

## Key Performance Advantages

- Improves chrome utilization
- Increases vegetable tannage's fixation
- Can be incorporated throughout leather production process



Leather Tanning

# ZOLDINE<sup>®</sup> ZE

## Oxazolidine for Leather Tanning and Finishing

ZOLDINE<sup>®</sup> ZE Oxazolidine is a unique crosslinking agent that reacts readily with proteins such as collagen and casein, as well as vegetable tanning materials (condensed tannins). This versatility allows ZOLDINE ZE to be incorporated into many leather production processes including pre-tanning, tanning, re-tanning and finishing.

ZOLDINE ZE improves processing and finished leather properties when used in combination with other tanning materials such as chromium sulfate, aluminum sulfate, vegetable extracts (mimosa, etc.), and phenolic syntans. ZOLDINE ZE is an excellent choice for both chrome and free-of-chrome (FOC) wet white tannages.

### The key benefits provided by ZOLDINE ZE include:

- Significantly improved chrome utilization and exhaustion
- Increased fixation of vegetable tannages
- Significant increase in shrinkage temperature (boil-proof leathers)
- Color stability (excellent for wet whites)
- Improved penetration of other tanning agents, dyes, waterproofing agents, etc.
- Improved perspiration and wash resistance

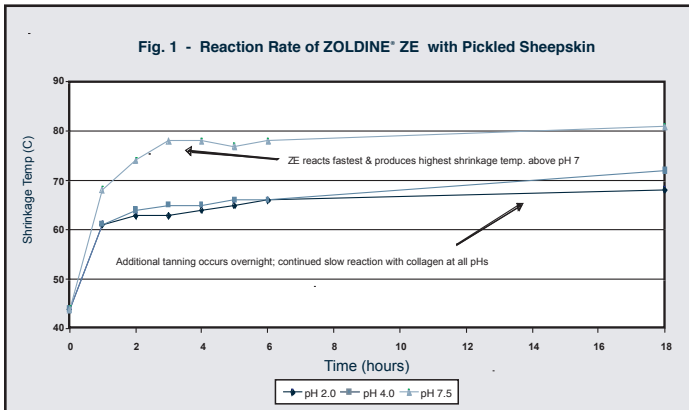
# Typical Properties

The following are typical properties of ZOLDINE ZE. They are not to be considered product specifications.

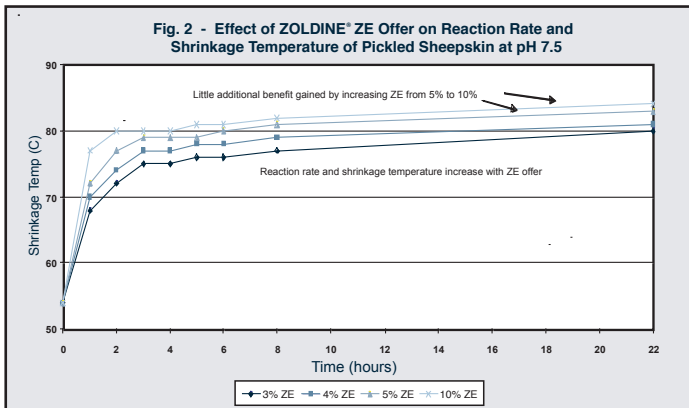
Properties	Values
Total Actives	97%
Specific Gravity @ 20/20°C	1.08
Flash Point (Tag Closed Cup)	79°C (175°F)
Freezing Point	0°C
pH (0.1M aqueous)	10
Color (Gardner)	3
Solubility	Soluble in water, ethanol, acetone, naphthenic oils

## Reactivity of ZOLDINE ZE Oxazolidine

In order to properly apply ZOLDINE ZE in leather processing, it is necessary to understand its reactivity. This material reacts readily with proteins, but the rate of reaction is governed by pH. In general, reaction of ZOLDINE ZE with collagen is faster above pH 7 than below, and leather with the highest shrinkage temperature is usually observed when tanning is done at the highest pH value. An example of the reactivity of ZOLDINE ZE is shown in Figure 1.



The rate of tanning also depends upon ZOLDINE ZE use level as shown in Figure 2 for sheepskin tannage. Addition of ZOLDINE ZE above 5% offers little additional benefit.



Temperature plays an important role in reactivity, and tanning with ZOLDINE ZE will occur faster as temperature is raised. This is also true when ZOLDINE ZE is used to crosslink casein finishes, where elevated temperature is required to obtain adequate curing.

