal position. The weight of the dry rubber plate with wet wrapped sample is then recorded as W_3.

The rubber plate with wet wrapped sample thereon is immediately returned to its original position in the inclined plate, and the stainless steel cover plate is gently applied thereto to result in a 1 p.s.i. loading on the wet sample. The 1 p.s.i. cover plate loading is maintained for 45 seconds while excess water is blotted from the rubber plate, as detailed above. The stainless steel cover plate is then removed, and the rubber plate with wet sample thereon is again wiped dry in a horizontal position. The weight of the rubber plate with pressed wrapped wet sample thereon is recorded as W_4.

The rubber plate and pressed wrapped wet sample is immediately returned to its original position on the inclined plate and resaturated with 500 ml. of water for 1 minute, as was originally done. Again, the excess water on the rubber plate around the sample is blotted up with the previous precautions, and the rubber plate is wiped dry in a horizontal position. The final weight of the rubber plate with wet precompressed and resaturated wrapped sample thereon is recorded as W_5.

In the foregoing manner the initial zero load wet weight (W_3) the 1 p.s.i. loaded weight (W_4) and the precompressed zero load weight (W_5), with tare of tape secured polyethylene wrap, tissue and rubber plate are determined for the 11 samples.

The weight determinations $W_{1\text{-}5}$ are determined separately for the tissue used as covering for the tested air-laid pads so that the tissue absorptive capacity can be eliminated from the air-laid pad absorbent capacity in calculating the test results. The combined tissue bottom and top cover sheets (32 sq. in. per pad) used in the present determinations had a total weight of 0.39 grams. The absorptive capacity of the tissue under test conditions was 12.80 grams H_2O/gram tissue under initial zero p.s.i. loading, 5.52 grams H_2O/gram tissue under 1 p.s.i. loading and 9.23 grams H_2O/gram tissue under final zero p.s.i. loading. Having determined the $W_{1\text{-}5}$ weights for the 11 samples and separate tissue data, the absorptive capacity of the air-laid pads is calculated according to the following formulas, wherein:

W_1 = weight air-laid pad with tissue, grams

W_2 = weight polyethylene wrapped air-laid pad, tissue and rubber plate, grams

W_3 = initial zero p.s.i. wet weight of tissue-backed wrapped air-laid pad and rubber plate, grams

W_4 = 1 p.s.i. wet weight of tissue-backed wrapped air-laid pad and rubber plate, grams

W_5 = final zero p.s.i. wet weight of tissue-backed wrapped air-laid pad and rubber plate, grams

A_0 = absorptive capacity of air-laid pad alone under initial zero p.s.i. load, grams H_2O/gram of pad weight

A_1 = absorptive capacity of air-laid pad alone under initial 1 p.s.i. load, grams H_2O/gram of pad weight

A_f = absorptive capacity of air-laid pad alone under final zero p.s.i. load, grams H_2O/gram of pad weight

$$A_0 = \frac{(W_3 - W_2) - (0.39)(12.80)}{W_1 - 0.39}$$

$$A_1 = \frac{(W_4 - W_2) - (0.39)(5.52)}{W_1 - 0.39}$$

$$A_f = \frac{(W_5 - W_2) - (0.39)(9.32)}{W_1 - 0.39}$$

The determination of A_0, A_1, and A_f for the 11 samples is considered desirable versus a single determination. Statistical determinations on replicate tests have revealed that the 11-sample arrangement detailed above allows both paired T-test and average T-test determinations to be made for comparison of the various absorptive results to determine confidence limits; all of which confidence limits are in excess of 90 **percent and most of which exceed 99 percent**.

The Cellulose Absorbency test (drip method) is carried out by preparing three 4 inch by 4 inch tissue-backed, air-laid pads as for the Absorptive Capacity test above, except that the air-laid pad weights are not graduated and have a weight of about 2 grams to about 3 grams. The top and bottom tissue sheets are carefully stripped from the air-laid pads as prepared. The tissue weights and absorbent capacities are thereby eliminated from the calculations in this Cellulose Absorbency test; the weight in grams of the air-laid pad, without tissue covering, is recorded.

