

Structure and recycling of vegetable parchment

N. Cartier, P. Escaffre, F. Mathevet, H. Chanzy,* and R. Vuong

ABSTRACT: *The ultrastructure of vegetable parchment was investigated by scanning and transmission electron microscopy together with electron diffraction analysis. It was found that within the parchment, the cellulose fibers which were almost intact, were held together by a glue-like precipitate of poorly crystallized cellulose II, that was deposited during the washing step of the parchmentization process. These observations have led to the devising of a recycling process for vegetable parchment where the cellulosic glue was loosened by a controlled digestion with cellulase. Within hours, the parchment became susceptible to aqueous disintegration and repulping. Handsheets made from 100% recycled fibers had mechanical properties slightly lower than those of control sheets.*

KEYWORDS: *Cellulose, enzymatic activity, parchment papers, parchmentization, reclaimed fibers, recycling, ultrastructure.*

In the conventional parchmentization process, which dates from the last century (1), a sheet of unsized paper is briefly immersed in concentrated sulfuric acid before being quickly washed and neutralized. The current belief is that the treatment involves a partial solubili-

zation of the cellulose fibers and that during neutralization the dissolved cellulose fraction is reprecipitated in the paper sheet. This leads to a filling of the sheet voids, imparting an outstanding grease proof character to the final product (2). As of today, the fine structure of parchmentized paper commonly named vegetable parchment is still a sub-

ject of speculation and debate, and there is a need of further ultrastructure studies if one wants to modernize the century old parchmentization process.

One of the crucial drawbacks of vegetable parchment is that it is hard or even impossible to recycle with conventional paper technology. After parchmentization, the cellulose fibers seem to be irreversibly glued to one another so that they cannot be disrupted by an aqueous mechanical treatment. On a laboratory scale, some attempts at redispersing vegetable parchment have been made. They include an extended immersion of the parchment in 50% sulfuric acid at 50–60°C (3) or its incubation with microorganisms (4). Both methods seem, however, impractical in an industrial process: the extended sulfuric acid treatment is extremely damaging to the cellulose fibers, whereas the microbial digestion requires at least 3–10 days to be effective.

The goal of this work was to find a practical way to achieve a successful recycling of vegetable parchment. For this, the structure and morphology of typical parchments were first investigated. The observations included scanning and transmission electron microscopy together with electron diffraction analysis. As it was found that the parchmentized fibers had kept their integrity but were glued together by reprecipitated cellulose of poor crystallinity, a selective enzymatic

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Recycling Parchment

treatment was devised to dissolve away this cellulosic glue before applying a conventional repulping. In this paper, both aspects are presented: the ultrastructure of vegetable parchment and a feasible route toward its recycling.

Experimental

Materials

The vegetable parchment used in this study had a basis weight of 70 g/m². It was produced from unsized and filler free paper made from a composition of bleached soda pulps containing 66% softwood and 33% hardwood.

Novozym 342 from Novo-Nordisk with an activity of 107 EGU/mL was received as a liquid preparation. This enzymatic complex from *Humicola insolens* "is applicable in all cases where the aim is modification and/or breakdown of cellulosic- or cellulose bonded-matter" (5). For optimum efficiency, it requires a maceration temperature of around 50°C and a neutral pH.