While it is important to understand the reactivity of ZOLDINE ZE alone, it is equally important to note that ZOLDINE ZE will not produce satisfactory tanned leather on its own. **It must be used in combination with other tanning agents such as chrome or vegetable extracts.** When used in combination with other tanning agents, the amount of ZOLDINE ZE can be reduced and still provide excellent finished leather properties.

## Chrome/ZOLDINE ZE Co-Tannage

ZOLDINE ZE Oxazolidine provides excellent results with chrome, improving the tanned leather properties and greatly increasing chrome utilization. As a result, the chrome can be reduced and its exhaustion significantly improved.

Pickled sheepskin was divided and tanned in separate drums with 20% chrome liquor (15/33) on drained pickled weight for 2 hours. The bath pHs at the end of this period were 2.5 and the shrinkage temperature 68°C. A 3% offer of ZOLDINE ZE was added to one of the drums (same float), and the pH and shrinkage temperature were monitored hourly; the results are shown in Table 1.

**Table 1 - Effect of ZOLDINE ZE Co-Tannage on Shrinkage Temperature - Sheepskin**

Time after ZOLDINE ZE Addition (hrs)	Bath pH	Shrinkage Temperature (°C)
1	3.6	>100 (stood boil)
2	3.6	>100 (stood boil)
3	3.7	>100 (stood boil)
4	3.7	>100 (stood boil)

Although the shrinkage temperatures for the chrome system alone (after tanning 3-6 hours) were not reported, it is likely that these samples had much lower shrinkage temperatures vs. that co-tanned with ZOLDINE ZE. As little as 1% ZOLDINE ZE produces boil-proof leather after 1 hour (total tanning time 3 hours), even without additional pH adjustment as is normally required with straight chrome tannage. After finishing, leather co-tanned with ZOLDINE ZE was described as fuller and softer than that tanned with chrome alone.

To demonstrate the excellent ability of ZOLDINE ZE to increase chrome uptake, pickled sheepskin was tanned with 20% chrome 15/33 with and without 4% ZOLDINE ZE co-tannage; total residence time in the tanning floats was 6 hours. The leathers were then finished and the final chrome content measured. Results are shown in Table 2.

**Table 2 - Effect of ZOLDINE ZE Co-Tannage on Chrome Uptake - Sheepskin**

Tannage	Cr <sub>2</sub> O <sub>3</sub> in Finished Leather (%)
Chrome	3.3
Chrome + ZOLDINE ZE	6.6

Increased chrome uptake means better chrome exhaustion. In an example with pickled cowhide, 0.25% ZOLDINE ZE was used together with chrome in a 7-hour tanning step. Atomic absorption analysis of the final floats gave 589 ppm chrome in the chrome control system vs. 55 ppm in that with the chrome/ZOLDINE ZE co-tannage. The chrome concentration in the effluent was reduced by more than 90%.

Other results with pickled cowhide demonstrate the ability of ZOLDINE ZE not only to increase shrinkage temperature and chrome uptake, but to produce softer leather. In this example, 10% chrome (described as Chromitan F) was used alone (6 hours tumbling, set overnight) or together with ZOLDINE ZE (10% Chromitan F for 1 hour, then 3% ZOLDINE ZE for 5 hours, set overnight). None of the floats were adjusted for pH after tannage. Results are shown in Table 3.

**Table 3 - Effect of ZOLDINE ZE Co-Tannage on Cowhide**

Property	Chrome	Chrome/ZOLDINE ZE
Shrinkage Temperature (°C)	97	124
Cr <sub>2</sub> O <sub>3</sub> (%)	2.7	4.5
Fullness (higher = better)	4.5	4.8
Softness (higher = better)	3.5	4.5

Skins and hides co-tanned with Chrome/ZOLDINE ZE also demonstrate excellent resistance to moist heat and perspiration. Results for sheepskin tanned with 20% chrome liquor 15/33 with and without 4% ZOLDINE ZE are reported in Table 4. The co-tannage with ZOLDINE ZE provides higher shrinkage temperature before and after exposure to moist heat and perspiration, and also gives significantly less area loss.

