The addition of fungicides in chrome tannage and their Penetration, absorption and distribution in the wet blue 1997

Dr. Christiane Hauber and Dr. Heinz-Peter Germann Lederinstitut Gerberschule Reutlingen, Germany

Leathers in the wet blue condition are susceptible to attack by micro-organisms, particularly moulds. Since the withdrawal of pentachlorophenol (PCP) as a means of preventing attack, alternative products are being offered. These are less of an ecological bürden, but are also less effective than PCP.

These substitutes are available as components of products that incorporate suitable emulsifiers to help ensure a homogeneous distribution in the tanning bath and within the hide material. These modern fungicides, however, are more sensitive to the conditions of application. On storage and transport of the wet blue frequently unexpected attacks of moulds and yeasts occur.

Optimum conditions are needed to produce the most satisfactory results, and these parameters were the subject of detailed investigation.

The approach to the investigation

After preliminary trials a conventional chrome tannage was used on pilot scale for the investigation.

The bovine hides processed were:

- lime split to 2.0mm substance
- unsplit but levelled to 4.5mm

Fungicides investigated

The fungicides used in the form of their commercial product were:

1. TCMTB (2-Thiocyanatemethylthiobenzothiazol)
2. CMK/oPP (p-Chlor-m-cresol together with a o-Phenylphenol)
3. OITZ(2-n-Octylisothiazoline-3-on)

The application concentrations used in the studies corresponded to the minimum and maximum values

recommended by the manufacturers:

1. TCMTB 0.06% and 0.15%,
2. CMK/oPP 0.2% and 0.5%
3. OITZ 0.05% and 0.1%.

Addition of fungicides to process

The fungicides were offered during:

1. pickle 30 minutes after the last acid addition
2. tannage five minutes after the addition of chrome tanning materials
3. basification 60 minutes after the addition of the basifying agent

Sampling for fungicide determination

Both the bath and pelts/wet blue were sampled:

1. prior to the addition of the chrome tanning material
2. after 60 minutes tannage
3. after 60 minutes of basiflcation
4. after a fatliquor addition and overnight running of the tannage
5. after two months wet blue storage

Hide areas and sections for analysis

Hide samples were taken from butt and flank areas for individual analysis.

The unsplit hides were split after sammying into grain, middle and flesh layers.

Findings from the investigation

The investigations are summarised and provide the foÜowing information.

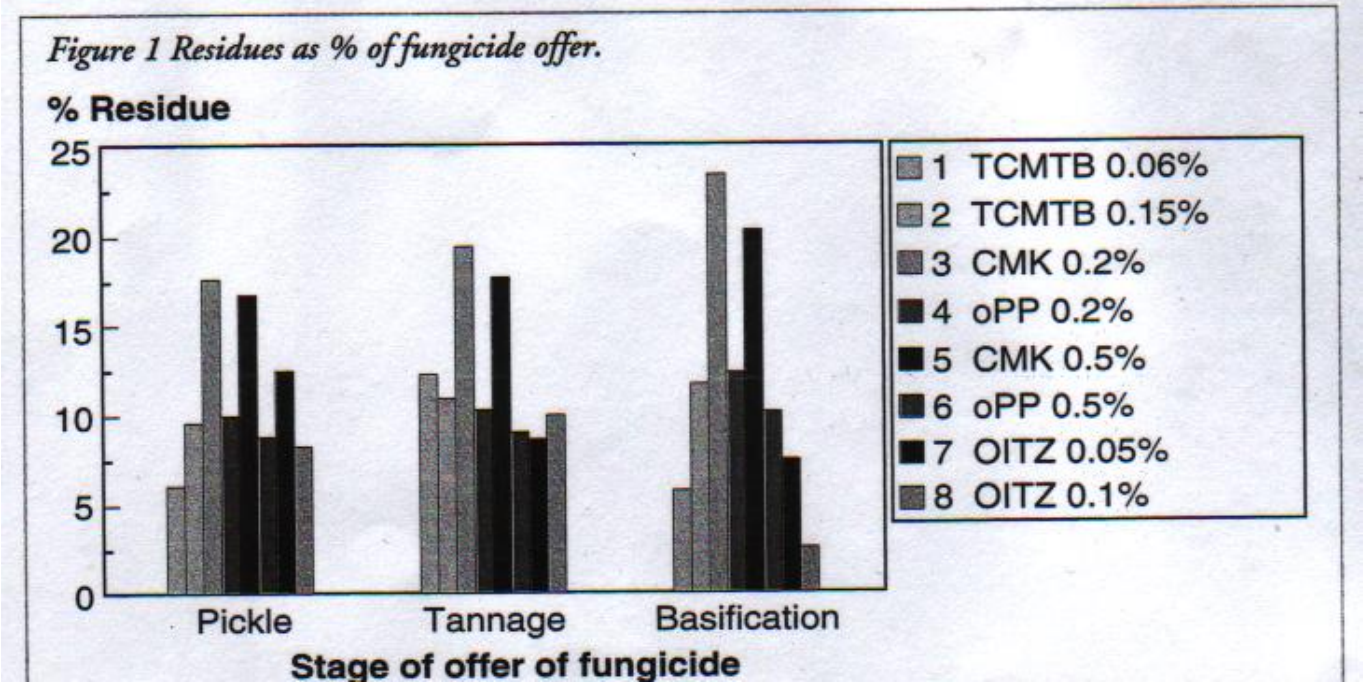
The active components remaining in the float Analysis of fungicide remaining in the bath shows that the uptake of all three chemicals is worse during pickle. In general, the active contents remaining in each float reduced as the process progressed through tannage, basiflcation, and overnight running period.

