

Preparation of Storable Standard Chrome Grain Leather for Dyeing

1 Purpose and Scope

- 1.1 By standard chrome grain leather is meant a box-calf type of leather, made from oxhide which, having been tanned with a cationic chrome liquor, takes up dye readily. The standard chrome grain leather is made with a defined chrome tanning agent according to a standardised procedure, which is simple and easily controlled and largely parallels industrial processing. The standard chrome grain leather is intended to remain unchanged on storage.
- 1.2 The preparation of the standard chrome grain leather is so designed that the customary reneutralisation of chrome leather before dyeing is unnecessary. Renutralisation, being difficult to control, particularly in small-scale experiments, is replaced by washing under defined conditions.
- 1.3 The standard chrome grain leather is intended for (see also Section 7.1):
 - 1.3.1 Determining the fastness of dyeings of specified dyestuffs;
 - 1.3.2 Determining the dyeing behaviour of specified dyestuffs;
 - 1.3.3 Testing dyeing auxiliaries.
- 1.4 This method describes the production of standard chrome grain leather, as well as its preparation for use. The process is checked at specified stages and tolerances are laid down for the values obtained (see also Section 7.2).
- 1.5 This method allows the preparation of standard chrome grain leather in small packs (3-6 hides) as well as in larger ones (about 100 hides) according to a laid-down schedule (see Section 7.8).

2 Methods for Process Control

- 2.1 Chrome oxide content and basicity of chrome liquors.
- 2.2 The Measurement of Shrinkage Temperature (see Section 7.1(b)).
- 2.3 pH determination:
 - 2.3.1 Of aqueous solutions: electrometrically with a glass electrode at 20 °C (see Section 7.1(c)).
 - 2.3.2 Of pelt sections: phenolphthalein solution, 0.1 g in 100 ml 70% v.v ethanol.
 - 2.3.3 Of leather sections: Bromocresol Green solution, 0.1 g in 100 ml 20% v.v ethanol.
 - 2.3.4 Of an aqueous leather extract: see Section 7.1(c).
- 2.4 Chrome oxide content of leather (see Section 7.1(d)).

3 Materials

- 3.1 *Raw hides*
Oxhides, salted, stored correctly, quality Ia, up to 24.5 kg.
- 3.2 *Tanning agent*
Chrome alum, $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, analysing as follows:
 - 3.2.1 Chrome oxide content, Cr_2O_3 : $15.1 \pm 0.1\%$.

- 3.2.2 Basicity (Schorlemmer): $0 \pm 1\%$.
- 3.2.3 Iron content, calculated as Fe_2O_3 : $<0.02\%$.
- 3.2.4 Ammonium sulphate: absent.
- 3.3 *Auxiliaries*
Chemicals of technical quality, as far as possible free from iron, suitable for tannery use:
- 3.3.1 Calcium hydroxide (hydrated lime in powder form).
- 3.3.2 Sodium sulphide, 60-62%.
- 3.3.3 Sodium chloride (free from additives).
- 3.3.4 Ammonium sulphate.
- 3.3.5 Sulphuric acid, concentrated (98% H_2SO_4 , $d_{20} = 1.84$ g/ml).
- 3.3.6 Sodium carbonate, anhydrous.
- 3.3.7 Sodium hydrogen carbonate (sodium bicarbonate).
- 3.4 *Water*
- 3.4.1 For soaking and tanning: water suitable for tannery use, total hardness <250 ppm.
- 3.4.2 For washing (neutralising): softened water, $\text{pH } 6.5 \pm 0.5$.
- 3.4.3 For washing out the preservative before dyeing: distilled water, $\text{pH } 6 \pm 1$, or demineralised water of the same quality.
- 3.5 *Preservative*
Ethylene glycol, 99-100%, technical quality, water-clear, neutral (content of organic acids $<0.01\%$), free from corrosion inhibitors and other additives.

4 Preparation of the Leather

- 4.1 *Soaking*
Percentages are based on the green weight.
Soak in a drum at 2-3 rev/min or in a paddle in water without additions, using successively three different floats:

	Float 1	Float 2	Float 3
Water (%)	500	500	500
Temperature ($^{\circ}\text{C}$)	20 ± 1	20 ± 1	20 ± 1
Duration (h)	1	6	17
of which movement	5 at end	5 at start	5 at start
for (min)		10 midway	10 at end
		10 at end	

Drain skins for 2 h after piling flat, then preflesh and determine soaked weight.

- 4.2 *Painting*
Composition of the paint:
66 parts by weight water
30 parts by weight calcium hydroxide
4 parts by weight sodium sulphide, 60-62%.

Room temperature and temperature of paint: 20 ± 1 $^{\circ}\text{C}$.
Apply about 20% paint, calculated on the soaked weight. Paint the flesh of the hides completely and uniformly, fold along the backbone, do not place more than ten hides in a pile, and unhair after 15 h.

