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REVIEW SUB-COMMITTEE
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NR0217E1

O. Eng.

Brussels, 17 January 2002.

PROPOSAL BY THE US ADMINISTRATION TO AMEND THE NOMENCLATURE TO CHAPTER 41

(Item III.A.7 on Agenda)

Reference documents :

NR0155E1 (RSC/23)
NR0165E2, Annex D/4 (RSC/23 – Report)
NR0177E1 (RSC/24)
NR0205E2, Annex C/9 – RSC/24 Report)

I. BACKGROUND

1. At its 24th Session, the Review Sub-Committee held a preliminary discussion on the proposal by the US Administration to amend the Nomenclature to Chapter 41. One delegate indicated that a criterion based on thermal stability would be more appropriate than a criterion based on putrefaction, whereas other delegates, while informing the Sub-Committee that some of them were currently in the process of consulting their industries, indicated that a further study was necessary to find out what the exact terminology should be. The Chairman invited administrations to submit their written comments.

II. SECRETARIAT COMMENTS

2. At the time of preparing this document, the Secretariat had not yet received any comments. It has, however, consulted some literature and the Internet vis-à-vis the tanning process and techniques, and offers the following information for possible consideration by delegates.

Note : Shaded parts will be removed when documents are placed on the WCO documentation database available to the public.

File No. 2745

McGraw-Hill Encyclopedia of Science & Technology, Volume 9, 8th Edition, pages 729 and 730

Leather and further processing

[. . .]

The epidermal tissue in the grain area of a typical hide includes the outer epidermal layers and the associated hair follicles, oil glands, sweat glands, and erector pili muscles. Collagen, a unique triple-helical biopolymer, is the leather-making substance; it predominates in the hide corium and is a major proteinacous component in the grain enamel and fibrous grain layer that surrounds the epidermal tissue.

[. . .]

Chromium tannage

The beamhouse processes remove the keratinous tissues from the hide and initiate the preparation of collagenous fibrous substances in the hide tannage. [. . .] Chromium tannage requires an acidic pickling process. The pickling solution is a sodium chloride brine solution [. . .]. Pickling, in addition to being a tannage process step, is also used for temporary storage of the skins and hides.

[. . .]

A characteristic manifestation of chromium tannage is the increase in the hydrothermal shrinkage temperature of the hide substance from around 65 °C to temperatures exceeding 100 °C. [. . .] The tanning complex is fixed by collagenous carboxyl groups, partially forming cross-links in the collagenous molecule.

The New Encyclopaedia Britannica, Volume 11, Micropaedia, page 546

Tanning, chemical treatment of raw animal hide or skin to convert it into leather. A tanning agent displaces water from the interstices between the protein fibres and cements these together. The three most widely used tanning agents are vegetable tannin, mineral salts such as chromium sulfate, and fish or animal oil.

[. . .]

Two methods are used for the tanning with chromium salts. In the double-bath method the hides are first bathed in a mild chromic acid solution. In the second bath, sodium thiosulfate and another acid react with the chromic acid to produce basic chromium salts, which are deposited on the fibres of the skins. In the more common single-bath method the hides are soaked in revolving drums filled with increasingly strong chromium sulfate solutions. Aluminium and zirconium salts are also used in tanning.

Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition, 2001 Electronic Release

7.3. Tanning Techniques

Vegetable tanning is used in the manufacture of leather for shoe soles, harnesses, saddles, belts, bookbinding, heavy shoes, and certain other products. The bated pelts

[hides and skins – *Secretariat*] are usually tanned in vegetable tan floats, starting with dilute solutions, followed by stepwise increases of the tan concentration.

[. . .]

Today tanning is performed with floats prepared from vegetable extracts and often syntans [= synthetic tanning agents – *Secretariat*]. [. . .] Tanning starts with used floats that contain no tannins, but high concentrations of salt and sugar left after tanning. These liquors have a soft, weak pretanning effect with low astringency. The grain is flat, penetration is fast, and the pH is higher. In the floats used in final tanning steps, the tannin concentration is high, the salt and sugar concentrations are low, the pH is lower and the astringency is high. This results in a good filling effect. This process avoids "dead tanning" in which tanning comes to a standstill when a pelt is treated straightaway with a concentrated tannin. Osmotic dewatering then causes a structural collapse producing a glueing together of the fibre network. The pores are sealed and penetration (i.e., tanning) stops. Many tanneries employ pretanning to stabilize the fibre structure and prevent the above-mentioned collapse.

