ZOLDINE® ZA-78
Oxazolidine for Leather Tanning and Finishing

ZOLDINE® ZA-78 Oxazolidine is a unique oxazolidine-based, fast-reacting crosslinking agent for collagen and casein, as well as vegetable tanning materials (condensed tannins). This versatility allows ZOLDINE ZA-78 to be incorporated into many leather production processes including pre-tanning, tanning, re-tanning and finishing. ZOLDINE ZA-78 improves processing and finished-leather properties when used in combination with other tanning materials such as chromium sulfate, aluminum sulfate, vegetable extracts (such as mimosa), phenolic syntans and others.

The key benefits provided by ZOLDINE ZA-78 include:

- Significant increase in shrinkage temperature during pre-tanning (allowing hot aqueous degreasing)
- High reactivity with collagen and casein allowing curing over a range of ambient temperatures
- Improved chrome utilization
- Increased fixation of vegetable tannages
- Color stability (good for wet whites)

ZOLDINE ZA-78 is an excellent choice for both chrome and free-of-chrome (FOC) wet white tannages. This document provides detailed information on the application, storage and handling of this unique material.

Key Performance Advantages

- Improves processing and finished-leather properties
- Reacts readily with proteins and condensed tannins over a range of temperatures
- Excellent candidate for formaldehyde replacement
Typical Properties

The following are typical properties of ZOLDINE ZA-78. They are not to be considered product specifications.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Actives</td>
<td>74-78%</td>
</tr>
<tr>
<td>Specific Gravity @ 25/25°C</td>
<td>0.98-0.99</td>
</tr>
<tr>
<td>Flash Point (Tag Closed Cup)</td>
<td>46°C (115°F)</td>
</tr>
<tr>
<td>Freezing Point</td>
<td>-20°C (&lt;-4°F)</td>
</tr>
<tr>
<td>pH (as supplied)</td>
<td>10.5-11.5</td>
</tr>
<tr>
<td>Color (APHA)</td>
<td>100</td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in water, alcohols, some hydrocarbons</td>
</tr>
</tbody>
</table>

Reactivity of ZOLDINE ZA-78

In order to properly apply ZOLDINE ZA-78 in leather processing, it is necessary to understand its reactivity. This material reacts quickly with proteins, and the reaction rate is generally unaffected by pH. An example of the reactivity of ZOLDINE ZA-78 is shown in Figure 1. This material rapidly increases shrinkage temperature independent of pH. Because of this property, ZOLDINE ZA-78 is an excellent choice for pre-tanning of greasy skins, allowing environmental-friendly degreasing processes to be used.

The rate of tanning depends upon ZOLDINE ZA-78 Oxazolidine as shown in Figure 2 for pickled sheepskin tannage. Reaction rate increases with ZOLDINE ZA-78, as expected. As little as 3% of this material raises shrinkage temperature above 80°C after 4 hours, while 4% achieves the same result after 1 hour. Minimal additional benefit is observed above 4%.

The high reactivity of ZOLDINE ZA-78 means that temperature is not a major factor. ZOLDINE ZA-78 will react readily with proteins and condensed tannins (i.e. vegetable tanning agents) over a range of ambient temperatures.

While it is important to understand the reactivity of ZOLDINE ZA-78 alone, it is equally important to note that ZOLDINE ZA-78 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 ZA-78 can be reduced and still provide excellent finished leather properties.

Chrome/ZOLDINE ZA-78 Tannages

ZOLDINE ZA-78 provides excellent results with chrome, improving tanned leather properties and increasing chrome utilization. As a result, the chrome can be reduced and its exhaustion significantly improved.

ZOLDINE ZA-78 Pre-tannage

Pickled cowhide was pre-tanned with 3% ZOLDINE ZA-78 Oxazolidine for an unspecified time; shrinkage temperature was 79°C. The pre-tanned hides were then washed and pH adjusted with formic acid, followed by chrome addition (1.5% Cr₂O₃) and tumbling for 4 hours. The float was then pH adjusted with MgO, tumbled 3 hours and allowed to stand overnight. The shrinkage temperature was 93°C.