TCMTB posed an exception as an addition of fatliquor during tannage caused an increase in active matter. This, however, became substantially lower by the time of analysis of the sammying liquors, the phenomenon being connected with the solubility of the TCMTB in fat. For this reason the lowest residual values were recorded by addition in the pickle and at the end of tannage.

The lowest residues in the sammying bath were found with the addition of OITZ, followed by TCMTB, while the values in the case of CMK/oPP were conspicuously high. The comparative results from additions of the products at three stages as a percentage remaining of the offer are presented as figure 1.

Figure 1

and flank areas for individual analysis. bath were found with the addition of



Uptake ofactive components into the wet blue

The total uptake of fungicide was calculated from analysis of all split and unsplit samples, and expressed with reference to the offer.

Although diese provide uptake values at the pickle, tannage, basification and final stages, the sammed wet blue values are the most important because of the need for good fungal resistance during storage.

Study of the uptake of the various fiingicides shows:

TCMTB: additions during pickle and start of tannage appear most favourable.

CMK/oPP: optimum point of offer is after basification.

OITZ: should be added in the pickle or at the start of chrome tannage. Uptake was poor when the addition followed basification being distincdy lower than found with the other fungicides.

The contrast in uptake of the fungicides from the different points of offer by the wet blue is presented in Figure 2.

Uptake of active components by flank and butt

With the hides that were lime split (2.0 mm) before tannage, analysis of the active components was carried out on the flank and butt regions.

With the unsplit hide (levelled to 4.5mm), the flank and butt regions were split after sammying into grain, middle and flesh layers. For comparison with the lime split samples the analysis results of the individual layers were calculated as a whole sample.

Study of the uptake of the various fungicides show:

TCMTB:

1.Wet blue produced from lime split hides.

- at minimum offer the uptake is a little higher in the butt than the flank.
- at maximum concentration, the uptake increases in the flank. This results in an almost equal fungicide content between the flank and butt regions of the samples.

2.Unsplit wet blue took up less active material than the limesplit leathers.

CMK/OPP:

1. Wet blue produced from lime split hides.

- at minimum offer in the pickle and after basification, uptake is higher in the flank than in the butt.
- at maximum concentration and with addition after basification, the uptake is distinctly higher in the flank area. The uptake from additions at other stages are comparatively uniform.

2. Unsplit wet blue tended to take up more active material in the butt area than the flanks. In a few cases the uptake was greater with unsplit than lime split hides.

OITZ:

1. Wet blue produced from lime split hides show no clear differentiation between uptake in the butt or flank at either level of offer.
2. Unsplit wet blue showed better uniformity between butt and flank,although the uptake was less than found with the lime split leathers.
3. In both lime split and unsplit wet blue the uptake was inferior when additions were made after basification compared to pickle and tanning stages.

The highest fungicide uptake resultedfrom addition stages summarised in Figure 3.

Figure 2 and 3

With the unsplit hide (levelled to 4.5 hides.

Figure 2 Fungicide uptake into wet blue as % of offer.