- 4.3 *Liming*
Percentages are based on the soaked weight.
Lime in a drum at 2-3 rev/min or in a paddle with:
500% water, 20 ± 1 °C
10% calcium hydroxide
2% sodium sulphide, 60-62%
5% sodium chloride.
Duration: 46 h, of which movement for 10 min at the start and for 5 min every 3 h thereafter.
Check: pH of fresh lime liquor: 11.8 ± 0.5 .
After liming, immerse the hides for 1 h without movement at 20 ± 1 °C in 500% water, which has been softened with calcium hydroxide (lime water at pH 8.5 ± 0.5). Flesh, split to about 3.5 mm, and scud. Determine pelt weight (see also Section 4.7.1).
- 4.4 *Deliming*
Percentages are based on pelt weight.
Delime in a drum at about 10 rev/min.
- 4.4.1 Washing: 500% water, 30 ± 1 °C, run 10 min. Drain.
- 4.4.2 Deliming: 300% water, 35 ± 1 °C.
3% ammonium sulphate.
Duration: Run continuously for 45 min. Leave in the float until the check has been carried out.
Check: pH after deliming: 8.75 ± 0.25 . If necessary, continue to run until this pH is reached. Drain.
Cut edge remains colourless with phenolphthalein or colours only weakly in the centre.
- 4.5 *Bating*
Percentages are based on pelt weight.
Bate in a drum at about 10 rev/min.
- 4.5.1 Bating: 300% water, 35 ± 1 °C
0.5% Oropo OR (see Section 7.3).
Duration: Run continuously for 45 min. Drain.
Check: pH of the float after 15 min and at the end of bating: 8.5 ± 0.2 .
Cut edge remains colourless with phenolphthalein.
- 4.5.2 Washing: 300% water, 25 ± 1 °C.
Duration: Run continuously for 15 min. Drain and unload pelts.
- 4.6 *Pickling*
Percentages are based on pelt weight.
Pickle in a drum at about 10 rev/min:
90% water, 20 ± 1 °C
8% sodium chloride
Add hides and run 20 min.
Check: Density determination: d_{20} not less than 10.45 g/ml (6°Be).
Addition: 0.8% sulphuric acid, concentrated, added after diluting 1:10.
Check: Acid content of fresh pickle: 7.0 ± 0.1 g/litre
Acid content of used pickle: <0.2 g/litre H_2SO_4 .
pH of used pickle: 3.3 ± 0.2 .
Duration: Run continuously for 1.5 h. Leave in the float overnight without movement. In morning, run 10 min. Drain.
- 4.7 *Chrome tanning*
Percentages are based on pelt weight.
- 4.7.1 Preparation of the tanning liquor:
The preparation of the chrome tanning liquor must be started immediately the pelt weight has been determined.
Chrome oxide offered: 2.5%.
Equivalent to chrome alum: 16.3%.
Add the chrome alum to 1.8 times its weight of boiling water and divide the resulting solution into three equal portions. Cool to

25 ± 5 °C before basifying. Basify each of these portions to the basicity specified below with the calculated amount of sodium carbonate solution (100 g/litre Na₂CO₃) within 30 min:

	Schorlemmer basicity (%)	Amount of Na ₂ CO ₃ required, calculated on pelt weight (%)
Portion 1	33	0.58
Portion 2	42	0.72
Portion 3	50	0.87

After basifying, make each portion up to 25% (based on pelt weight) by addition of water.

Checks: Chrome oxide content of each portion: 30 ± 2 g/litre.

Basicity (Schorlemmer) of

portion 1: 33 ± 1.5%

portion 2: 42 ± 1.5%

portion 3: 50 ± 1.5%.

4.7.2 *Tannage*

The basified portions of the chrome liquor must not be used until they have stood overnight. All portions must be at 20 ± 2 °C.

Percentages are based on the green weight.

Tan in a drum at about 10 rev/min:

Tannage: 60% water, 20 ± 2 °C.

1% sodium chloride.

Portion 1 of chrome liquor.

Load pickled pelt into drum and run for 1 h. Add portion 2 of chrome liquor. Run drum for 1 h. Add portion 3 of chrome liquor. Run drum for 2.5 h.

Basification: Add during 30 min 0.3% sodium carbonate (100 g/litre Na₂CO₃), with movement. Run drum for a further 3 h and allow to stand overnight.

Next morning, add during 30 min 0.3% sodium carbonate (100 g/litre Na₂CO₃), with movement. Run drum for a further 2 h.

Checks: If the tannage has been carried out correctly, the analysis of the spent chrome liquor is as follows:

pH: 3.7 ± 0.2.

Chromic oxide content: 9 ± 1 g/litre.

Basicity (Schorlemmer): 38.5 ± 1.5%.

The leather must have a shrinkage temperature above the boiling point (see Section 7.1(b)).

4.8 *Shaving*

Horse up the leather for two days. Samm, shave to a thickness of 1.5 mm, allow to rest at least overnight, and shave again to 1.5 mm. Determine the shaved weight.

