A Process for Drying a Superabsorbent Pulp

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The market for bleached pulp in absorbent sanitary products is rapidly expanding. Pulp, generally in fluffed form, is quite efficient for absorbing quickly fairly large quantities of liquid. Conventional pulp has, however, serious drawbacks. One is the bulk of the products, which require large storage space. Another is the relative ease with which a large proportion of the absorbed liquid is released under light pressure.

There is a need for an absorbent material, preferably in fibrous form, capable of absorbing larger volumes of liquid per gram of absorbent and to hold this liquid under moderate pressure. Several such "superabsorbent" products, some in powder form, some in fibrous form, have been developed in the last few years (1,2).

A superabsorbent in fibrous form has been developed at the Pulp and Paper Research Institute of Canada to the completion of the laboratory stage; its preparation and properties have been the subject of several publications (3,4,5). Essentially, it consists of wood pulp modified by graft-polymerization of polyacrylonitrile which is subsequently hydrolyzed into a copolymer of sodium polyacrylate and polyacrylamide which confers on the pulp an outstanding affinity for water.

In addition to its water absorption properties, this product, or variants of it, may have considerable interest in wet and dry forming of specialty papers.

Commercialization of such a material hinges upon the technical and economic feasibility of producing it in dry form. Conventional thermal drying is slow, causes the fibers to lose some of their absorptive capacity and furthermore produces a stiff and brittle sheet which is impossible to fluff. Freeze-drying or solvent exchange drying prove much too costly because of the huge quantity of water to be removed.

An unconventional drying method had to be developed; this report deals with the development of this novel drying process.

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I. Requirements to be met

The requirements that had to be met are listed below:
1. The drying process should not impair the absorption
   properties and should leave the product in fibrous form.
2. The dry product should be fluffable by ordinary means.
3. The product should be economical as judged by its cost/
   performance ratio when compared to regular pulp.

II. First Attempts

The first attempts to produce a product meeting these re-
quirements will be described as they point to a step critical
for success.
    1. Hydrolysis under non-swelling conditions. Under normal
conditions the grafted polyacrylonitrile was hydrolyzed in
boiling aqueous NaOH. The pulp was then filtered and washed to
remove excess NaOH. Typically, the quantity of liquid associated
with the fibers was of the order of 8-10 g/g fiber after hydrol-
ysis and of 30-40 g/g after washing, as compared to approximately
1 g/g for the untreated fibers.
    To avoid the large quantity of water taken up during hydrol-
ysis in aqueous NaOH, it was logical to attempt the hydrolysis
under low-swelling conditions. Hydrolysis experiments carried
out in the presence of alcohols showed that this could be
achieved. In this fashion the amount of liquid retained by the
fibers at the end of hydrolysis was considerably decreased, and
further solvent exchange drying was easy. However, this route
had disadvantages:
    a) hydrolysis at reflux temperature was quite long and
       sometimes incomplete unless substantial amounts of water
       were present, depending on the alcohol used.
    b) while the water absorption characteristics of the dried
       fibers were usually close to normal, the absorption of
       1% aqueous NaCl (simulating physiological fluids) was
       quite low and proportional to the amount of water pre-
       sent in the hydrolysis liquor.
    2. Hydrolysis at high pulp concentration. Another way to
reduce the amount of liquid taken up is to reduce the amount of
available liquid. Hydrolysis experiments with aqueous NaOH at
high fiber concentration followed by solvent-exchange drying,
produced fibers which swelled normally in water but not in NaCl.
Swelling in aqueous NaCl was inversely proportional to the fiber
concentration used, i.e., proportional to the amount of water
present during hydrolysis.
    3. Normal aqueous hydrolysis followed by solvent-exchange
drying. The preceding experiments seemed to indicate that the
swelling taking place during normal, low consistency, aqueous
hydrolysis was necessary. Since most of the total swelling takes
place in the washing stage (liquid associated with the fibers

increases from 8-10 g/g to 30-40 g/g), solvent exchange drying
was done immediately after hydrolysis. Again, while the water
absorbency was normal, the salt absorbency, while higher than in
the previous experiments, was still low (7-10 g/g), but became
normal after the fibers had been soaked in water prior to con-
tacting them with the salt solutions.