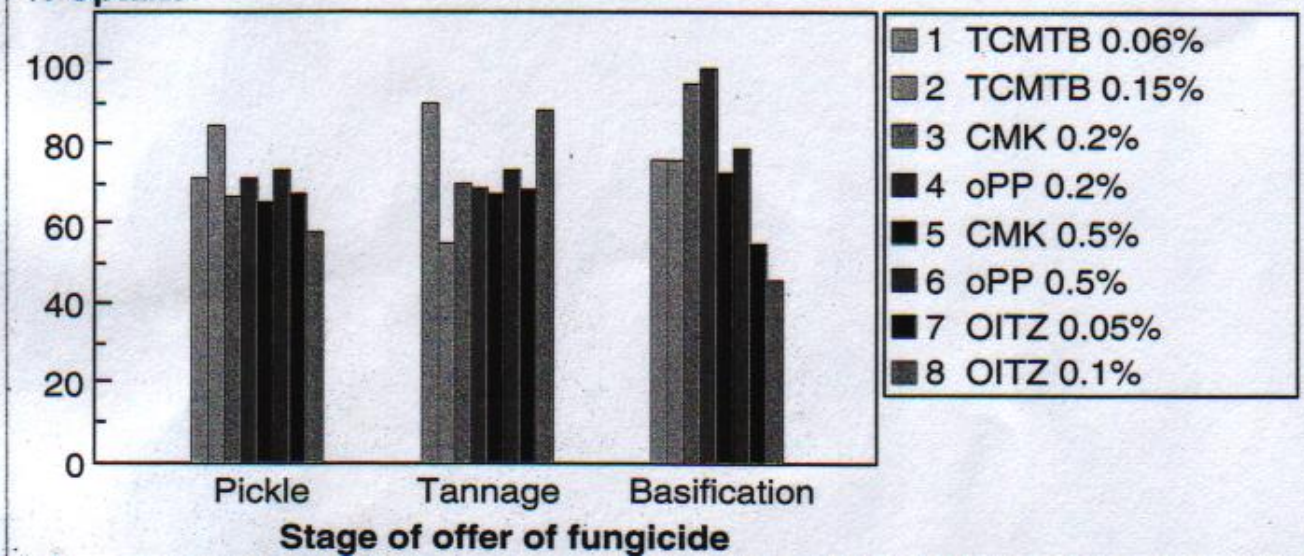


Figure 3 Optimum uptake of different fungicides.

	Lime split wet blue		Unsplit wet blue	
	Flank	Butt	Flank	Butt
TCMTB 0.06%	Basification	Basification	Basification	Basification
TCMTB 0.15%	Basification	Basification	Tannage	Pickle
CMK/oPP 0.2%	Basification	Basification	Basification	Basification
CMK/oPP 0.5%	Basification	Basification	Pickle	Basification
OITZ 0.05%	Tannage	Tannage	Pickle	Tannage
OITZ 0.15%	Tannage	Tannage	Tannage	Pickle

With both TCMTB and CMK/oPP the highest single values were observed from additions made after basification. With OITZ, however, the higher values were achieved with additions at the start of tannage, and even in the pickle bath.

Uptake of active components by grain, middle and flesh layers

The leathers produced from the unsplit (levelled) hides was split in the blue sammed State into grain, middle and flesh layers.

Study of the results shows that with all fungicides the highest uptakes were found in the grain split and lowest in the middle split layer.

TCMTB

1. The grain layer shows the highest level of uptake in the butt area.
2. In the flank area, however, the flesh layer shows higher uptake than the grain layer.

3. In the middle layer, the uptake in the butt area was less than found in the flanks.

CMK/oPP

1. The highest levels of uptake were found in the grain layer with little difference between butt and flank areas. Pickle additions, however, slightly favoured uptake in the flank area.
2. Uptake in the middle and flesh layers from both flank and butt regions do not significantly differ.

OITZ

1. In the butt area of the grain layer the uptake is slightly higher than found in the flanks.
2. The total uptake of fungicide is greater by additions made to the pickle.
3. The uptake in the middle layers is low compared to the other agents,especially in the butt area.

The analysis also shows that the percentage uptake of all fungicides tested is not significantly influenced by minimum and maximum offers. The distribution in the 3 layers as percentage uptake in butt and flank areas are presented in Figures 4 and 5 respectively.

Changes in active components caused by wet blue storage

To follow the behaviour of the fungicides in wet blue storage, the analysis was repeated after two months.

Both the lime split, and the unsplit wet blue were analysed as sammed samples (no Separation into grain, middle and flesh layers). Sample locations were butt and flank areas.

