



The resistance of wet-white pre-tanning systems to mould growth when supported by various fungicides

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The development of wet-white pre-tanning systems was to address environmental matters—in particular the reduction of chrome in effluent and solid waste—and for the production of chrome-free leather for specific applications. The largest user of chrome-free leather is the motor industry which requires high performance, particularly in manufacture and use.

There are several processes possible for manufacturing wet-white pre-tanned stock, and this approach to leather manufacture often involves holding periods. A delay at this interim stage can lead to mould growth, and hence potential loss in quality and value. To avoid these losses, it is customary to include preservatives in the pre-tanning system.

Combinations of pre-tanning process, fungicides, and different points of offer of these preservatives were investigated to see the effects on mould growth during storage, and possible ecological effects.

The investigation

The raw materials used in this investigation were south German bovine hides, as the main outlet for wet-white pre-tanned leathers is for auto and furniture upholstery leather. The wet-white pre-tannages investigated were:

- glutaraldehyde
- glutaraldehyde + polymer
- Tetrakis-hydroxymethylphosphonium sulfate (THPS)

It is noted that the glutaraldehyde was in the masked form and commercially available for leather manufacture. Evaluations were made under five different sets of conditions. One set omitted any addition of preservative, and four different products were used to preserve the other wet-white, i.e.:

- Non-preserved
- 2 phenylphenol (OPP)
- 2 octyl 2H-isothiazol-3 (OIT)
- 2-(thiocyanomethylthio)-benzothiazol (TCMTB)
- p chlormetacresol (CMK)

Panel 1

Point of addition of fungicide and running times in process

Wet-white Pre-tannage	Point of addition	Running time (mins)
Non-preserved	n/a	n/a
THPS	Pickle	410
	Commencement of pre-tannage	350
	End of pre-tannage	60
Glutaraldehyde + Polymer	Pickle	195 and overnight
	Commencement of pre-tannage	135 and overnight
	End of pre-tannage	60 and overnight
Glutaraldehyde	Pickle	520
	Commencement of pre-tannage	460
	End of pre-tannage	60

Panel 2

Detail of preservative offer

Fungicide agent	Content	Offer
OPP/OIT (blend)	33 - 38% / <3% (ratio of blend)	0.35%
OIT	20 - 22%	0.15%
TCMTB	30%	0.25%
CMK/OIT (blend)	35 - 40% / 1-5% (ratio of blend)	0.35%

The products were added at one of the following three process stages:

- to the pickle
- to the pre-tan float
- at the end of the pre-tannage ➤



THE RESISTANCE OF WET-WHITE PRE-TANNING SYSTEMS

The running times are given in *Panel 1*, and the content of the fungicide agents is given in *Panel 2*. These offers are slightly greater than the manufacturer's recommendations for wet-blue.

The retention of preservatives during storage

The quantity of preservative offered to process and retained after storage was measured. The decline in fungicide content as a consequence of storage by some of the samples was less than expected.

The effects of each of the four preservatives on the three different wet-white pre-tannages can be summarised:

SAMPLES PRESERVED WITH OPP

THPS samples: showed the highest OPP content when added at the end of the pre-tannage.

Glutaraldehyde: Best absorbed when added in the pickle.

Glutaraldehyde + polymer: Best absorbed when added either in the pickle or the pre-tannage float.

SAMPLES PRESERVED WITH OIT

THPS samples: Best absorbed when added in the pre-tannage. After storage for 8 weeks no OIT could be found.

Glutaraldehyde: Best absorbed when added at the end of pre-tannage.

Glutaraldehyde + polymer: Best absorbed when added at the end of pre-tannage.

SAMPLES PRESERVED WITH TCMTB

THPS samples: After 6 weeks no fungicide could be detected.

Glutaraldehyde: Best absorbed when added to the pickle bath. Over the 16-week storage period there was a continuous loss of fungicide.

Glutaraldehyde + polymer: Best absorbed when added to the

pickle bath. Over the 16-week storage period there was a continuous loss of fungicide.