8.3. Aldehydes and other tannages

Formaldehyde is a well-established cross-linking agent. It is used in aqueous solution up to 4 % formalin (40 % formaldehyde). Formaldehyde is never used alone as a tanning agent because it produces stiff, empty leather with an uneven grain. Uptake of formaldehyde is low under acidic condition and increases strongly above pH 7. The compound reacts with the primary amine groups of lysinyl residues in the protein chains. It is used in pretanning to accelerate vegetable tanning. It is regularly used to fix the hairs of fur and to fix sheep wool. Glutaraldehyde has been in use since the late 1960s; in contrast to formaldehyde, it cross-links under acidic conditions. Glutaraldehyde is a better tanning agent and gives a sift voluminous leather, but has a yellowing effect. Both aldehydes serve in pretanning, and glutaraldehyde in retanning; they are, however, harmful in the workplace. Formaldehyde concentrations in air are restricted. Glutaraldehyde forms higher molecular mass unsaturated aldehydes, and reacts with amines to give pyridine derivatives. Both formaldehyde and glutaraldehyde can be stabilized against polymerization and reaction with other compounds by acetalization with methanol.

Internet

(*http://www.unido.org/ssites/env/sectors/sectors45bk.html*)

Pretanning (Recycling of Used Floats)
[1] [5] [3] Pretanning is done between pickling and tanning when the pelt is pretanned with part of the accumulated waste baths from tanning including water from sammying and draining for 2 to 3 hours. The pretanned bath is discharged and then the pelt is tanned with a use of the residual part of the accumulated tanning waste baths after refilling their composition. The chromium composition of the discharged bath, about 1.3-3.0 gr/l of chromium, [5] must be treated to avoid chromium discharges to the treatment plant (chromium recovery by precipitation as an example).

[1] Techno-economic Study on Measures to Mitigate the Environmental Impact of the Leather Industry, Particularly in Developing Countries
Winters, D.
Third Consultation on the Leather and Leather Products Industry, Innsbruck, April 1984. UNIDO

[3] Expert Group Meeting on Pollution Control in the Tanning Industry in the South-east Asia Region
Ludvik, J.; UNIDO project US/RAS/89/246
Madras, 1991

[5] Introduction of Cleaner Leather Production Methods-Prospects and Constraints
Aloy, M.
Eleventh Session of the Leather and Leather Products Industry Panel, Nairobi (1993)

3. The Secretariat understands from the foregoing that the tanning process is done stepwise by increasing the tan concentration, starting with diluted solutions. It also understands that the starting point of this process could be called "pretanning", since the final tanning is being done with high concentrations of the tanning substance. In this context, the Secretariat has noted that some agents (e.g., glutaraldehyde) are referred to as a substance used in pretanning, as well as in retanning. Another aldehyde (i.e., glutardialdehyde) is mentioned as a pretanning agent in the wet-white tanning process, which is a process using chrome-free tanning agents, for example, titanium salts. Wet-white can be retanned with chrome, vegetable and synthetic tanning agents. Based on this information, the Secretariat considers that it might be difficult, if not impossible, to draw a dividing line between hides which have undergone a pretanning process, on the one hand, and those which have undergone a further tanning process, on the other hand. It would, therefore, not be in favour of saying, as suggested by the US, that pretanned hides are always to be classified in one of the headings 41.01 to 41.03, and not in the headings covering "tanned" hides and skins.

4. The Secretariat considers that the processes referred to in paragraph 3 above, which contribute to the cross-linking of the fibres of the hides, are part of the "tanning process", and, therefore, go beyond the provisions of headings 41.01 to 41.03. In other words, the hides and skins have undergone a further process than preserving and would be classifiable in headings 41.04 to 41.06, as the case may be.

5. Having said this, the Secretariat must leave it to the Sub-Committee to decide whether or not the provisions of Note 2 (A) to Chapter 41 should be amended.

6. The Secretariat has nothing to add to its comments in paragraphs 16 to 20 of Doc. NR0177E1, concerning the US proposal to replace the terms "hides" and "skins" by the term "leather" in headings 41.04 to 41.06.

III. CONCLUSION

7. The Sub-Committee is invited to take into account the comments of the Secretariat set out in paragraphs 3 to 23 of Doc. NR0177E1 and in paragraphs 2 to 6 above, when considering the US proposal vis-à-vis certain terminology used in Chapter 41, as set out in Annex II to Doc. NR0177E1.