**Table 4 - Effect of ZOLDINE ZE Co-Tannage on Moisture/Perspiration Resistance**

Property	Chrome	Chrome/ZOLDINE ZE
Shrinkage Temperature, °C (moist heat: 70°C, 48 hrs)	Before = 111 After = 114	Before = 129 After = 132
Area Loss, % (moist heat: 70°C, 48 hrs)	Δ Before/After = 7.6%	Δ Before/After = 4.0%
Shrinkage Temperature, °C (perspiration: 70°C, 48 hrs)	Before = 111 After = 95	Before = 129 After = 116
Area Loss % (perspiration: 70°C, 48 hrs.)	Δ Before/After = 11.8%	Δ Before/After = 3.4%

## Re-tannage of Chrome with ZOLDINE ZE Oxazolidine

ZOLDINE ZE can also be used as a re-tanning agent for chrome. The same or even greater benefits can be observed when ZOLDINE ZE is used as a re-tanning agent for wet blue (vs. co-tannage with chrome). For example, a piece of wet blue cowhide was treated with 2% ZOLDINE ZE for 1 hour followed by finishing (fatliquoring, etc.). When compared with the finished piece without ZOLDINE ZE, the re-tanned piece was described as fuller and whiter in appearance. The ZOLDINE ZE re-tanned piece also showed a tighter and clearer grain than the wet blue without re-tanning.

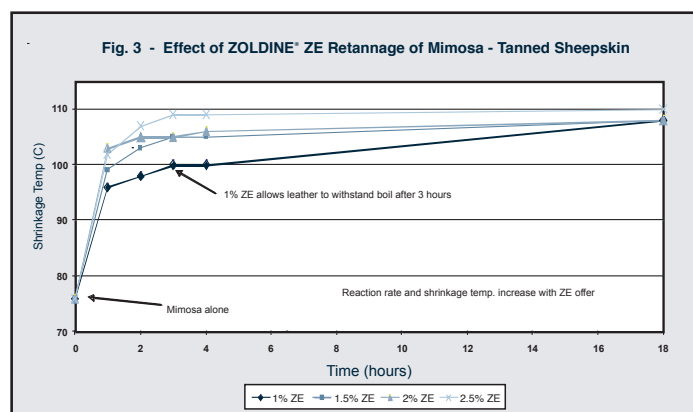
As a re-tanning agent, ZOLDINE ZE can be added at any convenient point, such as during dyeing or fatliquoring. ZOLDINE ZE will increase the penetration of these components and should have good chemical compatibility with most finishing chemicals.

## ZOLDINE ZE for FOC and Wet White Tannages

ZOLDINE ZE is an excellent choice for the production of FOC and metal-free wet white tannages, including white and pastel leathers. ZOLDINE ZE must be used in combination with other tanning agents to achieve satisfactory leather products. It can be used with vegetable extracts (condensed tannins), aluminum sulfate, glutaraldehyde and syntans (such as phenolics) to produce satisfactory leathers.

### Re-tannage of Mimosa with ZOLDINE ZE

ZOLDINE ZE provides excellent results as a re-tanning agent for mimosa extracts. Mimosa alone generally does not provide satisfactory shrinkage temperature, especially for more thermally demanding applications. Figure 3 shows the effect of ZOLDINE ZE re-tanning on the shrinkage temperature of mimosa-tanned sheepskin. In this case, 15% mimosa was used for the tannage, and ZOLDINE ZE re-tanning was performed at 45°C (final pH 6.5). As little as 1% ZOLDINE ZE produces boil-proof leather after only 3 hours.



## Re-tannage of Glutaraldehyde with Mimosa/ZOLDINE ZE

In this example a piece of shagreen (shark skin) was pre-tanned with modified glutaraldehyde, followed by mimosa tannage (21%), producing a shrinkage temperature of 85°C. The tanning float was changed and 2% ZOLDINE ZE added with the pH raised to 6-7 over 2 hours, followed by 5 hours of tumbling. The final shrinkage temperature was 95°C.

### Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>/ZOLDINE ZE Pre-tannage

Pickled cowhide was pre-tanned with 4% Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> • 18H<sub>2</sub>O, with and without 1% ZOLDINE ZE. The tannages were done for 4 hours (tumbling) followed by setting overnight. The next day, pH was adjusted using 2% MgO followed by 3 hours tumbling; the results are presented in Table 5. ZOLDINE ZE increases shrinkage temperature and produces softer leather.