SAMPLES PRESERVED WITH CMK

THPS samples: There is a continuous decline in fungicide concentration to 75% of that found immediately after addition in pickle.

Glutaraldehyde + polymer: Best absorbed if added at the end of the pre-tanning.

Glutaraldehyde: The retention of fungicide was between the other two variants, and declined more slowly during storage.

The growth of mould during storage

Mould resistance tests according to TEGEWA were carried out (*as recommended for wet blue*) after storage periods of between 108 days and 119 days. Samples 3cm in diameter were inoculated with the spores of three fungi for 21 days at 29°C, +/-2°C, giving a total of 12 samples for each wet-white variant. A satisfactory result was achieved if, at the end of the test period, a mould-free cut edge remained around the specimen. As a summary it can be said that:

THE NON-PRESERVED SAMPLES

- After 3 weeks the THPS samples were completely covered in mould.
- After 4 weeks the glutaraldehyde + polymer showed definite mould growth. This covered the complete specimen after a further 1.5 weeks.
- The glutaraldehyde product showed the beginning of mould at 6 weeks. After 12 weeks the material showed little mould with only some discolouration.

THPS PRE-TANNAGE

- OPP added at the end of the pre-tannage provided

Panel 3

**Protection provided to various wet-white pre-tanning systems by selected fungicides.
+ Fungicide as active content at start of test (based on dry weight mg/kg)**

	THPS				Glutaraldehyde				Glutaraldehyde + polymer			
Point of addition	OPP	OIT	CMK	TCMTB	OPP	OIT	CMK	TCMTB	OPP	OIT	CMK	TCMTB
Pickle	4378	0	2033	0	4909	905	3374	2163	5056	746	2955	1682
Commencement of Pre-tannage	3051	0	2160	0	3558	950	3022	1467	3967	816	3041	1234
End of Pre-tannage	3238	0	2360	0	3065	1021	3603	1467	3637	850	4595	1017

Completely ineffective
 Inadequate protection
 Some protection
 Adequate protection

WET-WHITE PRE-TANNING SYSTEMS



adequate protection against mould.

- OIT samples were completely covered in mould.
- TCMTB provided inadequate protection.

GLUTARALDEHYDE PRE-TANNAGE

- OIT at a concentration of 400 ppm was ineffective.
- OPP at >1200 ppm was satisfactory if added at the beginning and at the end of pre-tannage. Despite the fact that in the pickle higher values of ~2000 ppm were found, some specimens showed mould growth.
- CMK at a content >1500 ppm was satisfactory against mould.
- TCMTB provided adequate protection at >600 ppm.

GLUTARALDEHYDE + POLYMER PRE-TANNAGE

- OPP prevented mould growth at >1500 ppm.
- TCMBT prevented mould growth at >500 ppm.
- CMK was effective at 1400 ppm.
- OIT was ineffective at 300 - 400 ppm.

Independent of the pre-tannage, the most dependable of the fungicides were OPP and TCMTB.

The amount of preservative absorbed by the different wet-white was determined for each of the samples at the start of the test period, and expressed as active material on the dry pelt weight. These values, together with evaluations for mould growth, are presented as *Panel 3*.

Based on these findings, and over a sample holding period of 108 to 119 days, it was found that:

- Where there was a complete absence of preservative, the wet-white based on THPS were completely moulded after 3 weeks. This occurred with the glutaraldehyde + polymer in 6 weeks. The glutaraldehyde wet-white only showed the beginning of mould growth after 13 weeks.
- There were differences in the loss of the different fungicides during storage, and these varied according the method of pre-tannage.
- When using the THPS wet-white pre-tanning system, with the exception of an addition of OPP at the end of pre-tannage, no fungicide was effective against mould growth.
- With the glutaraldehyde pre-tannage, OPP and TCMTB were found effective against mould growth when added during tannage, and OPP, TCMTB and CMK when added at the end of the pre-tannage.
- With the glutaraldehyde + polymer pre-tannage, addition of OPP, TCMTB and CMK were effective against mould when added during tannage and at the end of tannage. 🌐

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