III. Stage of full swelling prior to drying: a requisite

During the course of this work it became evident that when-
ever fibers were dried without having undergone full swelling in
water at pH 6-9 in the absence of a significant concentration of
salt, they would reswell in water more or less to their normal
extent but not in a salt solution.

Many experiments then confirmed that taking the fibers
through their state of full swelling prior to drying was a re-
quisite for salt solution absorption.

In a previous article (3) it was explained that swelling
was due to osmotic pressure effects and that equilibrium was
reached when a balance was achieved between these swelling forces
and the fiber cohesion forces. While alkaline aqueous hydrolysis
contributes to a substantial reduction in the fiber cohesion, con-
siderably more weakening takes place during the swelling that
occurs during the washing operation and the transformation is ir-
reversible, as seen on Fig. 1, line ABC.

This requirement of a full swelling stage during the man-
ufacturing process meant that a new approach had to be thought
of.

IV. The drying process

1. **Principle.** The process makes use of the solution pro-
perties of the grafted polymer. This polymer is soluble in
water at pHs above 4 but insoluble at lower pHs and in alcohols.
As seen in Fig. 2, swelling as measured by the amount of water
retained after high speed centrifugation (water retention value,
WRV) decreases from 30 at pH 6-9 to 2.5 g/g when the pH is re-
duced to 3. At this pH, the grafted polymer is in its non-
ionized polyacrylic acid form. If the fibers are dried at that
point, they will not reswell in water to any extent. However if
the deswollen fibers are converted back into their sodium salt
form with NaOH under non-swelling solvent conditions before
drying them, normal reswelling in water and in salt solution will
take place.

The process then consists of three steps.
a. The hydrolyzed fibers are taken through their maximum
swelling state at pH 6-9 in the absence of any significant salt
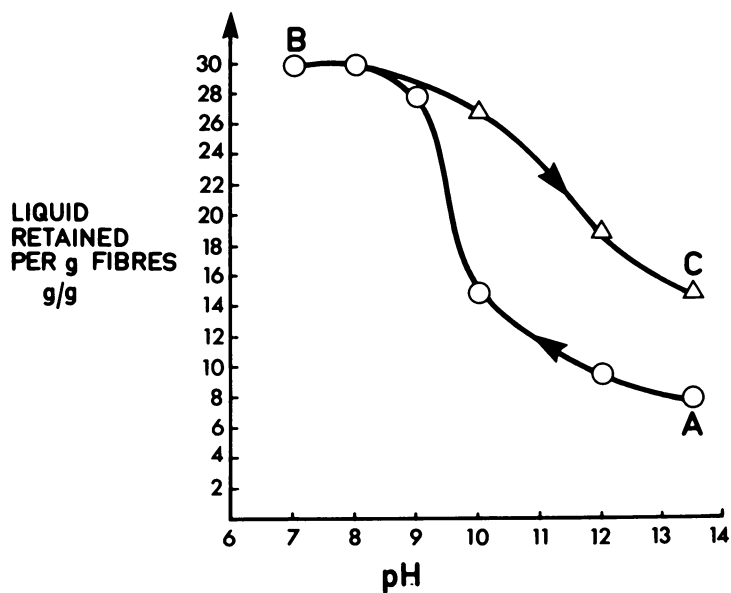concentration.

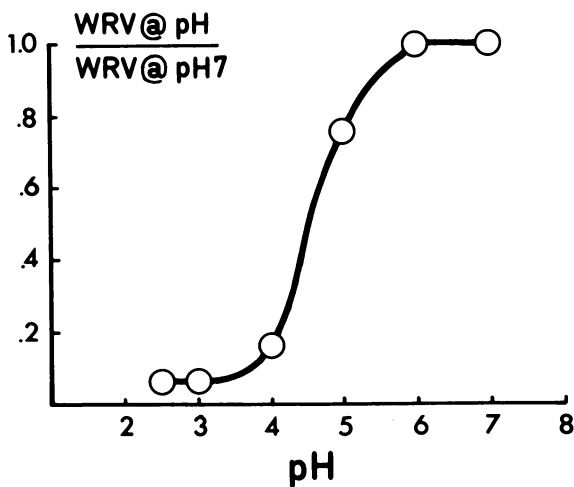Figure 1.   Liquid retained by the fibers as a function of the pH