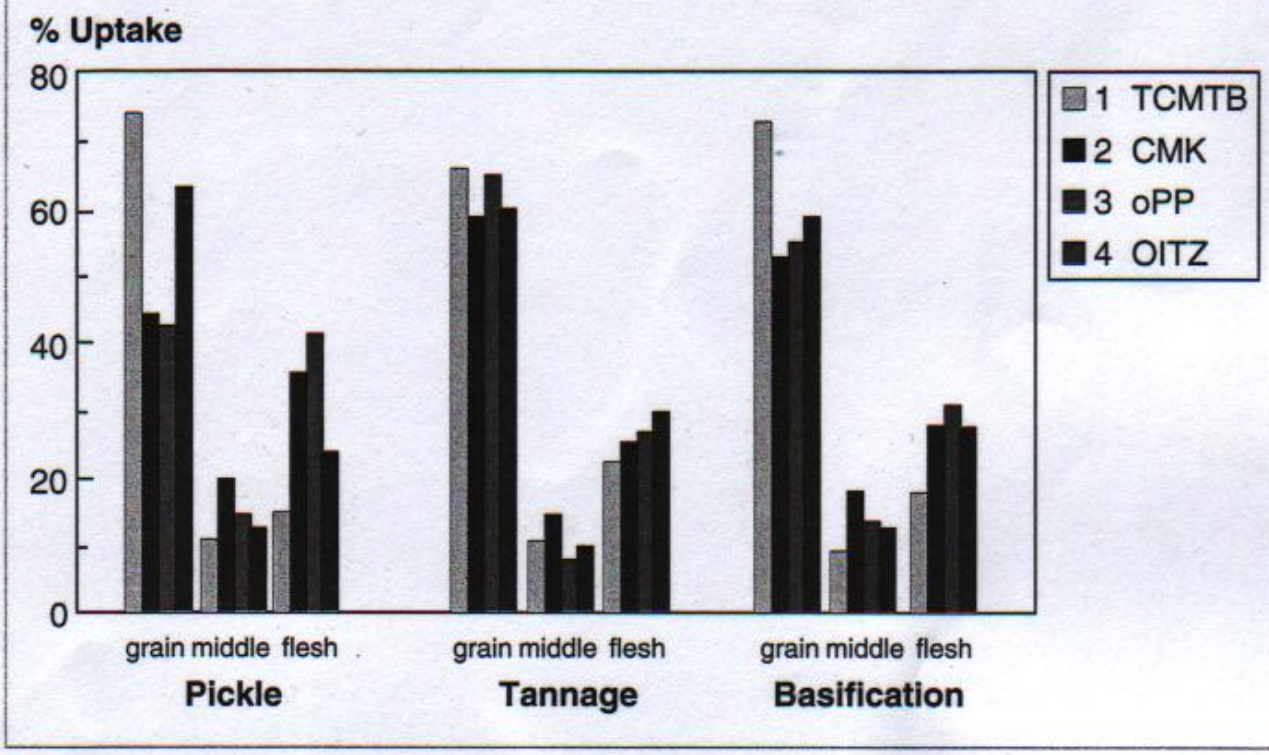
The study shows that at minimum offer the active chemical contents reduced on average to ca.80%, with best Performance from OITZ.

With maximum application levels the percentage decreases were greater, with the exception of TCMTB.

Regarding differences between the butt and flank areas:

Figure 4 and 5

Figure 4 Butt: distribution of fungicides into grain, middle and flesh layers as % of uptake.

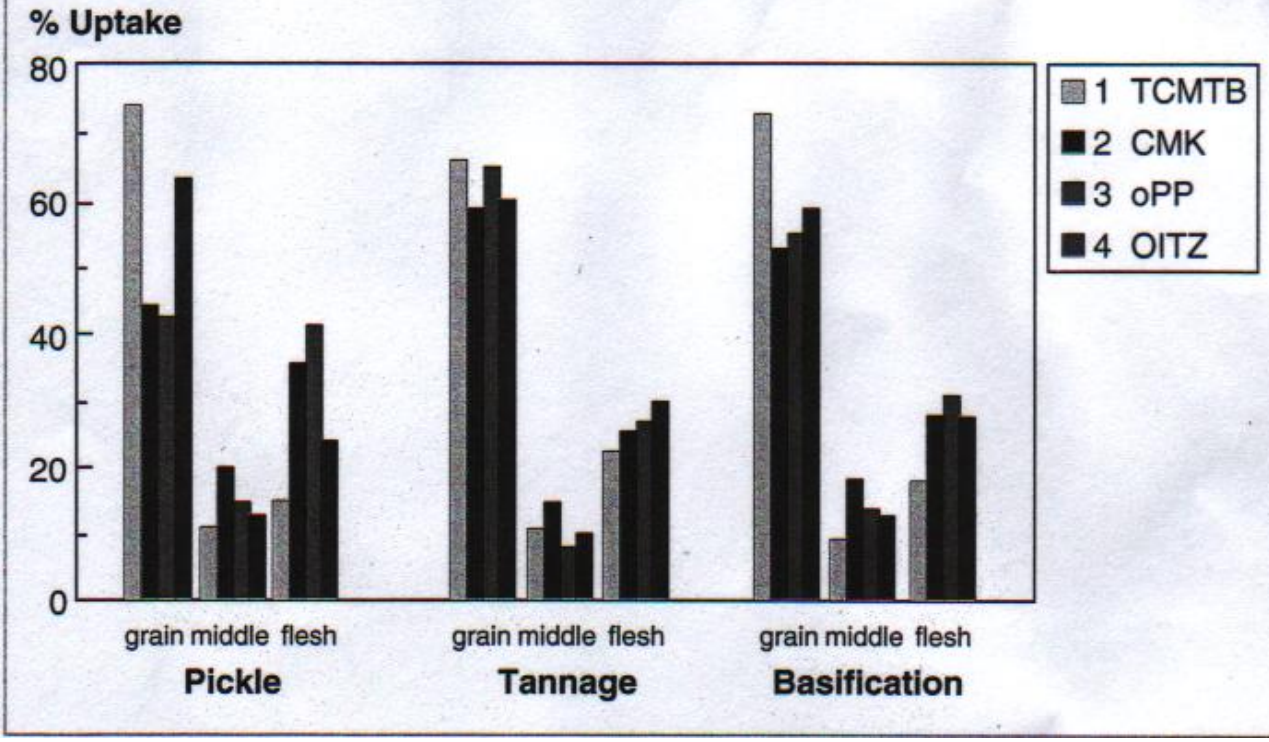


In the grain layer TCMTB shows the highest level of uptake. The values for the other active agents are comparable.

