Hornification - Its Origin and Meaning

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ABSTRACT

"Hornification" is a technical term in the recycling literature that refers to the physical change that takes place in a papermaking fiber upon drying. The term is currently not in common nontechnical use, but it does have a long and interesting history. Its introduction to the papermaking literature is attributed to G. Jayme in 1944. The manifestations of hornification in recycling and some methods of preventing or reversing it are briefly discussed.

KEYWORDS

Drying, Hornification, Reclaimed fibers, Recycling.

ORIGIN AND MEANING OF "HORNIFICATION"

When chemical pulp fibers are dried, either in sheet or pulp form, the internal fiber volume shrinks. If the fibers are resuspended in water, the original water-swollen state is not regained. The physical change manifested by this inhibited reswelling is termed "hornification."

This word has an interesting history. In a recent presentation at the oxford Symposium on Fundamentals of Papermaking (1), Laivins and Scallan attributed to G. Jayme in 1944 (2) the application of the term "hornification" to pulp fibers. They said, "The mechanism is proposed to be an increase in the degree of cross-linking between microfibrils due to additional hydrogen bonds formed during drying and not broken during rewetting." Indeed, at least one of Jayme's subsequent papers states that he originated the term (3). Jayme's papers, however, were published in German, and the term used was "irreversible Verhornung." The-German-English Science Dictionary by De Vries (4) translates Verhornung as cornification, although the verb verhornen translate as "to become horny." The translation "cornification" has appeared in at least one English summary of Jayme's papers (3) and in translations from other languages, such as Russian (5). The Random House Unabridged Dictionary lists the noun cornification but not the noun hornification (6).

Cornification is a biological term defined as: "The formation of a horny layer of skin or horny skin structures as hair, nails, or scales from squamous epithelial cells." The given date for the origin of the word is 1835-1845. The adjective "horny," defined as "consisting of a horn or horn-like substance, corneous," was given, with the date of origin being 1350-1400. Although perhaps not strictly variants of each other, the terms hornification and cornification have similar meanings and the same root in the Indo-European "ker-" (7), from which we get keratin. The Latin word for horn is cornu. In English language papermaking literature, hornification is the preferred term, so it is likely, with the interest in recycling, that hornification will find a renewed place in the dictionary.

APPLICATION IN RECYCLING

In addition to recycling, the term hornification has been in common usage in carbohydrate chemistry, although perhaps not appearing in publications or textbooks. Isolates of polysaccharides from natural products by water extraction have to be dried carefully by solvent exchange or freeze drying. Otherwise, if dried from water, the polysaccharides will dry from a gel state to a very hard, crusty material that will not swell in or redissolve in water. They are said to be hornified. It is likely that the mechanism on a molecular level is the same as that for hornification of pulp fibers. Fig. 1 is a photomicrograph of never-dried fibers while Fig. 2 shows recycled fibers. The recycled

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FIGURE 1: **Never-dried fibers after critical point drying.**

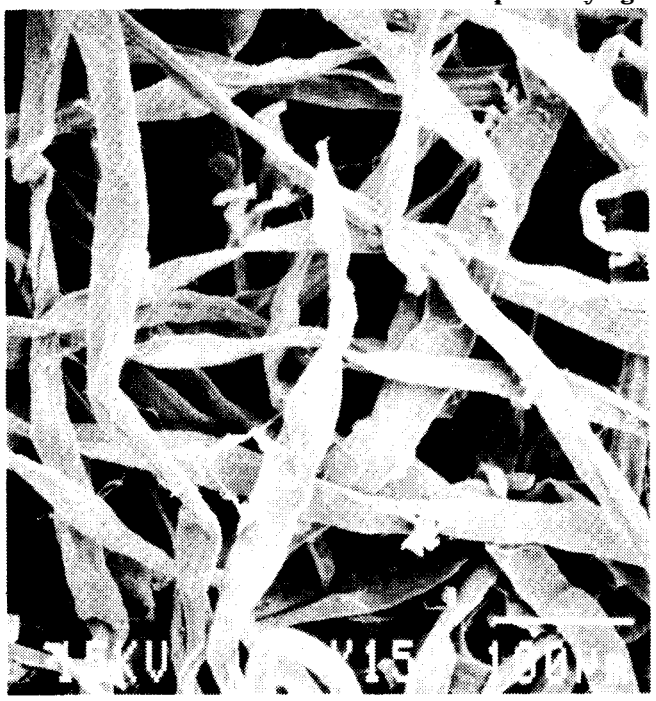
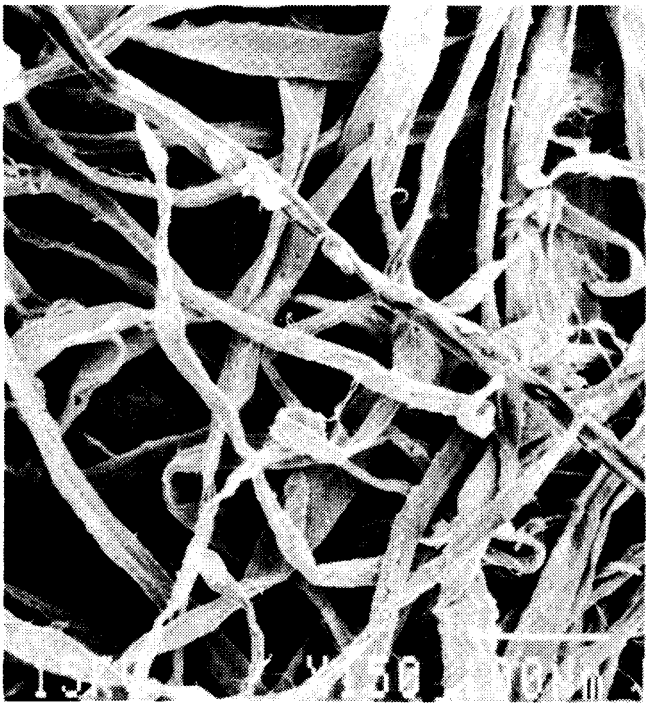