Figure 2.   Relative water retention value as a function of the pH

   b.   The pH is brought down to approximately 3 where the
fibers are in their minimum swelling state.
   c.   The acid groups are converted into sodium carboxylate
groups with NaOH in alcohol (a non-solvent for the polymer) and
the alcohol is evaporated.
   2.   Laboratory procedure. At the end of hydrolysis the
fibers are filtered, washed with one volume of water while on
the filter. The pH at that point is 9.5 - 10. The fibers are
then slurried in water at 1% consistency and sulfuric acid is
added with good agitation to avoid any local high concentration.
During the acidification, the fibers undergo full swelling in
the pH range 8-6 in the absence of any significant salt concen-
tration. As the pH continues to drop, the fibers start to de-
swell as evidenced by a rapid decrease in slurry viscosity. At
pH 4 flocculation starts and acidification is continued until pH
3. At that point, the fibers are in their minimum swelling state,
and are flocculated in large aggregates. They are soft and sticky
and will form strong wet bonds when pressed together. The slurry
is then drained freely or filtered with gentle suction until
water starts to recede from the fibrous pad surface. Suction is
released. This operation is critical when a fluffable pulp is
desired. Excessive compaction of the pad must be avoided because
of the tendency of the soft fibers to form strong interfiber
bonds which slows down further processing, and makes fluffing
very difficult.
   While the fibrous pad is still on the filter, a solution of
NaOH in aqueous methanol (e.g., NaOH/H_2O/MeOH - 1/9/90) is
poured on the pad to displace the interfiber capillary water
which is allowed to drain freely or under gentle suction. NaOH
converts the carboxylic acid groups into sodium carboxylate
while MeOH prevents swelling taking place. Once all the inter-
fiber capillary water has been replaced by the methanolic sol-
ution the fibrous mat becomes stiff because the polymer, which
is insoluble in methanol, "precipitates". From there on, strong
suction can be applied. A solution of aqueous methanol (e.g.
H_2O/MeOH-8/92) is poured to wash out the excess residual NaOH,
followed by pure methanol to remove the last traces of water.
The methanol is then evaporated to yield a bulky mat of loosely
held fibers.
   3.   Suggested industrial drying process. Two alternative
drying process schemes are offered for consideration. The first
one is continuous; the second is a batch progress.
   a.   As shown schematically in Fig. 3, the acidified fiber
slurry is delivered through a headbox on an endless screen.
Water drains freely in the first section. This stream is dis-
carded. Alkaline aqueous methanol is sprayed on top of the web
while gentle suction is applied. Once the solution has dis-
placed the water, strong suction is applied to remove most of
the excess liquid, from which methanol and NaOH may be recovered
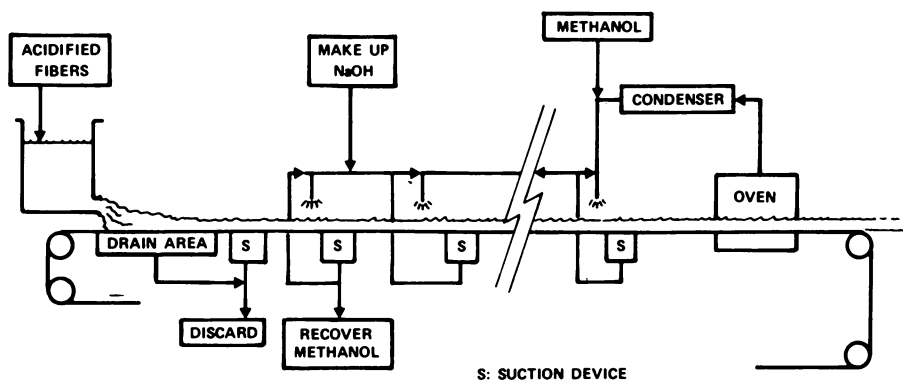in a separate recovery cycle. The web is then sprayed with NaOH-