The prepared air-laid pad is then placed on a horizontally oriented and supported piece of ½-inch-square mesh, galvanized hardware cloth. An overhead gravity-flow reservoir containing aerated distilled water and equipped with a ¼-inch rubber tubing for delivery thereof is provided. The ¼-inch rubber tubing is provided with a pinch clamp which is adjusted to give a controlled flow rate of 60 ml. per minute. The waterflow is directed to the center of the horizontal sample from the tubing tip positioned 1 inch above the sample pad. Waterflow is continued until the first drop of water is observed to drip from the bottom side of the supported sample pad. The time elapsed in seconds between first waterflow and first drip is recorded and is equal to the grams of water absorbed by the pad under the Cellulose Absorbency test conditions. The test results are reported as grams H_2O absorbed per gram pad weight, as calculated by multiplying the seconds of waterflow by the grams of H_2O flowing per second to first drip and dividing the result by the weight of the sample pad in grams. The results for the three pads are calculated individually and mathematically averaged to record a test result. The Cellulose Absorbency test (drip method) constitutes a different procedural method for determining initial zero-loading absorptive capacity.

The Bulk Fiber Sink test measures the rate of water absorption into comminuted cellulose fibers at a bulk density of 0.05 grams/cubic centimeter. The selected cellulose bulk density is substantially equivalent to the bulk density of a cellulose fiber pad as formed in conventional air-laying procedures. The Bulk Fiber Sink test has advantage in that it is convenient, fast and reproducible to confidence limits of 99.9 percent.

In carrying out the Bulk Fiber Sink test a plexiglass tube having an ID of 1.5 inches, an OD of 1.75 inches and a length of 12 inches is fixed in a vertical position. The plexiglass tube is provided with a 20-mesh screen for foraminously closing its bottom end. The plexiglass tube is loaded with 16.9 grams of

comminuted cellulose fibers in a volume of 338 cubic centimeters to result in the test bulk density of 0.05 grams/cubic centimeter. Plexiglass tube loading is accomplished by taking small undensified increments of comminuted cellulose fibers and introducing them into the plexiglass tube to provide 16.9 grams of sample; the sample is then lightly compacted to result in the specified bulk density.

After tube loading, a 1,000 ml. graduated Pyrex cylinder is filled to the 800 ml. mark with distilled aerated water at 72 ± 2° F. The fiber-loaded plexiglass tube is then positioned vertically with its screen one-half inch above the water surface in the Pyrex graduated cylinder; the plexiglass tube is then released. The time in seconds from release to complete submersion of the compacted cellulose fibers within the plexiglass tube is recorded. Ten replicate tests are run with new fillings of distilled aerated water in the graduated cylinder and newly loaded comminuted fiber samples. The mathematical average of time for submersion in seconds for the 10 tests is recorded as the test result.

The Embossed Pad Wicking test measures the time for water to proceed under the impetus of capillary action along a vertically oriented zigzag linear embossed region, with a total length of 5.6 inches, in a tissue-backed air-laid pad. The zigzag embossed line has a width of about one-thirtysecond inch. The zigzag linear embossed region is formed by part of an enclosed rectilinear embossing pattern formed by two sets of parallel embossed lines. The embossed lines in each set are spaced 1 inch apart, and the intersections of the lines in the two sets have included angles of 53.2° and 126.8° where they cross. A sample cut to include an unbroken zigzag embossed line and oriented so that the 126.8° included angles are vertically opposed is held by a clip in a vertical position. The bottom one-eighth inch of the sample resides in an aerated distilled-water reservoir maintained at 72 ± 2° F. The time in seconds, from first dipping, for water to proceed vertically and upwardly by capillary action for a total vertical distance of 2.5 inches, along a zigzag embossed line length of 5.6 inches, is observed and recorded.

The tissue-covered air-laid pads for the Embossed Pad Wicking test are prepared in the same manner as pads for the Absorptive Capacity test with exception that six pads having a weight per 4 inch by 4 inch pad of 2 to 3 grams are prepared. These tissue-covered pads are then embossed with the pattern described above by use of an embossing platen on which the test pad and 0.002 inch metal shim for final plate clearance are laid. The pad is then pressed in a hydraulic press (Carver Press pressure of 20,000 p.s.i.g.) to emboss the pattern on the pad. The water is changed after each six samples, and the mathematical average time in seconds for the six samples is taken as the test result.