In the middle layer CMK and oPP penetrate the best and show the highest uptakes. The values for OITZ are slightly higher than those of TCMTB.

In the flesh split OITZ shows high percentage uptake. The active chemical TCMTB is the least absorbed by the flesh split.

Figure 5 Flank: distribution of fungicide into grain, middle and flesh layers as % of uptake.



TCMTB:

Generally, at minimum offer, the reduction in TCMTB is higher in the flank areas than in the butt regions. This is also apparent at maximum offers.

CMK/oPP:

No uniform difference between the flank and the butt could be established.

OITZ:

No uniform difference between the flank and the butt could be established. The findings. for lime split and unsplit wet blue at minimum offer are presented grain middle flesh Basification in Figures 6 and 7.

Findings from fungistatic testing ofthe wet blue leathers

After two months storage a fungi resistance test was carried out on all of the wet blue samples.

In this test the samples were exposed under conditions favourable for the growth of mould to attack by three kinds of fungi spores commonly found on unprotected wet blue leathers.

TCMTB:

1. At minimum offer the use of TCMTB at the pickle stage proved to be least effective. At least one type of fungi spore could grow on the wet blue surface of all of the samples.
2. With the addition in the tannage the same results were observed with the lime split samples. The unsplitleathers showed no growth of fungi on the surface, but as growth occurred on the cut edges of thesample further storage of these leathers would be inadvisable.
3. With the addition after the basification only the split flank was regarded as insufficiently preserved.Further storage of these leathers,however, would be inadvisable.
4. At maximum offer, all samples were classed as sufficiently preserved. In most cases areas free from fungal growth were noticed in the medium around the samples under test. The most pronounced clear areas were around samples treated after basification, with slightly better results obtained from the lime split samples.

CMK/oPP

1. At minimum offer the samples were regarded as adequately preserved, but storage exceeding two months could not be recommended.
2. The most unfavourable stage of addition was in the pickle bath. This could also be detected at maximum offer where storage exceeding two months could not be recommended.
3. The best results were obtained with additions made after basification.

OITZ

1. In general, at minimum offer in the tanning and basification stages the preservation was unsatisfactory. Better results, however, were obtained by addition to the pickle bath.
2. At maximum offer satisfactory protection was achieved at the pickle and tannage addition stages.
3. In both lime split and unsplit wetblue samples there were indications of better protection in the flank rather than butt regions.

According to these results for adequate preservation the fungicide content of the wet blue should be:

TCMTB minimum 250ppm.

CMK/oPP minimum 580/280ppm.

OITZ minimum 80ppm.

Figure 6 and 7

Figure 6 Lime split wet blue: Change in active fungicide component at minimum recommended offer after 2 months storage.