FIGURE 2: **Recycled fibers after being dried and rewetted three times.**



fibers appear thinner than the never-dried fibers.

The inhibited reswelling of hornified fibers is important in recycling because such fibers are stiffer and less conformable than never-dried fibers. The effect of hornification is expressed in those physical paper properties that are related to hydration or swelling, such as burst or tensile. Repeated recycles show progressive decreases in these properties for several cycles (8). The problem of hornification in recycling is dependent on pulp yield and is greatest with chemical pulps and least with mechanical pulps (1). It appears that if sufficient lignin is present in the fiber cell walls, the polysaccharide polymers will not dry down upon themselves and create the hornified state. The phenomenon and its possible prevention were extensively studied by Laivins and Scallan (1). They proposed that in delignifed fibers, hydrogen bonds are formed between microfibrils upon drying, and that some of these additional hydrogen bonds are retained after rewetting.

PREVENTION OF HORNIFICATION

Proposed preventive measures focussed on methods of interfering with the formation of new hydrogen bonds or intensified methods of breaking hydrogen bonds. It is experimentally known that derivatizing some of the polysaccharide hydroxyls prevents hydrogen bond formation and, consequently, prevents hornification; however, researchers realize that this approach is not practical for the commodity recycled paper.

An alternative preventive approach would be to take a lesson from the fact that lignified pulps do not hornify to the extent that chemical pulps do. High-yield pulps can be utilized as much as specifications permit, or high-yield pulps from the first cycle can be upgraded by delignification upon recycling. At least one mill is taking the latter approach (9). A related procedure would be to add materials to never-dried pulps that would penetrate and adsorb to the cell wall structure in a manner similar to lignin and hemicelluloses. Laivins and Scallan repeated the experiments of Higgins and McKenzie (10) and confirmed that the addition of sucrose or glycerol prevented hornification by acting as bulking agents within the fiber wall. A U.S. patent has been issued on a process that is claimed to prevent hornification (11). Heating dissolving pulp under 120 psi of saturated steam at pH 8.1 improved the subsequent reactivity of the pulp. The patent authors proposed that the reason for the improvement was an inhibition of hornification.

REVERSAL OF HORNIFICATION

If hornification has already occurred, can it be reversed? Part of the original definition was "irreversible." Mechanical beating can restore the swelling capacity of hornified fibers (1, 12), but two factors restrict this approach in papermaking. Additional fines are produced by the extra beating, and it appears that the original fines in chemical pulps lose their

beneficial effect to bond strength upon hornification (13). The latter effect cannot be reversed by beating.

Derivative formation has also been found to reverse the effects of hornification (1), but again, the approach is not practical. The addition of alkali to the repulper is commonly practiced and does improve the bonding strength of repulped newsprint compared to that of untreated pulp (14). Tensile properties of recycled linerboard pulps can be restored with alkali and mechanical beating (15), and the compression strength of old corrugated containers can be improved by soaking in sodium hydroxide solutions (16). However, the extent of reversibility of hornification of chemical pulps by treatment with alkali does not appear to have been fully examined.

SUMMARY

To review, "hornification" is a term that describes a phenomenon important in paper recycling. The term has not been commonly used in textbooks nor is it defined directly in general dictionaries, but it has been used in the pulp and paper literature since its introduction by Jayme in 1944. The word is used to describe something that becomes hard or horn-like, and in the case of dried pulp fibers, it describes the stiffening of the structural polysaccharides of the cell wall through an increase of intermolecular hydrogen bonding. Hornified fibers have a lower interfiber bonding capability. It is possible to prevent or reverse hornification, but the present methods are either too costly to be practical or create other papermaking problems. Alkali treatment or alkali soaking seem to partially reverse hornification, but more research is needed to understand the effect of alkali on recycled fiber structure.

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