The Loft test, which determines the bulk density of an air-laid pad with tissue backing, is carried out by preparing 4 inch by 4 inch tissue-backed pads as in the Absorptive Capacity test, with the exception that 10 pads are prepared at a 2- to 3-gram tissue-backed pad weight. The 10 pads are stacked and the height measured. The volume is then taken as 4 inches × 4 inches × the stack height in inches and converted to cubic centimeters. The bulk density (neglecting the neglible volume of the thin tissue backing sheets) is equal to the weight of the 10-pad stack minus 3.9 grams of tissue weight divided by the determined volume in cubic centimeters. A lower bulk density figure is indicative of greater bulk or loft.

The cellulose fibers used to prepare air-laid pads in the foregoing test procedures can be prepared by hammer-milling comminution pulp sheets in a mill equipped with an 8-mesh screen plate and dull hammers to avoid fiber cutting. A Sprout-Waldron mill was also used effectively to prepare cellulose fibers for test purposes.

For comparative testing, comminution sheets of Southern pine bleached fiber woodpulp were formed and dried to have a basis weight, at a 5 percent by weight moisture content, of 210 lbs. per ream of 500 sheets measuring 19 inches by 24 inches. The sheet had an average thickness of 0.050 inches. During the formation of the pulp sheets on the Fourdrinier wire of the paper machine they were passed under a dandy roll, whereon a distribution system of showers delivered approximately 300 g.p.m. of an aqueous solution containing 0.0005 lbs. of active surfactant per pound of aqueous solution. This amount of surfactant resulted in a pulp sheet containing about 0.2 percent active surfactant by weight based on the weight of bone dry pulp. The paper machine sheet speed was 300 f.p.m. For comparison, comminution pulp sheets were prepared containing the stated amount of the zwitterionic surfactant, N-tallowalkyl-N,N-dimethylammonioacetate (supplied under the trade name Culveram TDG by Culver Chemical Co.) and the cationic surfactant, dimethyl dihydrogenated tallow alkyl quaternary ammonium chloride, (supplied under the trade name Formonyte 1703 by the Foremost Chemical Products Co.). Indentical comminution pulp sheets containing no surfactant were also prepared. The described tests were performed on the compared comminution pulp sheets, and the test results are tabulated in table I below.

In reviewing the comminution and absorbency data tabulated in table I, it is noted that the results of the Quick Disintegration test illustrate that the zwitterionic surfactant-impregnated sample was easily comminuted or fiberized to retain only 21.9 percent of the sample on the standard 14-mesh screen. The fiberization of the zwitterionic surfactant impregnated sample, as measured by percentage was better than twice as complete as the Standard Pulp sample without surfactant and was significantly improved over the cationic surfactant-impregnated sample.

The results of the Tappi T-233 test illustrate that the Standard Pulp sample without surfactant was not only incompletely fiberized, but was, in part, reduced in fiber length by comminution; since 51.4 percent of the sample was retained on the standard 14-mesh screen prior to fiberization, and only 44.4 percent of the sample was retained after fiberization. The Tappi T-233 test illustrates that the zwitterionic surfactant impregnated sample not only provided ease of comminution

TABLE I.—ABSORPTIVE CAPACITY

Test designation	Quick disintegration (percent)	TAPPI T-233 (Clark classification) (percent)	Avg. pad wt. (grams)	0 p.s.i. (initial g. H_2O/g. pad)	1 p.s.i. (g. H_2O/g. pad)	0 p.s.i. (final g. H_2O/g. pad)	Cellulose absorbency (drip method) (g. H_2O/g. pad)	Bulk fiber sink test (seconds)	Wicking (embossed fiber batts) (seconds)	Loft (g./cc.)
Sample description:										
Standard pulp sheet		51.4								
Standard pulp sheet (fiberized)	51.5	44.4	2.50	25.89	8.46	16.30	25.29	53.4	33.8	.0269
Standard pulp sheet impregnated with 0.2% cationic surfactant, dimethyl dihydrogenated tallow alkyl quaternary ammonium chloride and fiberized	26.1	53.2	2.51	25.78	8.16	15.85	25.39	104.9	117.0	.0254
Standard pulp sheet impregnated with 0.2% zwitterionic surfactant, N-tallowalkyl-N,N-dimethylammonioacetate and fiberized	21.9	51.5	2.50	26.03	8.30	17.27	27.54	87.4	55.4	.0245