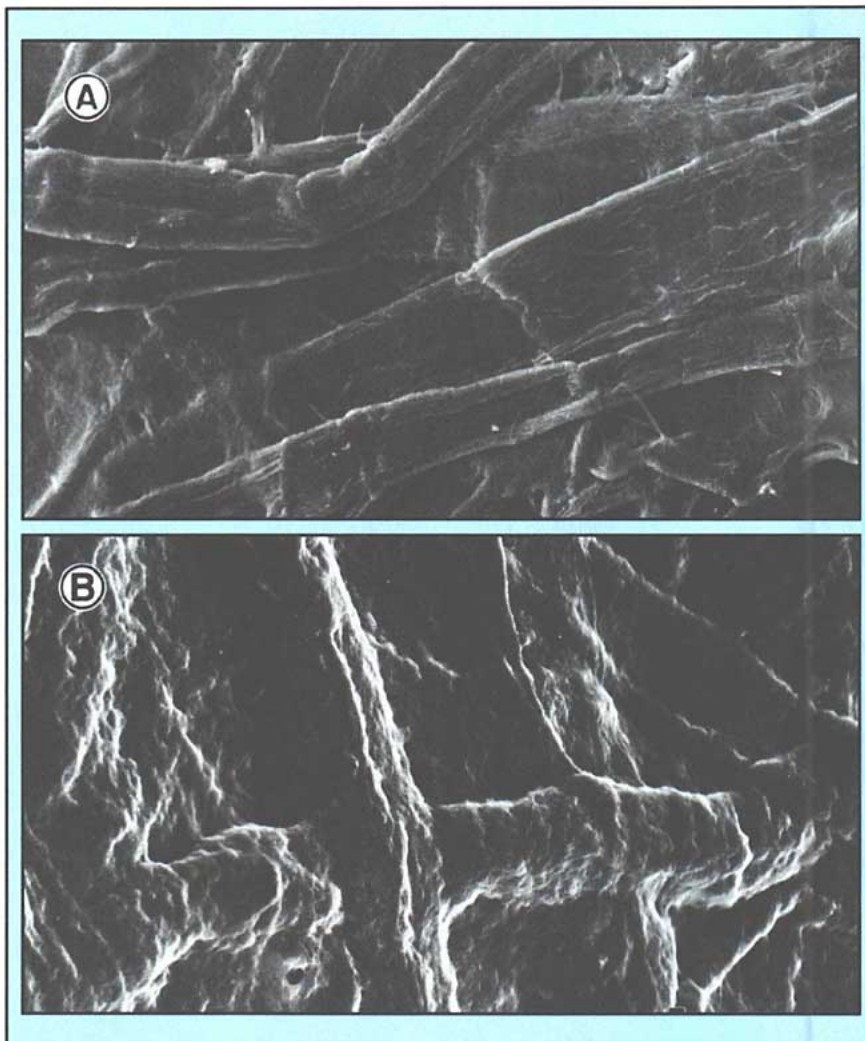
Maceration and repulping test

100 g of parchment paper was cut into square pieces having edges of 5 cm. They were soaked with 600 mL of tap water (pH 7–7.5) containing various amounts of Novozym 342 and brought to 55°C. The macerations were conducted in an oven kept at 55°C for various lengths of time ranging from 1 hour to 2 days.

At the end of the maceration time, the parchment fragments were diluted to 2% concentration. They were then subjected to a Waring blender action at 18,500 rpm for 30 s. A test for repulping was then made by dispersing a small amount of the disintegrated pulp into a graduated cylinder filled with water. If the maceration had been successful, all the parchment fibers were redispersed and no flake could be detected by visual observation.

The yield of the maceration and repulping was calculated by weigh-

1. Scanning electron micrographs: A, surface of a sheet of paper before parchmentization. B, surface of the same paper after parchmentization.



ing 10 g of dry vegetable parchment and comparing it to its weight after maceration, disintegration, filtering, and drying.

Mechanical properties of the recycled sheets

Handsheets of the recycled vegetable parchment were made with a Franck handsheet former. These sheets were tested for breaking and tear strength, elongation at break, bursting factor, brightness, and opacity using the AFNOR standards. Control handsheets were also made with the same furnish as that of the vegetable parchment.

Electron microscopy

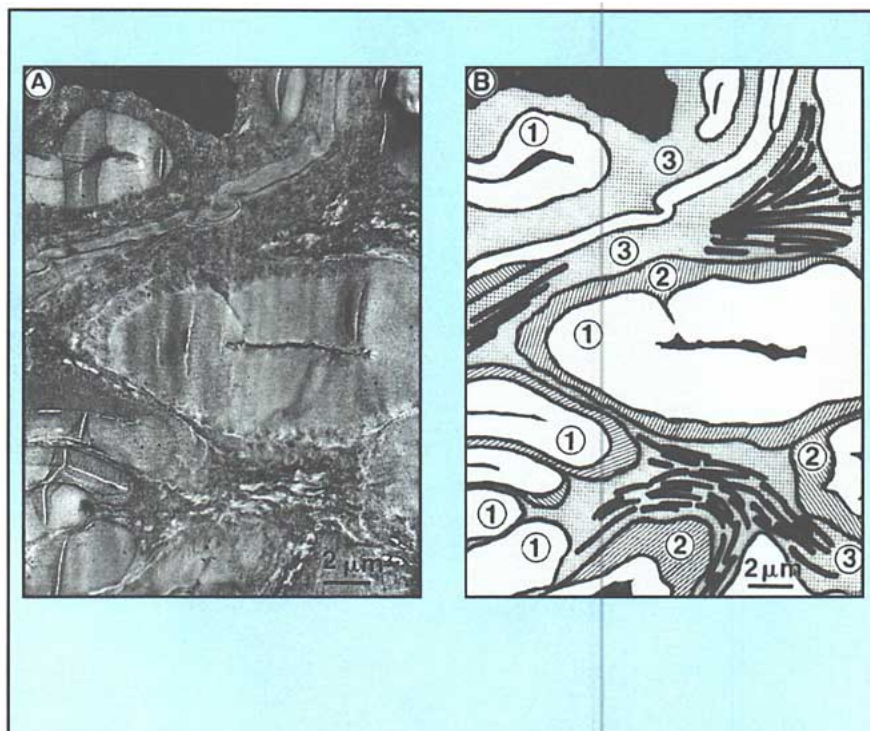
Scanning Electron Microscopy.