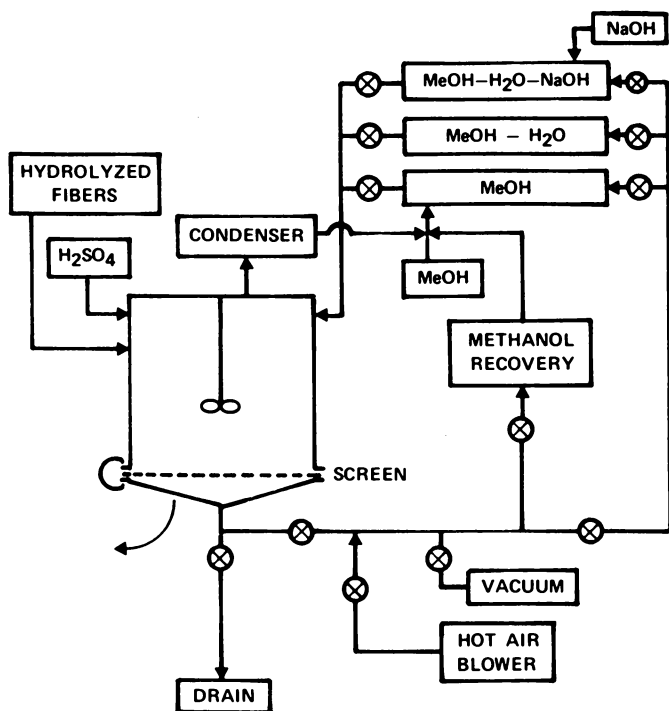*Figure 3.   Continuous drying process*

Figure 4.   Batch drying process

free, aqueous methanol to remove excess NaOH and continue the dehydration process. It passes over another strong suction device to remove the excess liquid which is sent to the first treatment zone after NaOH make-up. The web then receives a spray of pure methanol, passes over another suction device and goes to an oven where methanol is evaporated and recycled.

It should be understood that dehydration of the fibers takes place continuously throughout the sequence. The solvent solution runs counter-current to the web and its concentration is adjusted at each treatment zone so that, at no point, do the fibers pick up water from the solvent solution. In the first section, dehydration is favored when both the concentrations of NaOH and MeOH are increased. However, increased NaOH concentration means a longer washing zone. In the second section, dehydration is favored by higher MeOH concentration but removal of excess NaOH is slowed down. (The equilibrium isotherm between concentration of water in the solvent and absorbed water in the fiber, though not available now, will be required for this control).

b. The alternative process is a batch operation. It is really a scaled-up version of the laboratory procedure and is shown in Fig. 4. It has the disadvantage of being discontinuous but would seem to be much easier to control and be lower in capital cost. The acidification tank is equipped with a rotating bottom fitted with a screen. The washed hydrolyzed fibers are fed to the acidification tank and H_2SO_4 is added tobring the pH down to 3.0. Then the free draining liquid is removed from the slurry through the screen until water starts to recede from the interfiber capillaries. The filtrate is discarded. At that point, a quantity of alkaline methanolic solution equivalent to at least one pad volume is poured on top of the fiber pad. Its flow-rate is adjusted so that friction caused by the flow is minimized to avoid compaction of the pad and the alkaline methanolic solution has had time to diffuse into the fiber flocs. When NaOH - depleted aqueous methanol arrives at the bottom, the drain valve is closed, and the filtrate is sent for recovery of methanol. One volume of aqueous MeOH solution is run through the pad to wash out the excess NaOH followed by one volume of methanol. The filtrates, depending on their composition, are recycled to the storage tanks.

After the pure methanol wash, suction is applied through the pad by the vacuum source to remove most of the methanol. Then hot air is blown up through the fibrous cake and methanol is condensed. Finally, the dry cake is discharged through the revolving bottom, shredded and baled.