as shown by the Quick Disintegration test results, but the fibers of the zwitterionic surfactant-impregnated sample resisted shortening in fiberization. The Tappi T-233 test result (51.5 percent) for the zwitterionic-impregnated sample was substantially the same as the Tappi T-233 test result (51.4 percent) for the Standard Pulp sample prior to fiberization, illustrating that no substantial change in fiber classification, i.e. fiber length distribution, occurred. Taken together, Quick Disintegration and Tappi T-233 test results illustrate the comminution superiority of the zwitterionic surfactant-impregnated sample over the Standard and cationic surfactant-impregnated samples.

Having established the comminution superiority of the zwitterionic-impregnated sample, it is apparent that so great an advantage in the use of the zwitterionic impregnated pulp sheets exists in comminution that only the absorbency characteristics of surfactant-impregnated pulp sheets should be further considered, although comparison test results are presented for the Standard Pulp sheet for completeness.

The test results presented for the Absorptive Capacity test illustrate an overall advantage for the zwitterionic surfactant-impregnated sample over both the Standard Pulp sheet and the cationic surfactant-impregnated sample; the superiority of zwitterionic surfactant impregnation is also illustrated by the results of the Cellulose Absorbency test.

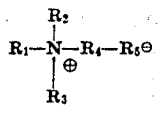
The results tabulated for the Bulk Fiber Sink and Wicking tests illustrate the clear superiority of zwitterionic surfactant impregnation over cationic surfactant impregnation in pulp sheet samples which otherwise exhibit the characteristic of improved comminution. The tabulated results of the Loft test illustrate the superiority of the zwitterionic-impregnated sample in the bulk and resiliency properties desirable in absorbent disposable batts, pads and sheets.

Standard Pulp sheets impregnated, at both the 0.1 and 2.0 percent by weight of active (or 100 percent surfactant in a formulation) surfactant based on the weight of bone dry pulp, with the zwitterionic surfactants N-tallowalkyl-N,N-dimethylammonio-2-hydroxy-3-propane-1-sulfonate, N-eicosyl (and docosyl)-N,N-dimethylammonioacetate and N-octadecyl-N,N-dimethylammonioethylsulfate will exhibit similar comminution, absorbency and bulk characteristics to those impregnated with N-tallowalkyl-N,N-dimethylammonioacetate, as do pulp sheets impregnated with other zwitterionic surfactants having the herein disclosed structures. The absorbent air-laid pads comprised of zwitterionic surfactant impregnated fibers have specific utility in bandages, diapers, sanitary napkins, tampons and like articles.

While preferred embodiments of the invention have been described, the descriptions are intended to be illustrative only, and it is to be understood that many variations which will be readily apparent to those skilled in the art may be made without departing from the spirit and scope of the inventive contribution to the art, as defined by the appended claims.

Having thus described the invention, what is claimed as new and desired to be secured by Letters Patent is:

1. A method for the manufacture of a comminution pulp sheet, which method comprises impregnating the cellulosic fibers of said pulp sheet, prior to final dewatering in sheet formation, with about 0.1 percent to about 2.0 percent, based on the weight of active surfactant and the bone dry weight of said pulp sheet, of a zwitterionic surfactant having the general structure:



wherein R_1 is a alkyl or alkenyl group containing about 16 to about 22 carbon atoms, R_2 and R_3 are selected from the group consisting of hydrogen and alkyl groups containing one to two carbon atoms, R_4 is an alkylene group containing one to about 11 carbon atoms, which alkylene group can have one or more hydroxyl groups attached to carbon atoms, and R_5 is selected from the group consisting of $-COO^1$, $-SO_3^1$, and $-OSO_3^1$, whereby the comminution of said pulp sheet and the absorbency characteristics of air-laid absorbent pads produced therefrom are improved.