The observations were made with a JEOL JSM 6100 scanning electron microscope operating at an acceleration voltage of 10 kV and in secondary electron mode. Before viewing, the samples were sputtered with gold in a JEOL JFC sputterer.

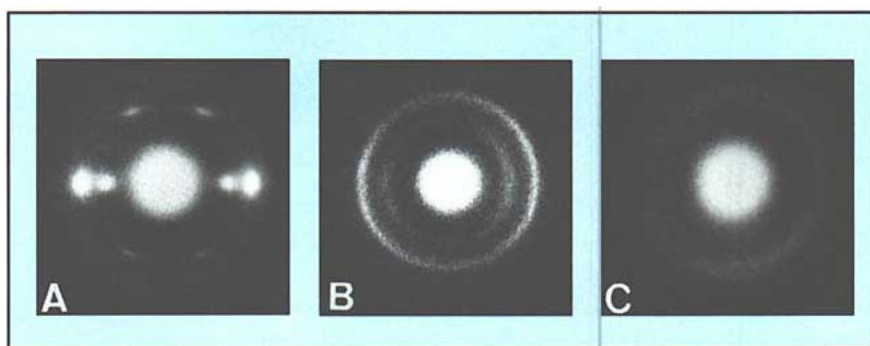
Transmission electron microscopy.

Fragments of parchment were embedded in Nanoplast resin (Agar Scientific, Essex, U.K.) which consisted of 10 g of aqueous melamine resin MME 7002 activated with 0.3 g of acid catalyst B 52. Ultrathin sections were made with an Ultratome III ultramicrotome from LKB.

2. Transmission electron micrograph obtained by low dose electron microscopy of a section of the sheet of vegetable parchment shown in Fig. 1B. 2A, actual micrograph. 2B, schematic interpretation. Three different zones can be identified: 1, white areas correspond to part of the fibers that have not been touched by sulfuric acid. 2, hatched areas correspond to the skin of the fibers that have been dissolved in or highly swollen by the sulfuric acid. 3, dotted areas correspond to the precipitate of cellulose II that covers the fibers and fills the voids of the sheet.



3. Typical electron diffraction diagrams recorded on sections of parchment sheets such as in Fig. 2A. Fig. 3A and 3B correspond to areas in intact fibers (white areas in Fig. 2B); 3C corresponds to the granular precipitate of cellulose II (dotted areas in Fig. 2B).



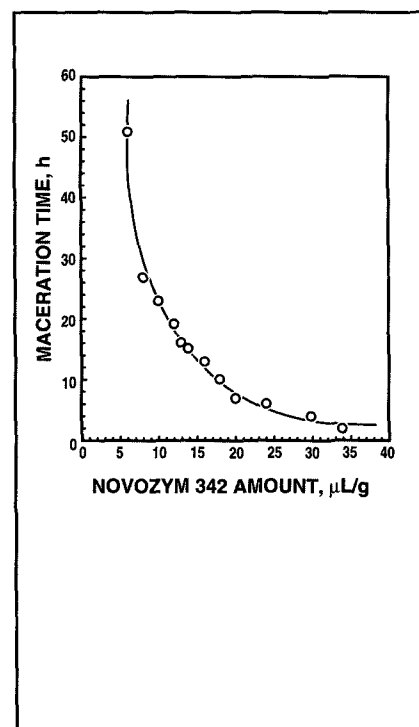
The grids holding the sections were observed under low dose mode with a Philips EM400T electron microscope operated at 120 kV. Selected area electron diffraction were achieved on one square micron of the sections. All micrographs and diffractograms were recorded on Mitsubishi electron image emulsions.