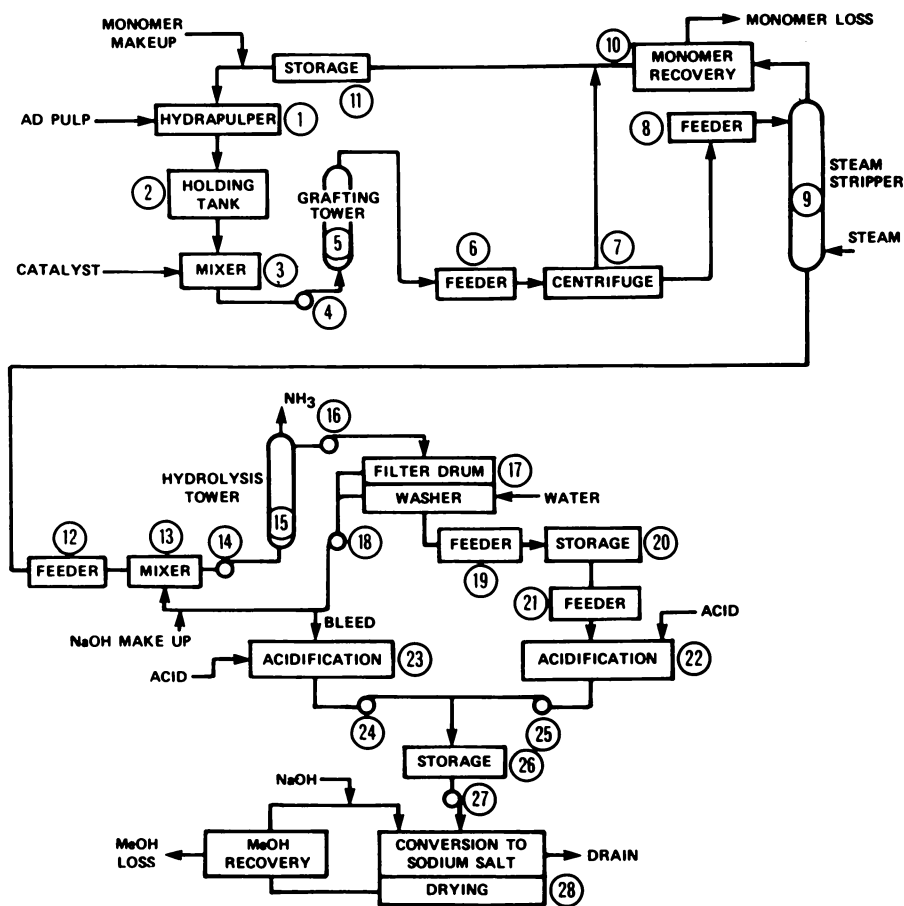The process has been sucessfully proven in the lab on fiber cakes 2 feet high and 2 inches in diameter.

Figure 5.   Process flowsheet

V.   Flow-sheet and Mass Balance for the Complete Process

A.   Flow-sheet

Fig. 5 shows the flow-sheet for the complete production
process from grafting through to drying.

    1.   Grafting of polyacrylonitrile. Air-dried pulp is
slurried at 4.35% consistency using recycled streams (water,
HNO_3, acrylonitrile) in a hydrapulper or similar equipment equip-
ped for handling acrylonitrile (toxic) solution and acid resist-
ant to pH 2.5.   The slurry is pumped to a holding tank.   (In an
integrated mill operation, wet lap pulp would be used and no
hydrapulper is necessary).

The grafting reaction is done in a continuous fashion.   From
the holding tank the slurry is sent to a small (residence time ~
30 sec) mixer where the catalyst is introduced.   Consistency is
now 4%.   The slurry is pumped to a "grafting tower" where no
further mixing takes place.   Laboratory adiabatic grafting ex-
periments have shown that polymerization is complete after 3-4
min., suggesting a residence time of 5 min.

The very bulky, free-draining grafted pulp is then fed to a
centrifuge (residence time 1 min.) and the liquid containing the
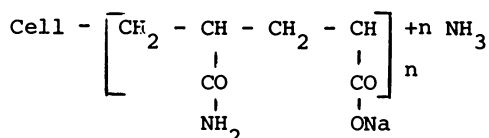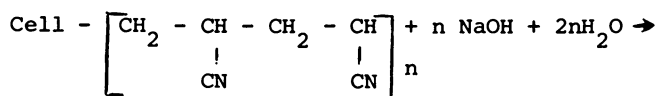unreacted monomer is recycled to the hydrapulper.

The centrifuged grafted pulp is then steam-stripped of its
residual monomer which is recovered.   Residence time: 15 min.

    2.   Hydrolysis.   After the steam-stripping operation, the
pulp is slurried in a small mixer at 2% consistency in the re-
cycled hydrolyzing liquor (residence time: 30 sec.) and pumped
to a hydrolysis tower equipped with steam jacket.   Residence
time is 15 min.

From the hydrolysis tower the slurry is pumped to a drum
filter where it is dewatered and washed.   Provision is made to
separate the filtrate and washings to minimize NaOH carry over in
the bleed.   (See mass balance for reasons for this bleed).   This
bleed is acidified to recover the dissolved polymer.   The bleed
and the fibers are acidified separately since the substantial
quantity of Na_2SO_4 produced in the acidification of the bleed
would be detrimental to the full swelling of the fibers.

