

[54] **ABSORBENT FIBERS OF
PHOSPHORYLATED CELLULOSE WITH
ION EXCHANGE PROPERTIES AND
CATAMENIAL TAMPONS MADE
THEREFROM**

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[22] Filed: **Nov. 1, 1971**

[21] Appl. No.: **194,748**

Related U.S. Application Data

[62] Division of Ser. No. 34,878, May 5, 1970, Pat. No. 3,691,154.

[52] U.S. Cl. **128/285**, 8/116, 260/212

[51] Int. Cl. **A61f 13/20**

[58] Field of Search 128/284, 285, 290,
128/296; 260/212, 219; 8/116; 162/157

[56] References Cited

UNITED STATES PATENTS

2,437,265 3/1948 Manning 128/285

3,052,593 9/1962 Battista 260/212
3,067,745 12/1962 Burgeni et al. 128/285

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[57] ABSTRACT

Absorbent dressings, such as tampons, made from highly absorbent cellulose fibers with ion exchange properties. These fibers are obtained by phosphorylating cellulose fibers, hydrolyzing the fiber walls with acid, converting the phosphorylated fibers to the sodium salt form, mechanically refining these fibers to rupture the primary fiber wall and permit subsequent swelling or ballooning, acidifying the refined fibers to reconvert the phosphorylated cellulose into the acid form, and drying the fibers in a manner to substantially avoid appreciable hydrogen bonding.

3 Claims, No Drawings

ABSORBENT FIBERS OF PHOSPHORYLATED CELLULOSE WITH ION EXCHANGE PROPERTIES AND CATAMENIAL TAMPONS MADE THEREFROM

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a division of copending application Ser. No. 34,878 filed May 5, 1970 and now U.S. Pat. No. 3,691,154. A related application is copending application of Leo J. Bernardin, Ser. No. 30,811, filed April 22, 1970 and now U.S. Pat. No. 3,658,790.

BACKGROUND OF THE INVENTION

It is well known that the normal healthy vagina is acidic, having a pH in the neighborhood of about 3.8 to 4.5. At that pH, numerous species of microorganisms are present which play a beneficial role in providing protection and resistance to infection. During menstruation, however, a slightly alkaline pH is frequently established. Under such conditions growth of favorable microflora is inhibited while undesirable types thrive. This causes the vagina to be more susceptible to infection and inflammation during menses.

Various attempts have been made to control this condition by providing catamenial devices which act to lower the alkaline pH during menstruation to the desired pH of 4.5 or less while simultaneously absorbing discharged menstrual fluids. One of these may be found in U.S. Pat. No. 3,091,241 to Kellett which employs glyceryl triacetate in an absorbent tampon as a physiological biostat or automatic pH controller.

In another U.S. Pat. No. 3,187,747 to Burgeni et al., catamenial tampons are made from multicomponent alloy fibers in which one of the components is absorbent, such as regenerated cellulose, while the other is an acidifying polymer, such as carboxymethyl cellulose in hydrogen form.

In each of the above patents, the tampon structure required at least two components, one performing the necessary absorbency function, while the other acts as the pH controller.

The present invention is directed to a cellulose fiber product which combines the pH control and the absorbency function in one fiber, without requiring chemical adjuvants or alloys.

In the copending Bernardin application, referenced above, phosphorylated cellulose fibers in sodium salt form were found to have a markedly increased absorbency over unmodified cellulose. The product was obtained by chemically substituting phosphate groups for hydroxyls on the cellulose, hydrolyzing the fiber walls with acid, then converting the substituted and hydrolyzed fibers to the salt form by ion exchange, and solvent drying or otherwise drying the fibers in a manner to substantially avoid appreciable hydrogen bonding. It was found that the phosphorylated fibers in their acid form, before conversion to salt form, and whether solvent dried or not, showed no improvement in absorbency over unmodified cellulose, while the salt form was found to be up to 5 times as absorbent. These results appeared to confirm the belief, at that time, that in order for substituted celluloses to have a sufficient increase in absorbency to warrant commercial use, it was necessary for the cellulose to be in an alkaline salt form. Prior art developments involving carboxymethyl

cellulose having particular degrees of substitution also supported this belief.

However, as work continued it was found that even greater absorbency could be developed in the phosphorylated cellulose in salt form if the fibers were refined for at least one minute before drying. Such refining increased absorbent properties almost threefold over the unrefined fibers. It was then found, rather unexpectedly, that if these refined fibers were reconverted to the acid form, they retained much of the increased absorbency developed by refining and exhibited by the salt form fibers. This finding seemed to contradict the earlier conclusion that the acid form of phosphorylated cellulose shows no increase in absorbency over unmodified pulp. This unexpected result immediately opened up a number of possibilities for use of the product in areas where absorbency and ion exchange complement one another.