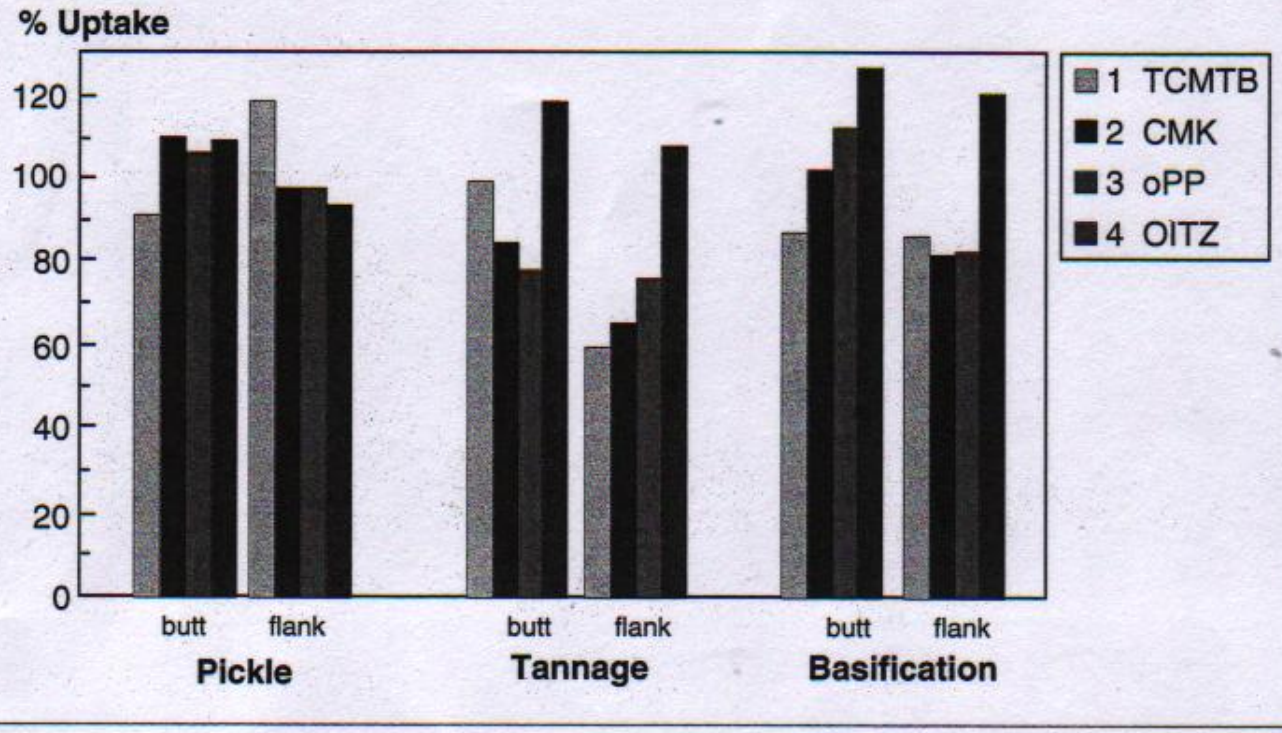
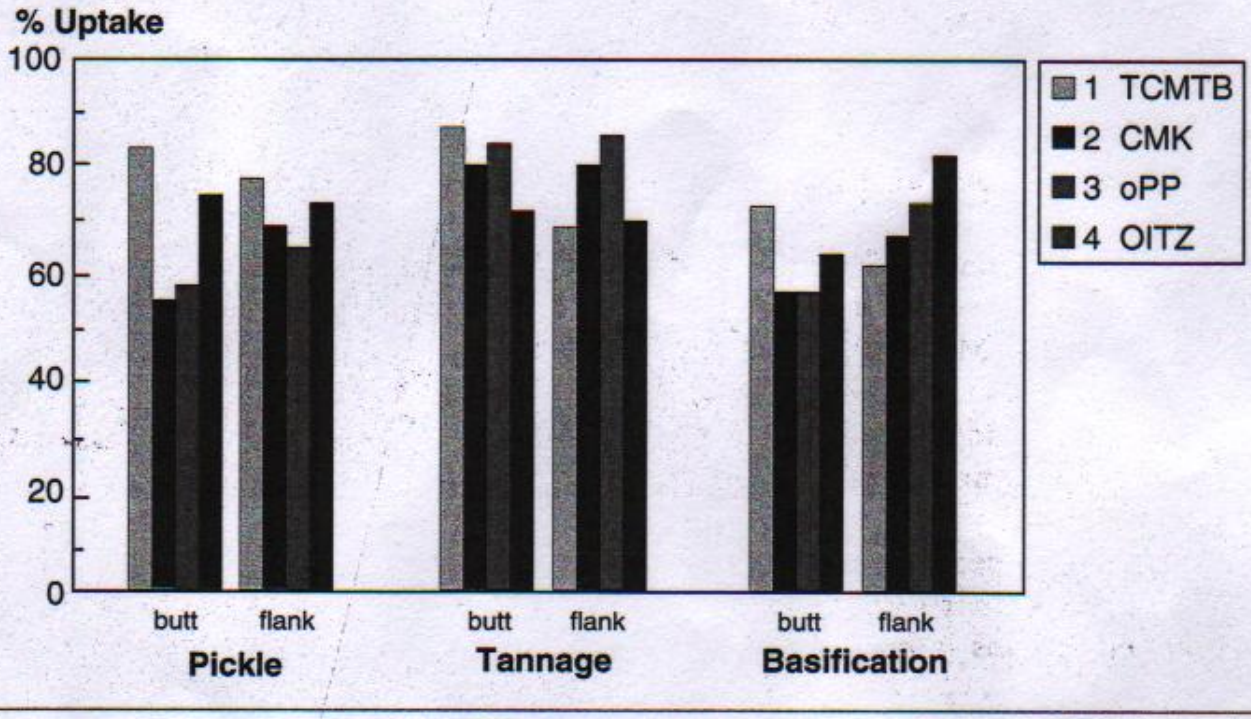


Figure 7 Unsplit wet blue: Change in active fungicide component at minimum recommended offer after 2 months storage.



From pilot trials to commercial scale chrome tannage

The OITZ containing product provided the greatest level of protection in pilot trials. The effects of an increase in scale was investigated by applying the fungicide to a conventional füll size chrome tannage.

In this. study, the hides were lime split to 4.5mm, and the fungicide offered in the pickle at a concentration of 0.075%.