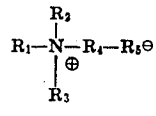
2. A method for the manufacture of a comminution pulp sheet, which method comprises impregnating the cellulosic fibers of said pulp sheet, prior to final dewatering in sheet formation, with about 0.1 percent to 2.0 percent of a zwitterionic surfactant selected from the group consisting of N-octadecyl-N,N-dimethylammonio-12-dodecanoate, N-eicosyl-N,N-dimethylammonio-3-propane-1-sulfonate, N-tallowalkyl-N,N-dimethylammonio-2-hydroxy-3-propane-1-sulfonate, N-C_{16}-C_{18}alkyl (and alkenyl)-N,N-dimethylammonioacetate, N-(2-hydroxy, C_{16}-C_{18}alkyl)-N,N-dimethylammoniacetate, N-tallowalkyl-N,N-dimethylammonioacetate, N-soyaalkyl (and alkenyl)-N,N-dimethylammonioacetate, N-eicosyl (and docosyl)-N,N-dimethylammonioacetate, N-octadecyl-N,N-dimethylammonioacetate, N-octadecyl-N,N-dimethylammonioethylsulfate, and N-(1-methyl,C_{16}-C_{18}alkyl)-N,N-dimethylammonioacetate, whereby the comminution of said pulp sheet and the absorbency characteristics of air-laid absorbent pads produced therefrom are improved.

3. The method for the manufacture of a sheet of claim 2 wherein the comminution of pulp sheet is comprised of wood fibers, and said pulp sheet is impregnated with about 0.2 percent of zwitterionic surfactant.

4. The method for the manufacture of a comminution pulp sheet of claim 2 wherein said pulp sheet is impregnated with a zwitterionic surfactant by a displacement shower, prior to find dewatering in sheet formation.

5. A method for the manufacture of a comminution pulp sheet, which method comprises impregnating the cellulosic fibers of said pulp sheet prior to final dewatering in sheet formation with about 0.1 percent to about 2.0 percent of N-tallowalkyl-N,N-dimethylammonioacetate, whereby the comminution of said pulp sheet and the absorbency characteristics of air-laid absorbent pads produced therefrom are improved.

6. A comminution pulp sheet, the cellulosic fibers of which pulp sheet are impregnated with about 0.1 percent to about 2.0 percent, based on the weight of active surfactant and the bone dry weight of said pulp sheet, of a zwitterionic surfactant having the general structure:



wherein R_1 is an alkyl or alkenyl group containing about 16 to about 22 carbon atoms, R_2 and R_3 are selected from the group consisting of hydrogen and alkyl groups containing one to two carbon atoms, R_4 is an alkylene group containing one to about 11 carbon atoms, which alkylene group can have one or more hydroxyl groups attached to carbon atoms, and R_5 is selected from the group consisting of $-COO^1$, $-SO_3^1$, and $-OSO_3^1$, whereby the comminution of said pulp sheet and the absorbency characteristics of air-laid absorbent pads produced therefrom are improved.

7. A comminution pulp sheet, the cellulosic fibers of which pulp sheet are impregnated with about 0.1 percent to about 2.0 percent, based on the weight of active surfactant and the weight of bone dry pulp, of a zwitterionic surfactant selected from the group consisting of N-octadecyl-N,N-dimethylammonio-12-dodecanoate, N-eicosyl-N,N-dimethylammonio-3-propane-1-sulfonate, N-tallowalkyl-N,N-dimethylammonio-2-hydroxy-3-propane-1-sulfonate, N-C_{16}-C_{18}alkyl (and alkenyl)-N,N-dimethylammonioacetate, N-(2-hydroxy,C_{16}-C_{18}alkyl)-N,N-dimethylammonioacetate, N-tallowalkyl-N,N-dimethylammonioacetate, N-soyaalkyl (and alkenyl)-N,N-dimethylammonioacetate, N-eicosyl (and docosyl)-N,N-dimethylammonioacetate, N-octadecyl-N,N-dimethylammonioacetate, N-octadecyl-N,N-dimethylammonioethyl-

sulfate, and N-(1-methyl,C_{16}-C_{18}alkyl)-N,N-dimethylammonioacetate, whereby the comminution of said pulp sheet and the absorbency characteristics of air-laid absorbent pads produced therefrom are improved.

8. The comminution pulp sheet of claim 7, which comminution pulp sheet is comprised of wood fibers impregnated with about 0.2 percent of N-tallowalkyl-N,N-dimethylammonioacetate.

9. An air-laid absorbent pad produced from the comminution pulp sheet of claim 7.

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