The washed fibers, as a swollen fibrous mat, are best
handled by a screw-type extruder, and sent to storage.

    3.   Acidification and drying.   The next step, acidification,
is carried out batch-wise at a consistency of 1.5%.   The acid-
ified slurry is then processed as described in IV, 3.   A special
type of pump, possibly a plug-flow piston pump, is required to
avoid the compaction of the soft, sticky fiber aggregates.
Gravity flow should be utilized as much as possible.

$$\text{Cell} - \left[\begin{matrix} CH_2 - CH - CH_2 - CH \\ \qquad | \qquad\qquad\quad | \\ \qquad CN \qquad\qquad\;\; CN \end{matrix} \right]_n + n\ NaOH + 2nH_2O \rightarrow$$

$$\text{Cell} - \left[\begin{matrix} CH_2 - CH - CH_2 - CH \\ \qquad | \qquad\qquad\quad | \\ \qquad CO \qquad\qquad\;\; CO \\ \qquad | \qquad\qquad\quad | \\ \qquad NH_2 \qquad\qquad ONa \end{matrix} \right]_n + n\ NH_3$$

Yield, as experimentally determined, was 1.53 part of hy-
drolyzed copolymer per part of PAN. This corresponds to ca.
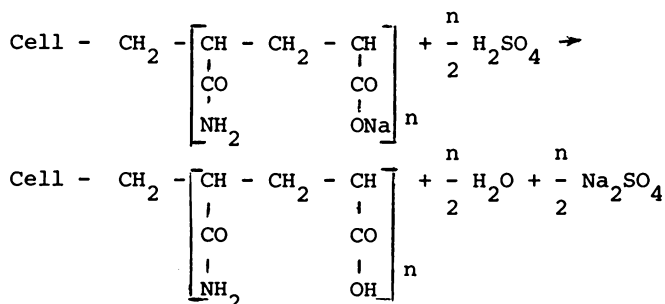50/50 w/w ratio of amide to acid groups.

Hydrolysis causes a loss in both cellulose and polymer:
a) Cellulose loss has been set at 5% (experimental finding) and
is not recovered. It is assumed to leave with the liquid drained
after acidification. b) Polymer loss during hydrolysis has been
set at 13% (experimental finding). However the dissolved polymer
may be recovered by bleeding enough of the washings to maintain
the concentration of dissolved polymer in the hydrolyzing liquor
at approximately 2%., acidifying the bleed and adding the pre-
cipitated polymer to the acidified fibers.

3. Washing. The quantity of water used to wash the hydro-
lyzed, filtered fibers has been set as equivalent to the quantity
of liquid carried over with these fibers. Laboratory experiments
using drop-wise addition of that amount of water to the filter
cake under suction showed that the amount of NaOH left with the
fibers was sufficiently low that the Na_2SO_4 produced during sub-
sequent acidification did not prevent full swelling of the fibers.
The pH of the washed fibers is approximately 10.

4. Acidification. Since the fully swollen fibers are them-
selves about 3% solids, the provision of adequate free water for
mixing and homogeneous acidification requires a lower consistency
and 1.5% has been chosen.

Chemical reactions:

$$\text{Cell} - CH_2 - \left[\begin{matrix} CH - CH_2 - CH \\ | \qquad\qquad\quad | \\ CO \qquad\qquad CO \\ | \qquad\qquad\quad | \\ NH_2 \qquad\qquad ONa \end{matrix} \right]_n + \frac{n}{2}\ H_2SO_4 \rightarrow$$

$$\text{Cell} - CH_2 - \left[\begin{matrix} CH - CH_2 - CH \\ | \qquad\qquad\quad | \\ CO \qquad\qquad CO \\ | \qquad\qquad\quad | \\ NH_2 \qquad\qquad OH \end{matrix} \right]_n + \frac{n}{2}\ H_2O + \frac{n}{2}\ Na_2SO_4$$

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$

B. Mass Balance

The mass balance is shown in Fig. 6 and the conditions used are based on laboratory results.

A PAN graft level of 120% was chosen for the mass balance calculations used in estimating the cost, because the absorption properties measured on undried fibers level off at this point (3). Recent data have indicated that, in the case of fibers dried by this process, the leveling off effect occurs at a somewhat higher graft level (150-160%). Typically the WRV and SRV of fibers at 120% PAN graft level are 30 and 13.5 g/g respectively while at 150% the WRV is in excess of 30 and the SRV is 16 g/g.