Results

Structure and ultrastructure of vegetable parchment

The parchmentization process has a strong influence on the morphology of paper. This is clearly visualized by comparing both scanning micrographs shown in Fig. 1, where 1A corresponds to the paper before and

4. Time of maceration at 55°C as a function of enzyme concentration to achieve successful repulping of vegetable parchment samples of 70 g/m². The units of enzyme are given as a function of microliters/gram of dry parchment.



1B after parchmentization. In Fig. 1A, the sheet consists of a superposition of individual cellulose fibers with sharp contours. In Fig. 1B, one still recognizes the outline of the cellulose fibers, but their contours are smoothed and their surface covered by a granular coating. In addition the interstitial voids between the fibers are also filled with the same granular material.

By cross sectioning and transmission electron microscopy, the inner structure of vegetable parchment is further revealed. This is shown in Fig. 2 where 2A is an actual micrograph and 2B its schematic explanation. Three areas can be identified: a granular structure (dotted in Fig. 2B) covers the surface of the sheet and fills all the inner voids. Its thickness ranges from 1–2 μ at the surface to 1/2 μ , and even less within the voids. The fibers (seen in white in Fig. 2B) are still present throughout the

Recycling Parchment

parchment sheet. Within the fibers, an external layer (hatched in Fig. 2B) corresponds to areas of the fibers that were in contact with the sulfuric acid during the parchmentization process. In particular, this layer was totally absent in the initial paper (not shown here).

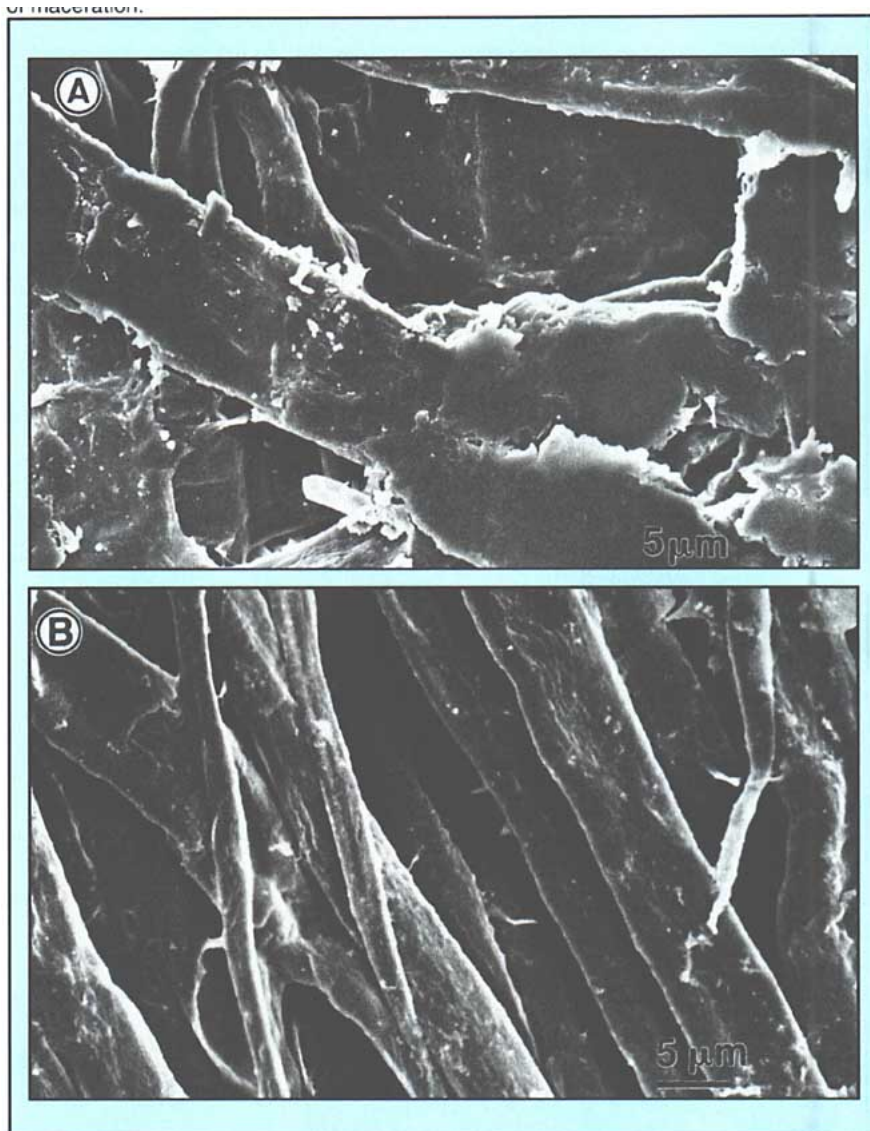
A section such as that shown in Fig. 2A can be analyzed by electron diffraction analysis at the square micron level. Typical diffractograms are shown in Fig. 3. 3A and 3B correspond to patterns recorded on the cellulose fibers (white areas in Fig. 2B). Both patterns can be identified as native cellulose I patterns: 3A is a fiber diagram corresponding to an area where the cellulose microfibrils are aligned vertically. On the other hand, in 3B the equatorial spots of cellulose occur as circles. This indicates that in the corresponding area, the microfibrils axes are parallel to the electron beam. Figure 3C corresponds to the granular part of the sample (dotted in Fig. 2B). This pattern is a powder pattern that can be identified as poorly crystallized cellulose II.