**Table 5 – Effect of ZOLDINE ZE in Pre-tannage with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>**

Property	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + ZOLDINE ZE
Final pH	4.0	5.0
Shrinkage Temp (°C)	74	79
Relative Softness	Firmer	Softer

### ZOLDINE ZE Pre-tannage of Mimosa/Myrabolam

Pickled sheepskin was pre-tanned with 4% ZOLDINE ZE Oxazolidine for 1 hour. Subsequently, the pre-tanned skins were tanned with 20% mimosa + 7% myrabolam for 5 hours at pH 4.5. The final leather properties (with and without ZOLDINE ZE pre-tannage) are described in Table 6. ZOLDINE ZE not only increases the degree of tannage significantly, but greatly enhances fixation of the vegetable extracts; this is expected since ZOLDINE ZE is known to react readily with condensed tannins. Improved utilization of the vegetable extracts means lower residuals in the effluent as demonstrated by a reduced level of water soluble organics.

**Table 6 - Effect of ZOLDINE ZE Pre-tannage of Mimosa/Myrabolam**

Property	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + ZOLDINE ZE
Final pH	4.0	5.0
Shrinkage Temp (°C)	74	79
Relative Softness	Firmer	Softer

## ZOLDINE ZE Oxazolidine for Casein Finishes

Casein finishes are often crosslinked with formaldehyde. With the current downward pressure on formaldehyde due to health and safety concerns, leather producers are looking for alternatives. ZOLDINE ZE is a good candidate for formaldehyde replacement. This product contains less than 0.1% free formaldehyde and reacts readily with casein at elevated temperatures. The optimum cure temperature depends upon the desired rate and degree of cure. If possible, a temperature of 40°C or higher should be used for initial evaluations.

In addition to generating less formaldehyde during cure and in the finished leather, ZOLDINE ZE does not discolor the finish. This is important for maintaining the desired appearance of the finished leather.

## Formaldehyde and Formaldehyde Analysis

ZOLDINE ZE contains less than 0.1% free formaldehyde. However, the active ingredient can break down under certain conditions releasing formaldehyde. The degree of formaldehyde release depends upon many factors including pH and other formulation ingredients. Higher pH favors complete reaction of ZOLDINE ZE with collagen and other proteins (casein, etc.); therefore, free formaldehyde should decrease with increasing tanning/finishing pH. Other formulation ingredients, particularly condensed tannins, can influence the amount of free formaldehyde produced by ZOLDINE ZE. Since the active ingredient in ZOLDINE ZE reacts with condensed tannins, systems containing vegetable tannages should generally have lower free formaldehyde levels than those which don't. Increasing the ratio of condensed tannins to ZOLDINE ZE should reduce the level of free formaldehyde.

Certain analytical methods for formaldehyde rely upon acidic reagents (Nash Reagent, etc.). Since these reagents decompose ZOLDINE ZE, such tests may give false positives for formaldehyde. Accurate quantification of free formaldehyde in the presence of ZOLDINE ZE therefore requires a method which is specific for formaldehyde and does not use an acidic pH environment. For a discussion regarding appropriate test methods, please contact an ANGUS technical representative.

## Safe Storage and Handling

This product emits pungent vapors which are irritating to the respiratory tract, so personnel should avoid breathing vapor (or mist) when handling or using the product. Use with adequate ventilation. This product is an alkaline liquid which may cause burns to the eyes and skin irritation following contact. Do not allow undiluted product to contact skin or eyes; wear personal protective equipment including goggles and chemical-resistant clothing during handling or use. Wash thoroughly after handling.


This product should be stored in the original container, in a cool, dry location. The containers should be kept closed when not in use. The product is considered combustible with a flash point of 79°C (175°F). Keep away from heat, sparks and flame. Vapors are heavier than air and may travel a long distance and/or accumulate in low lying areas.

Small amounts of formaldehyde may be generated in use at acidic pH. Airborne monitoring should be conducted, if applicable, to prevent possible exposure.

For further information and precautions regarding the handling, storage and disposal of ZOLDINE ZE Oxazolidine, please consult the current Safety Data Sheet for this product.

# Product Stewardship

ANGUS encourages its customers to review their applications of ANGUS products from the standpoint of human health and environmental quality. To help ensure that ANGUS products are not used in ways for which they are not intended, ANGUS personnel will assist customers in dealing with environmental and product safety considerations. For assistance, product Safety Data Sheets, or other information, please contact your ANGUS representative at the numbers provided in this document. When considering the use of any ANGUS product in a particular application, review the latest Safety Data Sheet to ensure that the intended use is within the scope of approved uses and can be accomplished safely. Before handling any of the products, obtain available product safety information including the Safety Data Sheet(s) and take the necessary steps to ensure safety of use.

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