1. Grafting. Grafting is performed using the ceric ammonium nitrate initiation method.

Catalyst requirement was found to be independent of pulp concentration when the latter was 3% or greater (5), so that it is more economical to operate at as high a pulp concentration as possible. However, the grafting reaction is very fast and a concentration of 4% has been chosen in order to have a rapid homogeneous mixing of the catalyst. A graft level of 120% can be achieved by various combinations of catalyst and monomer concentrations, (3). Increasing catalyst concentration increases grafting cost but leads to higher conversion of monomer to polymer thereby reducing monomer recovery cost. The conditions used (catalyst 1.3% of pulp, monomer concentration 9%) are in the range where cost is optimized. The fate of the ceric ion is still undetermined, and it has been left out of the mass balance.

2. Hydrolysis. The concentration of NaOH in the hydrolysing liquor has been set at 3% w/w. Hydrolysis rate is enhanced by higher NaOH concentration, so that the residence time, and thereby the hydrolysis tower size, could be reduced. However, higher NaOH concentration causes:

a. increased pulp degradation and loss.
b. increased residual NaOH at the washer, thereby slowing down the operation.

A consistency of 2% has been chosen because the hydrolyzed pulp is already significantly swollen. It might however be possible to operate at 3% consistency, which could permit a smaller tower size.

Chemical reactions during hydrolysis:
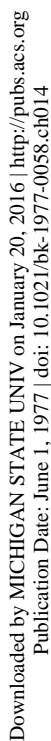
Figure 6.   Overall mass balance

5. Conversion to Sodium Salt and Drying by Methanol Exchange. No detailed balance is made for this operation as no data are available for counter-current continuous operation.

It is assumed, again based on static laboratory experiments, that approximately 7 parts of methanol are required per part of product, and are recovered by distillation.

0.125 part of MeOH per part of product (250 lbs/ton product) is assumed to be lost in the bottoms of the distillation tower and in leaks. This represents approximately 2% of the methanol flow.

VI. Modification of Process for Improved Saline Retention Value

It has been explained earlier that swelling is restricted by the fiber cohesion forces. If this cohesion is weakened by some means, e.g. by beating, the water and sodium chloride retention values may be improved by as much as 30%. A saline retention value of 20 g/g has been achieved.

The beating may be performed either on the pulp prior to grafting or on the hydrolyzed pulp.

a. **Beating the pulp prior to grafting.** In addition to increased absorbency as shown in Fig. 7, beating of a dried pulp leads to higher grafting efficiency (5).

Care should be taken not to overbeat the pulp as this would create serious problems when filtering and washing the hydrolyzed product.

b. **Beating the hydrolyzed pulp.** This is best achieved by submitting the fragile swollen fibers to violent mixing before the acidification step. Here again, care should be taken not to overbeat the fibers as they could be transformed eventually into a very thick colloidal solution (4). An example of the improvement to be expected is shown in the following Table I.

TABLE I.
Improvement in SRV by Shearing the Hydrolyzed Fibers

Initial SRV	SRV after stirring at high speed for	
g/g	5 min.	20 min.
13.5	16	18.5*
16.6	19.8	22*
18	24*	

* Fibers begin to lose their fibrous character.