Maceration and recycling of vegetable parchment

When the parchment was macerated with Novozym 342, it lost about 10% of its weight and was easily disintegrated after a 30-s mixing in a Waring blender. The success of disintegration is, however, directly related to the quantity of enzyme and maceration time. This relation is illustrated in Fig. 4 where one sees that with an amount of enzyme of 30–40 $\mu\text{L}/\text{mg}$ of parchment, total recycling can be obtained already after 1–2 h of maceration. On the other hand, when the quantity of enzyme is minimized, more than two days are necessary. These two limits seem to be impossible to cross with the present system and our laboratory equipment.

In Fig. 5, two scanning electron micrographs illustrate the effect of the enzymatic treatment on the structure of vegetable parchment.

5. Scanning electron micrograph of a parchment as in Fig. 1B but after 5A: 1 h of maceration with Novozym 342 at a concentration of 30 $\mu\text{L}/\text{g}$ of dry parchment. 5B, same as 5A but 2 h of maceration.



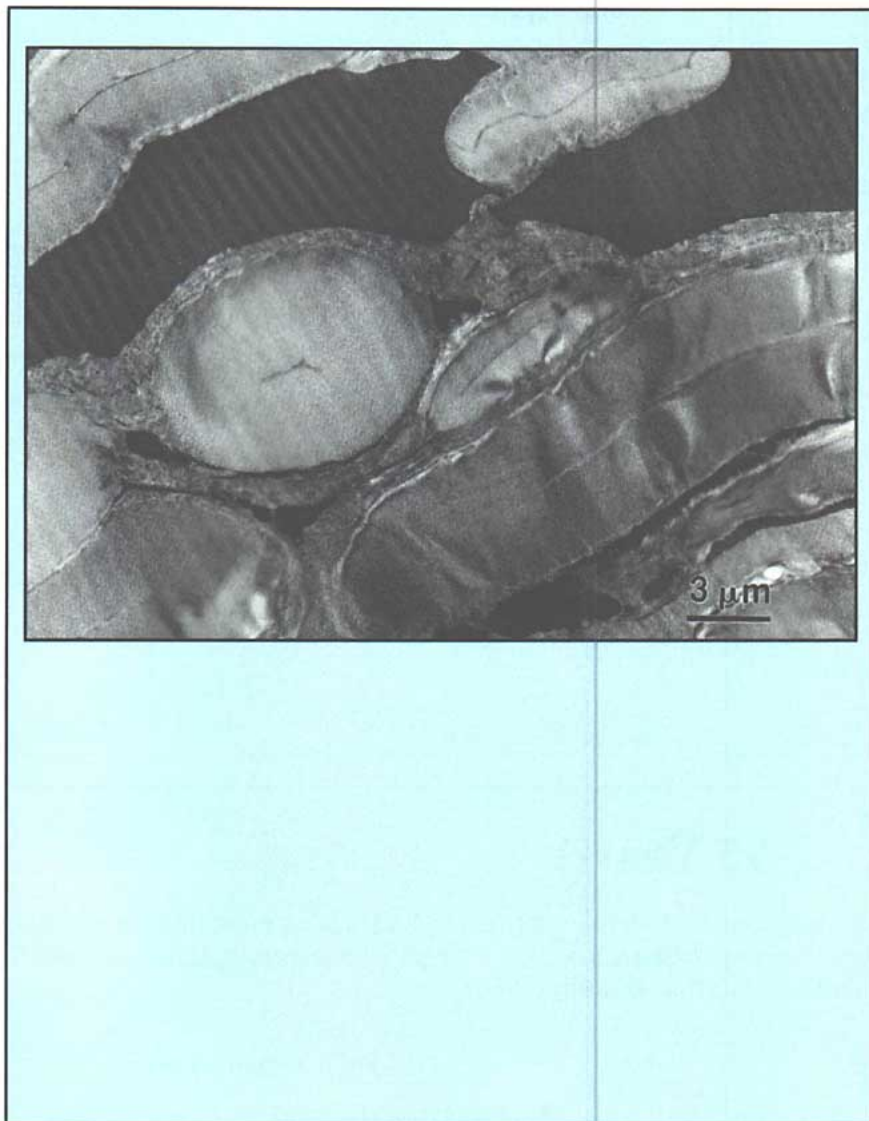
The specimen corresponds to a sheet of parchment macerated with 30 μL of enzyme per gram of paper. After 1 h (Fig. 5A), part of the fibers have lost their granular structure. After 2 h (Fig. 5B), most of the granular structure has disappeared and the surface of the paper has recovered most of its initial integrity. This is supported by the transmission micrograph in Fig. 6, which corresponds to a section of the same sample as in Fig. 5B. In this section, the cellulose fibers are no longer glued to one another. The granular material is still present but more as