Leather samples were taken at the end of tannage from butt and flank regions of the hides, and these were split into grain, middle and flesh layers. The OITZ levels were determined at the end of tannage and after storage for two months and are presented as Figure 8.

The findings show that:

1. The residual flot contained 3,2 % of OITZ offer. This value is lower than found on pilot scale.
2. The mean OITZ content of four samples from the butt and four samples from the flank regions amounted to 53 ppm. By chance this figure represents the value found with OITZ pickle addition in the pilot investigations.
3. Grain midle and flesh layers from butt and flank samples show values for OITZ similar to those found in the earlier investigations. Penetration was slight in the middle layer: ca. 30% was found in the flesh layer, and ca. 50-60% in the grain layer.
4. The OITZ content of the samples before and after two months storage do not differ substantially. A reduction was found in only half of the examined samples. Some increases were found, but can be attributed to a scattering of analytical values.
5. Fungistatic tests performed in parallel to the chemical analysis show that all samples were provided with resistance to fungal growth.
6. With an OITZ content of about 55-75 ppm the wet blue samples were adequately preserved against fungal attack.

Findings from the investigations

Application and behaviour of fungicides:

- The three fungicides examined are fundamentally suitable for several months preservation of wet blue.
- Differences in fungicide residues in the float and uptake by the wet blue occurred due to varying the stages of addition.
- Fungicide absorption into the wet blue is greatest with TCMTB, followed by CMK/oPP. OITZ has the lowest uptake.
- Additions after basification resulted in the highest levels of uptake with TCMTB and CMK/oPP. The greatest uptake with OITZ occurred with additions made at the beginning of tannage, or even in the pickle float.
- At minimum recommended offers, the active content of the fungicides after two months storage had fallen toca.80% of the initial value. OITZ maintained the highest level (92%) probably due to good stability of the bond.

At maximum offer, the percentage loss of CMK/oPP and OITZ was greater during storage period than found with minimum offers.

Distribution of fungicides between butt and flank

- TCMTB:

At minimum recommended offers made to lime split goods, higher fungicide contents in the butt regions were produced. At maximum offer, no significant differences were found between the butt and flank regions.

Uptake by lime split wet blue was always greater than found with unsplit leathers.

- CMK/oPP:

In general, uptake with lime split

wet blue is greater in the flank area than in the butt. Unsplit wet blue, however, shows higher values in the butt region.

In many cases the uptake by lime split wet blue is lower than found in unsplit samples.

- OITZ:

There are no significant differences in uptake between butt and flanks. The uptake is greater in the lime split wet blue compared to unsplit leathers.

Protection of unsplit wet blue

- All three fungicides provide best protection in the grain layer, with the least protection in the middle split.
- TCMTB: The butt areas of the grain layer show slightly greater uptake than the flanks. However, on the flesh layer, the flanks show higher uptake than the butt.
- OITZ: Uptake is particularly high - up to 40% - on the flesh layer, and for this reason is considered of value for protection of unsplit wet blue.
- For unsplit wet blue, it appears that the application concentration of TCMTB and OITZ should be approximately 30% greater than manufacturers' recommended levels to provide adequate preservation of all layers.

Fungicidal evaluations

- Findings from fungistatic tests essentially confirm the analytical results. The samples proved to be „adequately protected“ when TCMTB and CMK/oPP were applied after the basification, and OITZ before tannage.

- For an adequate fungicidal protection the minimum fungicide content of wet blue (as investigation) should be:

TCMTB 250 ppm.

CMK/oPP 580/280 ppm.

OITZ 80 ppm.