VII. Other Products

1. **Non-hydrolyzed PAN Absorbent Pulp.** The intermediate product, unhydrolyzed PAN grafted pulp, has quite interesting properties which warrant its consideration as an absorbent
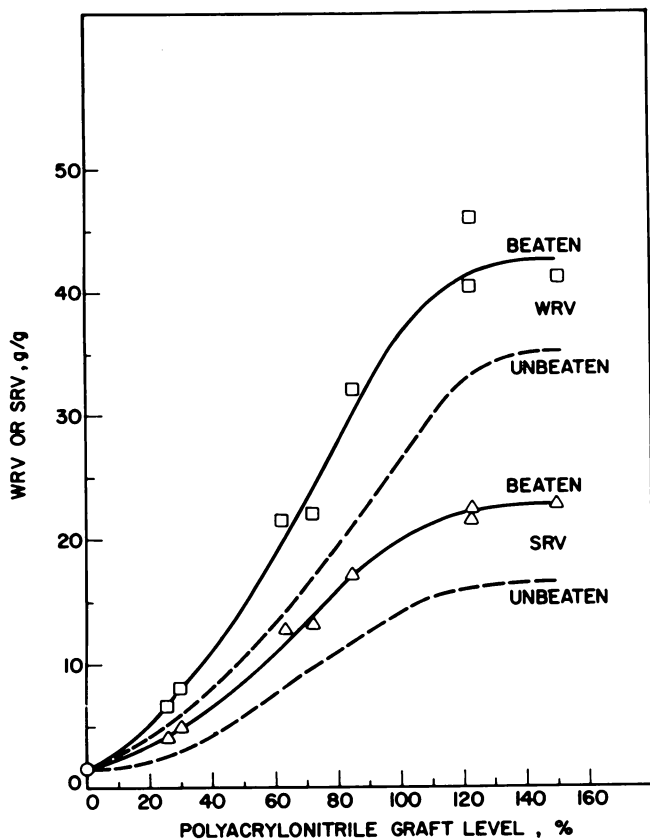
Figure 7.   Influence of beating on WRV or SRV

material as such. It may be compared to cross-linked cellulose
fibers.

Cross-linked cellulose fibers in mat or fluff form are
superior to regular pulp in rate of absorption of fluids and in
total capacity, particularly when absorption takes place under
moderate pressure. This is because the cross-linked fibers have
a higher wet modulus so that the mat or fluff does not collapse
when absorbing fluids under moderate pressure. In addition,
little or no interfiber bonding takes place during drying so
that the comminution of the pulp is easily accomplished. Several
patents have been issued in this area.

Pulp fibers grafted with PAN, a glassy, water-insensitive
polymer, behave quite similarly to cross-linked cellulose fibers.
They are bulky, stiff when wet, and do not form interfiber bonds
during drying. For the same reasons as stated above, PAN
grafted pulp is superior to regular pulp in fluid absorbency
under moderate pressure, as shown in Table II. Furthermore, the
absorption being of a capillary nature, it is not affected by
the ionic strength of the fluid.

TABLE II

Pulp	1% NaCl absorption capacity, g/g	
	under 1.7 KPa	under 6.9 KPa
Bleached Spruce Kraft A	12	8
Bleached Soft Kraft B	13	9
Pulp B grafted with PAN	18	13

A plant producing the superabsorbent pulp could also supply
the cheaper PAN graft intermediate for applications where intra-
fiber absorbency is not required.

2. Superabsorbent Pulp in Sheet Form. In some applica-
tions, the superabsorbent pulp may be used in sheet form. Then,
fluffability is no longer a requirement, but good sheet formation
becomes important.

As indicated before, acidification to pH 3.5 - 3.0 causes
flocculation of the fibers into aggregates and this results, of
course, in poor sheet formation. However, a further decrease of
the pH to approximately 2.2 will create ionization of the amide
groups and redispersion of the flocs. Very good sheet formation
is then obtained.

Since fluffability is no longer a requirement, the sheet
can be compacted and suction can be applied immediately after
sheet formation. This permits considerable reduction in the
quantity of methanol to be recovered by distillation.

   3. Application in Dry Forming. Preliminary laboratory ex-
periments have demonstrated that fibers prepared by this process
and dry-laid, can form sheets with good interfiber bonding when
pressed as ca 80% RH. The moisture content at this RH is suffic-
ient to plasticize the fibers and to lead to the development of
interfiber bonds. These bonds however are not water resistant.
   More attractive is the possibility of utilizing solvent-ex-
change dried fibers in the acid form (no conversion to sodium
carboxylate). Here, the interfiber bonds exhibit temporary wet
strength. Considerably more work is required to confirm their
potential as self bonding fibers in dry-forming processes.

ABSTRACT

   A process for the production of a fibrous superabsorbent is
described. The superabsorbent is obtained by grafting poly-
acrylonitrile on a bleached pulp, hydrolysing it to a copolymer
of sodium polyacrylate and polyacrylamide and removing the water
from the swollen fibers by a combination of chemical dehydration
and solvent-exchange drying. Fibers are obtained in an easily
fluffable form and have water and 1% aqueous NaCl retention
values of up to 40 g/g and 20 g/g respectively. Process flow-
sheets and mass balance are given.

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