SUMMARY OF THE INVENTION

Phosphorylated fibers in acid form with improved absorbency characteristics combined with high ion exchange capacity are produced by first saturating cellulose pulp sheets in a phosphorylating bath; drying and reacting the saturated sheets at elevated temperature; dispersing the reacted sheets in water, which preferably is deionized, and washing the reactant therefrom; converting the washed phosphorylated fibers to the acid form by treatment with acid; converting the acidified fibers to sodium salt form; mechanically refining the fibers in aqueous dispersion; reconvert the refined fibers to acid form; and finally drying the fibers in a manner to substantially avoid appreciable hydrogen bonding of the fibers to each other during the water removal process. When formed into mats the resulting fibers exhibit high ion exchange capacity and much higher capillary suction pressure and absorbent capacity than unmodified cellulose fibers.

These fibers are markedly superior in absorbent capacity to phosphorylated fibers in the acid form which have not been refined. They are also superior in absorbency to fibers which have been refined while in acid form. Accordingly, in order to obtain this improved absorbency in the acid-form fibers of this invention, it is necessary to first refine the fibers in salt form and then reconvert the refined fibers to acid form.

The preferred method of phosphorylating is the urea phosphate method, wherein the fibers are reacted at a temperature of from about 130° to 195°C for about 5 to over 30 minutes in a solution of urea and phosphoric acid. Other known but less satisfactory methods of phosphorylation may be used including treatment with phosphorous oxychloride and pyridine; phosphorous oxychloride and phosphoric acid; phosphorous oxychloride and dioxane; phosphorous oxychloride alone, and alkali metal salts of phosphoric acid.

When converting the washed phosphorylated fibers to acid form immediately after phosphorylation, cold acid may be used, but it is preferred to use hot acid because the latter more readily hydrolyzes the fiber walls which is highly desirable in developing the improved capillary suction pressures described herein.

In converting the phosphorylated fibers to salt form the alkali preferably employed is a dilute solution of sodium hydroxide. However, other solutions of basic salts such as sodium carbonates, phosphates and the like may be used.

In order to dry the fibers in a manner to avoid hydro-
gen bonding, conventional solvents such as acetone,
alcohol, alcohol followed by hexane, and the like may
be used.

Freeze drying may also be used since such a drying
method also substantially avoids hydrogen bonding.

It is the primary object of this invention to provide
chemically modified cellulose fibers which in their acid
form have markedly improved fluid absorbency char-
acteristics.

Another object is to provide absorbent pads from fi-
bers which have high absorbency combined with high
ion exchange capacity.

Other features, objects and advantages of the inven-
tion will become apparent by reference to the following
specification.

DESCRIPTION OF THE PREFERRED
EMBODIMENTS

In a preferred embodiment, four sheets of unbeaten,
bleached, northern softwood, kraft pulp weighing
about 14 grams each were immersed for about 30 min-
utes in a bath consisting of 50 percent urea, 18 percent
orthophosphoric acid, and 32 percent water by weight.
The saturated pulp sheets were drained to a consis-
tency of 1 part fiber to 3 parts by weight of solution.
The moist sheets were dried and reacted or cured in an
oven for 20 minutes at 160°C. The cured sheets were
dispersed in deionized water and the resulting slurry
washed free of the treating solution by several rinses
with deionized water using a suction filter.

The filtered material which is believed to be com-
prised of cellulose monoammonium monohydrogen
phosphate was dispersed in a 3 percent solution of hot
hydrochloric acid and soaked at a temperature of be-
tween 60° and 70°C for one-half hour. The acid form
of phosphorylated fiber thus obtained was washed free
of excess acid and separated into two portions. One
portion was refined in a conventional PFI laboratory
refiner for 2¼ minutes at 10 percent consistency and
solvent dried from acetone, the other portion was con-
verted to salt form by soaking in a 5 percent solution
of Na₂CO₃ for one-half hour. The fiber was washed
again and then refined at 10 percent consistency in a
conventional PFI laboratory refiner for 2¼ minutes.
The refined pulp was reconverted to acid form, i.e., a
pH of 3, with hydrochloric acid, washed free of excess
acid, and then solvent dried from acetone.

Absorbency characteristics in terms of capillary suc-
tion pressure of the two kinds of phosphorylated cellu-
lose in acid form obtained by the above described pro-
cess were then compared to each other and to an un-
modified cellulose which was also refined for 2¼ min-
utes and solvent dried.

Results were as follows:

WATER CONTENT IN GRAMS OF H₂O PER GRAM
OF FIBER

Capillary Suction Pressure (In Cm of H ₂ O)	Unmodified Pulp Refined	Phosphorylated Pulp in Acid Form		
		Unrefined	Refined in Acid Form	Refined in Salt Form
60	1.1	0.8	2.0	5.9
40	2.1	1.8	2.8	7.1
25	3.5	3.5	3.8	8.7
15	5.8	6.0	7.1	10.4
10	8.5	7.8	8.0	11.5

5	11.0	9.3	10.4	14.0
0	13.0	11.0	11.7	17.0

Absorption of liquid water as a function of capillary
suction pressure on airlaid mats of fiber is measured by
means of a known capillary tension cell apparatus of
the type described in an article from the Textile Re-
search Journal, Vol. 37, No. 5, May, 1967, pp.
356-366, A. A. Burgeni and C. Kapur, "Capillary Sorp-
tion Equilibria in Fiber Masses." Absorption capabili-
ties for a fiber mass are cited in the number of grams
of water per gram of fiber which a mat of fibers will ab-
sorb under the specified capillary suction head or pres-
sure indicated.