Chrome/ZOLDINE ZA-78 Combination Tannage

Cowhide was tanned with chrome for 1 hour, followed by addition of 3% ZOLDINE ZA-78 to the same float. The drum was tumbled 5 hours and held overnight, followed by neutralization, oiling and drying. The test results are shown below in Table 1. ZOLDINE ZA-78 re-tannage improves chrome uptake and produces softer leather.

Table 1 - Effect of ZOLDINE ZA-78 Re-tannage of Chrome

<table>
<thead>
<tr>
<th>Property</th>
<th>Chrome Control</th>
<th>Chrome/ZA-78</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shrink Temp (C)</td>
<td>97</td>
<td>99</td>
</tr>
<tr>
<td>Cr₂O₃ (% )</td>
<td>2.7</td>
<td>3.3</td>
</tr>
<tr>
<td>Fullness (5 best)</td>
<td>4.5</td>
<td>3.8</td>
</tr>
<tr>
<td>Softness (5 best)</td>
<td>3.5</td>
<td>4.3</td>
</tr>
</tbody>
</table>

ZOLDINE ZA-78 Oxazolidine for FOC Wet White Tannages

ZOLDINE ZA-78 is a good choice for the production of FOC and metal-free wet white tannages. ZOLDINE ZA-78 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 ZA-78

ZOLDINE ZA-78 provides good results as a re-tanning agent for mimosa extracts. Mimosa alone does not generally provide satisfactory shrinkage temperature, especially for more thermally demanding applications. Figure 3 shows the effect of ZOLDINE ZA-78 re-tanning on the shrinkage temperature of mimosa-tanned sheepskin. In this case 15% mimosa was used for the tannage, followed by ZOLDINE ZA-78 re-tanning (2.5% offer). The shrinkage temperature was raised from 81°C to more than 90°C.

![Fig. 3 - Effect of ZOLDINE ZA-78 Retannage of Mimosa (Sheepskin)](image)

In addition to generating less formaldehyde during cure and in the finished leather, ZOLDINE ZA-78 should not discolor finishes. This is important for maintaining the desired appearance of the finished leather.

**Formaldehyde and Formaldehyde Analysis**

ZOLDINE ZA-78 contains less than 0.1% free formaldehyde. However, the active ingredient can break down under certain conditions releasing formaldehyde. The amount of formaldehyde released depends upon several factors including pH and other formulation ingredients. Acidic pH conditions favor formaldehyde release while an alkaline pH suppresses release. ZOLDINE ZA-78 reacts readily with condensed tannins such as mimosa, and systems containing vegetable tannages should have lower free formaldehyde levels than those that do not. If free formaldehyde levels are unacceptable, increasing the ratio of condensed tannins to ZOLDINE ZA-78 should help.

Certain analytical methods for formaldehyde rely upon acidic reagents (such as Nash Reagent). Since these reagents decompose ZOLDINE ZA-78, such tests may give false positives for formaldehyde. Accurate quantification of free formaldehyde in the presence of ZOLDINE ZA-78 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 46°C (115°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 potential exposure.

For further information and precautions regarding the handling, storage and disposal of ZOLDINE ZA-78 Oxazolidine, please consult the current Safety Data Sheet for this product.

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**Al₂(SO₄)₃/ZOLDINE ZA-78 Oxazolidine Combination Tannage**

Pickled cowhide was tanned with 4% Al₂(SO₄)₃ • 18H₂O plus 1% ZOLDINE ZA-78 (same float). Tanning was done for 4 hours (tumbling) followed by setting overnight. The following day, pH was adjusted using 2% MgO followed by 3 hours tumbling; the results are presented in Table 2. ZOLDINE ZA-78 increases shrinkage temperature and produces softer leather.

![Table 2 - Effect of ZOLDINE ZA-78 in Combination Tannage with Al₂(SO₄)₃](image)

**ZOLDINE ZA-78 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 ZA-78 is an excellent candidate for formaldehyde replacement. This product contains less than 0.1% free formaldehyde and reacts readily with casein over a wide range of ambient temperatures. Initial replacement of formaldehyde should be on an equal equivalents basis, with ZOLDINE ZA-78 having a formaldehyde equivalent weight of 130 (as supplied basis).
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.