patches than a continuous layer.

Mechanical properties of the recycled paper

After recycling, the physical properties of handsheets made from recycled pulp were compared with the properties of handsheets made from the initial pulp. These results shown in Table I indicate a drop of 10–20% in the mechanical properties of the recycled paper. On the other hand, the value of brightness and opacity does not appear to be affected by the recycling treatment.

6. Transmission electron micrograph obtained under low dose conditions of a section of the sample shown in Fig. 5B



Discussion

The results presented in this study bring some new light on the process of parchmentization by elucidating the phenomena that occur during the acidification step and the subsequent washing. Our data show that, during the brief immersion of the untreated paper sheet into sulfuric acid, it is only the outer skin of the cellulose fibers that is dissolved or affected. From the above micrographs, this dissolution corresponds to surface layers that are only 1–2 μ deep. During washing, the dissolved cellulose reprecipitates as a granular substance which coats the fibers and fills the voids of the paper sheet. The granular substance which consists of poorly crystallized cellulose II is responsible not only for the cohesion of the parchment sheet and its outstanding grease proof property, but also for the extreme difficulty encountered if one wants to recycle vegetable parchment with mill equipment.

Given these observations, a sheet of vegetable parchment still contains cellulose fibers that are almost intact, and are therefore worth reusing. For this, however, one needs to loosen or dissolve the cellulosic glue that holds the fibers together. In the present work, this was successfully achieved by enzymatic digestion. The commercial cellulase from *Humicola insolens* was selected, as it is highly effective in dissolving only the poorly crystalline fractions of a given cellulose material (6, 7). In paper technology, the addition of this enzymatic preparation improves the drainage of the pulp (7) without affecting the mechanical properties of the paper. Another advantage of the *H. insolens* system is that it requires neutral pH and is therefore quite easy to adapt in the mill. The laboratory conditions that are described above take full advantage of the potential of this enzymatic complex: the treatment seems to affect only the poorly crystalline cellulosic glue but

I. Mechanical properties of handsheets made from 100% recycled vegetable parchment

	Control sheets ^a	Sheets from 100% recycled paper
Basis weight, g/m ²	66	64.5
Caliper, μ m	110	115
Breaking length, km	5.1	4.1
Elongation at break, %	2.5	1.4
Tear index, mN	630	540
Burst factor, kPa	3.1	2.0
Brightness, %	87	88.5
Opacity, %	83.5	80

^aThe control sheets were made from the same furnish as that of the vegetable parchment.

Recycling Parchment

not the underlying cellulose fibers. These could thus be recycled easily to yield paper handsheets whose strength was only slightly lower than that of the control sheets before parchmentization. It may be noticed that the slight loss in mechanical properties may be due more to the parchmentization treatment than to the enzymatic degradation of the fibers. However, it is not possible at this stage to differentiate between the effect of one or the other step.

The above experiments were conducted at bench scale. Their extrapolation to pilot trials are underway and look promising. Recycling re-

sults with mill equipment have shown that for a given concentration in enzyme, the time of enzymatic treatment could be divided by ten if the maceration was conducted under strong agitation. ■

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