The results indicate that when phosphorylated pulp
is merely converted to acid form and then refined, it
shows no measurable improvement over unmodified
pulp.

The results also show very clearly that when the
phosphorylated pulp is refined in its salt form before
converting back to acid form there is a dramatic in-
crease in its absorbent properties.

It became apparent that the refining of the fibers in
salt form and converting to acid form has a different ef-
fect on the fibers than when they are originally refined
while in acid form.

Microscopic examination of the fibers, before and
after refining, indicated that, before refining, the fibers
of the phosphorylated pulp in acid form look very
much like ordinary wood pulp fibers when wet with the
fiber walls substantially intact, while the walls of the
phosphorylated pulp in salt form showed signs of rup-
ture of fraying with some ballooning of the internal
structure in a number of places. Refined unmodified
pulp and phosphorylated pulp in acid form also ap-
peared quite similar, showing some fraying of the fiber
wall, but little ballooning or swelling. The refined phos-
phorylated fibers in salt form, on the other hand, exhib-
ited considerable ballooning and swelling, as the inter-
nal structure expanded down the length of the fiber
with only a few confining rings appearing where the pri-
mary fiber wall remained unruptured and intact. The
ballooned and swelled form of the main internal body
of the fiber structure was retained when these fibers in
salt form were converted back to acid form.

Refining phosphorylated fibers in the salt form prior
to reconversion to the acid form is therefore consid-
ered to be a necessary step in the preparation of the
highly absorbent fibers in the acid form of this inven-
tion. Without such refining the acid form of phosphory-
lated fibers show no improvement in absorbency. In
structure therefore, the acid form of phosphorylated
fibers must be substantially stripped or denuded of the
primary fiber wall in order to obtain the demonstrated
improvement in absorbency.

In considering this improved acid form of phosphory-
lated cellulose fiber for tampon useage it was also de-
termined that ion exchange capacity is significant. Ac-
cordingly, ion exchange capacity was tested by poten-
tiometric titration with 0.1N sodium hydroxide. As in-
dicated in the Burgeni et al. U.S. Pat. No. 3,187,747,
the acidifying capacity of a tampon in vivo can be ap-
proximated in terms of the volume of 0.1N sodium hy-
droxide consumed by the fibers in an environment of
0.8 percent NaCl solution at pH values up to about 4.5.
It is also indicated that in distilled water, less sodium
hydroxide would be required for equivalent capacity
because NaCl tends to aid in the liberation of hydrogen

ions. Accordingly the ion exchange capacity exhibited under actual use would be higher than the capacity indicated by titration in distilled water.

A number of samples of the acid form of phosphorylated cellulose fibers refined in salt form as described above were titrated in distilled water with 0.1N NaOH to determine ion exchange capacities. One gram of fiber was found to consume about 12.5 ml of 0.1N sodium hydroxide in reaching a pH of about 4.5. Accordingly a normal tampon weight of about 3 grams would have adequate capacity for maintaining an acid pH in the vagina under even the most severe conditions of use. Since such a tampon acts to maintain the menstrual fluids at an acid pH, the surrounding skin surface is also maintained slightly acid whereby the environment for the useful microflora stays favorable.

In view of this high ion exchange capacity it is not necessary to make the entire absorption device of the phosphorylated fibers of this invention. They may be admixed with ordinary wood pulp fibers, with phosphorylated fibers in salt form, with other absorptive fibers, or with resilient fibers as set forth in the prior art to provide better expansion properties when used in compressed form.

While the improved pulp fibers are indicated as being of particular use in catamenial tampons, they may also

be employed where the dual characteristics of high absorbency and high ion exchange capacity are required.

The invention is particularly applicable to fibers converted from wood pulp because of their low cost and ready availability. However, other fibers normal to the papermaking art may also be employed such as hemp, jute, esparto, cereal straws, flax, bagasse, bamboo, reeds, cotton linters, kenaf and the like.

What is claimed is:

1. An improved absorbent dressing for absorbing and simultaneously acidifying body fluids in contact therewith, comprising a fibrous mat of phosphorylated cellulose fibers in acid form, said fibers being characterized by a structure in which a major portion of the primary wall of each of said fibers is broken away leaving the main internal body of each of said fibers substantially unconfined by said primary wall, said internal body structure being in a swelled and ballooned condition, whereby said fiber mat provides improved capacity for absorbing aqueous fluids.

2. The dressing of claim 1 in which said mat is in the form of a tampon suitable for internal deployment in body cavities.

3. The dressing of claim 1 in which said mat has other absorbent fibers admixed therewith.

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