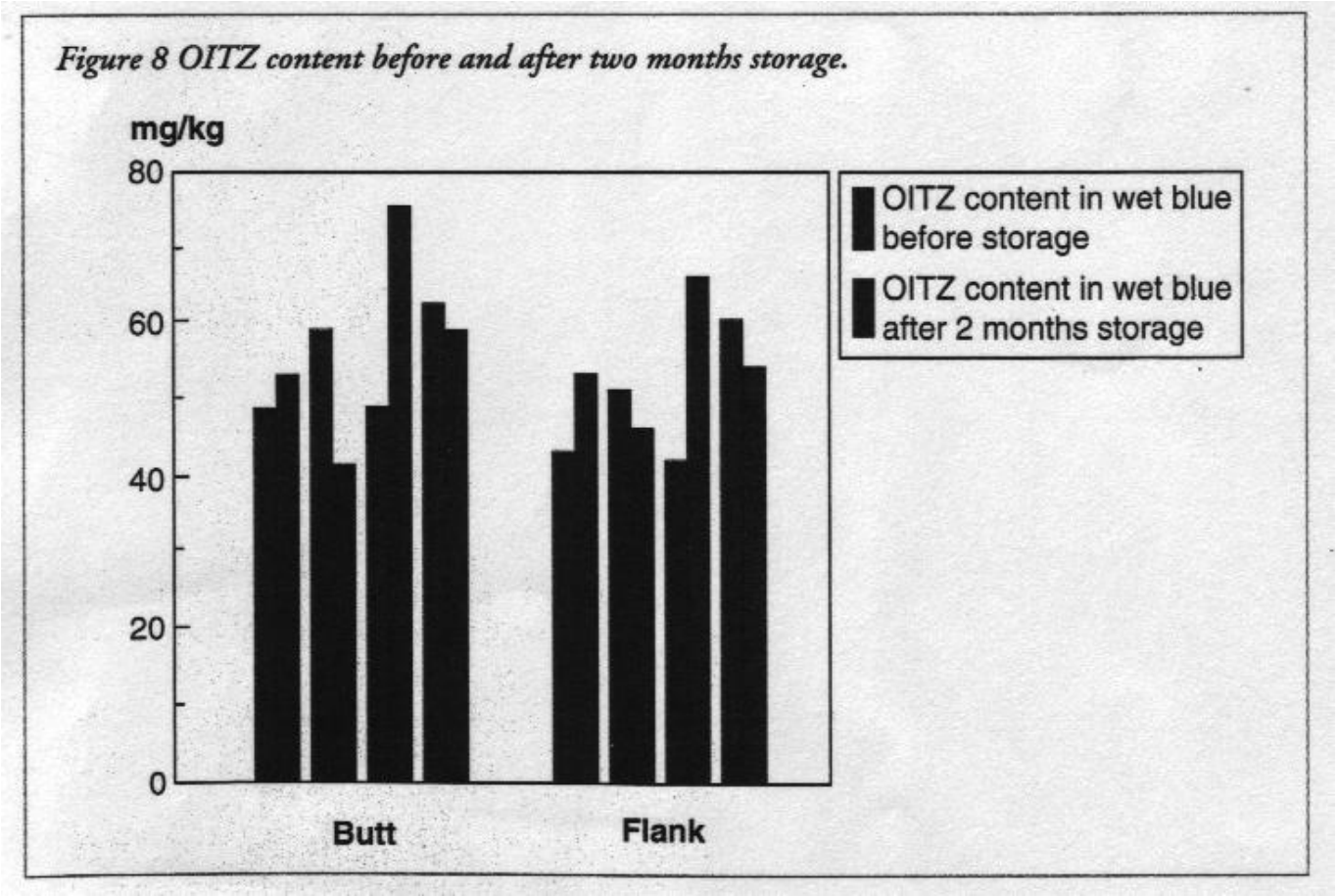
- Fungicides applied at minimum recommended concentrations can only be suitable for a short term storage.
- In practice, for three months storage an application concentration between the minimum and

maximum offers is recommended.
- The results from a production scale application of OITZ corresponded with the findings from pilot investigations.

After two months storage the wet blue preserved with 0.075% product (75 ppm.) showed adequate fungicidal protection.

Fungicide analysis of many single samples showed a wide scattering of results. To determine whether a wet blue has adequate protection, fungistatic tests should be carried out in parallel with chemical analysis.

Figure 8:



Acknowledgement

The authors thank all their colleagues of the LGR, who were involved with the project, particularly Mr. Tanju Yaldir for the execution of the tannages and the fungicidal treatment. Thanks are also due to Mrs. Scheck, Mrs. Kailer and Mrs. Eisinger for their cooperation in carrying out the chemical analysis. Special thanks to the „Bundesministerium für Wirtschaft“ (German Ministry of Commerce) for financial support via „Arbeitsgemeinschaft industrieller Forschungsvereinigungen“ (AiF).

References

1. Gattner, H., W. Lindner, H.U.Neuber : Das Leder 39 (1988), 66
2. Christner, J. : Das Leder 47 (1996), 44
3. Stosic, R.G. et al.: JALCA 88 (1993), 171
4. Bugby, A.: JSLTC 71 (1987), 138

Legend

1. These products contained 30% TCMTB, 35% CMK and 15% oPP as sodium salts, and 13% OITZ.
2. Full analytical details and findings can be made available through LGR.
3. The sum of the residues in the float and the fungicide content of the wet blue did not total 100%.
4. This was attributed to different levels of extraction of the fungicides by the solvent used. The Option of using different solvents for the different components was not taken to maintain analytical uniformity.

Publication:

C. Hauber, H.-P. Germann, The addition of fungicides in chrome tannage and their Penetration, absorption and distribution in the wet blue, World Leather 10, 5/1997, No 3, p. 75-82

Kategorien:

Alle-Seiten, Gesamt, antischimmel-fungizid, Gerbung, Veröffentlichungen, Umwelt, english-content

---

Quellenangabe:

Quellenangabe zum Inhalt

Zitierpflicht und Verwendung / kommerzielle Nutzung