Check: Cut pieces of leather, weighing 10 g each, from the butt of several hides and determine their water content (see Section 7.4). Use the average water content and the shaved weight to calculate the equivalent shaved weight for a 60.0% water content, on which calculations for neutralising are to be based.

4.9 *Neutralisation*

Percentages are based on the equivalent shaved weight for a 60.0% water content:

Carry out all operation in a drum at about 15 rev/min.

4.9.1 Preliminary wash: Drum three times, each time with 250% softened water at 30 ± 1 °C for 10 min.

4.9.2 Neutralisation: 250% softened water, 30 ± 1 °C. Add all at once 1% sodium hydrogen carbonate (50 g/litre NaHCO₃). Drum 1 h. Leave in the float until the check has been carried out.

Checks: pH of spent liquor: 6.0 ± 0.5. If necessary, neutralise further with sodium hydrogen carbonate (50 g/litre) until the correct pH is reached. Then drain.

Cut edge with Bromocresol Green appears blue in the outer thirds and greenish blue in the centre.

- 4.9.3 Final washing: Drum three times, each time with 250% softened water at 30 ± 1 °C for 10 min.
- 4.9.4 Samming: Samm to a water content of $62.5 \pm 2.5\%$, based on the equivalent shaved weight for a 60.0% water content.

5 Preservation of the Standard Chrome Grain Leather

5.1 Impregnation

Percentages are based on the weight of the shaved neutralised leather, sammed to a water content of $62.5 \pm 2.5\%$.
Impregnate in a drum (see Section 7.5) at about 15 rev/min with 200% ethylene glycol at 20 °C.
Drum for 1 h, then leave for at least 18 h before drumming for a further 1 h. Strike out lightly.

5.2 Storage

Packed in polyethylene bags at room temperature. The leather may be stored for at least four years.

6 Preparation of the Standard Chrome Grain Leather for Use

Start the preparation one day before use.

6.1 Cutting of standard chrome grain leather rectangles

Slick out the impregnated leather so that it lies flat, but has not been deliberately stretched. Cut the required number of rectangles of standard size, 150 x 90 mm, with their shorter sides parallel to the backbone and 2 cm from it (see Sections 7.6 and 7.7).
Equivalent shaved weight of each standard chrome grain leather rectangle, 150 x 90 mm: 25 g.

6.2 Removal of the preservative

Percentages are based on the equivalent shaved weight of 25 g.
Wash the required number of rectangles five times, each time with 500% distilled water at 10 ± 1 °C in a drum at about 15 rev/min or in some other suitable rotating apparatus as follows:

1st wash: 0.5 h	Movement only for
2nd wash: 1 h	first and final 15 min
3rd wash: 2 h	of each wash
4th wash: 4 h	
5th wash: about 16 h	

After each wash, drain and centrifuge or strike out the leather. Leave the leather in the final liquor until required for use.

Checks: pH of 5th wash liquor: 4.0 ± 0.5 .

After final wash, cut edge with Bromocresol Green: uniformly green.

6.3 Analysis of the leather

If all the operations have been carried out correctly, the analysis of the leather, dried after washing, but neither dyed nor fatliquored, will give results as follows:

pH of aqueous extract, 1:20: 4.0 ± 0.2 (see Section 7.1(c)).

Chromic oxide content of the leather at a moisture content of 18%: 5.0 ± 0.2 (see Section 7.1(d)).

7 Notes

7.1 See:

- General Principles of Colour Fastness Testing of Leather, IUF 120.
- The Measurement of Shrinkage Temperature, IUP 16.
- Determination of the pH Value and Difference Figure of an Aqueous Leather Extract, IUC 11.
- Determination of Chromic Oxide, IUC 8.

- 7.2 In cases of dispute it is advisable to employ a standard chrome grain leather which has been prepared by an independent institute, ie, Eidg Materialsprüfungs- und Versuchsanstalt, EMPAC, Unterstrasse 11, CH-9001 St Gallen, Switzerland.
- 7.3 Oropon OR is a product of Röhm GmbH, D-61 Darmstadt, Germany. Other enzyme preparations may be used, provided they give the same bating effect as Oropon OR under the conditions of Section 4.5.
- 7.4 For the determination of the water content, take samples after the first shaving. Determine the water content by drying overnight at 120 °C to constant weight.
- 7.5 Wooden drums are not suitable for the impregnation, since ethylene glycol dehydrates the wood and may thus cause leakage. Stainless steel drums are suitable.
- 7.6 If no press-knife is available, it is recommended first to mark the outline of the rectangles by means of a template, 150 x 90 mm, made of, eg, polyethylene or polyvinyl chloride, and to cut subsequently. Stainless steel tools only must be used.
- 7.7 It is recommended to mark the rectangles so that the hide from which they have been taken can be identified, as well as the position within that hide, which is best done by means of a diagram.
- 7.8 A timetable for the preparation of standard chrome grain leather is appended.