# New Generation Fungicide for the Leather Industry

*by*
D.L. Dalton*
*Zenith Industrial Chemicals Pte Ltd*
Singapore 628628

## Abstract

Fungicides are used in leather production to protect semi processed and finished leather against mold growth during storage and shipping. These chemicals are essential in leather manufacture to ensure that the leather is not degraded by mold growth and to safeguard the leather's quality, usefulness and commercial value. Over the years the use of some fungicides has been disallowed due to their toxicity or other issues, while others may be restricted in the future. Consequently, tanners are faced with a more limited number of products to choose from when it comes to these chemicals. In an effort to address this need, Zenith undertook a development project that led to a product specifically designed for the leather industry, which has good fungicidal effectiveness, an acceptable toxicology/eco profile and competitive cost. This paper provides an overview of the performance characteristics of this new leather fungicide.

## Resumen

Los fungicidas se utilizan en la producción de cuero para proteger a los cuero semiprocesados y terminados contra el crecimiento de moho durante el almacenamiento y el transporte. Estos productos químicos son esenciales en la fabricación de cuero para asegurar que la piel no se vea afectada por el crecimiento de moho y para salvaguardar la calidad del cuero, así como su utilidad y valor comercial. Con los años el uso de algunos fungicidas han sido prohibidos debido a su toxicidad y a otras cuestiones, mientras que otros podrán ser restringidos en el futuro. En consecuencia, los curtidores se enfrentan a un número más limitado de productos para elegir cuando se trata de estos productos químicos. En un esfuerzo por satisfacer esta necesidad, Zenith llevó a cabo un proyecto de desarrollo que dio lugar a un producto diseñado específicamente para la industria del cuero, que tiene buena eficacia fungicida, un perfil aceptable de toxicología/ecología y costos competitivos. Este documento ofrece una visión general de las características de funcionamiento de este nuevo fungicida para cuero.

## Introduction

There have been a number of changes over the years in the fungicides used to treat leather against fungal attack. In the 1930's we saw the emergence of phenyl mercury compounds, chlorinated phenols and phenolics. Products like phenyl mercuric acetate (PMA), pentachloro phenol (PCP), orthophenyl phenol (OPP) and parachlorometacresol (PCMC) came into common use. However, some of these classes of chemicals fell out of favor or became restricted due to their toxicity, their environmental problems and/or their aggressiveness in handling. The fungicide 2-(thiocyanomethylthio) benzothiazole (TCMTB) became the new standard starting in the 1970's and remains in use today. With ever increasing demands for safer and environmentally sound fungicides, tanneries continue to look toward new products that can meet these demands. The relatively limited market size for fungicides in the leather industry has largely prevented new products from being introduced, however.

We set out to develop a new fungicide product specifically for the leather industry, focusing on suitable existing active ingredients that could be used to develop new leather fungicides utilizing latest formulation technologies. Several key technical parameters were established to drive product formulation development. A first objective was to identify the preferred actives possessing a good balance between fungicidal efficacy and favorable toxicological properties.

The second development parameter called for a liquid formulation with such properties that maximum uptake by the leather would be achieved with minimum fungicide residuals remaining in the tanning liquor. This has the dual objective of achieving maximum benefit of the fungicide in the leather and minimizing residual fungicide to be treated in the effluent plant. Improper formulation of good fungicidal actives can result in products that largely remain in the tanning liquor and do not get taken up optimally by the leather, resulting in poor product efficiency, higher treatment cost and greater load on the effluent system.

*Corresponding author's email: dldalton@zenith-industrial-chemicals.com
A Technical Note presented at 107th Annual Convention of the American Leather Chemists Association,
Red Wing, Minnesota, June 10, 2011
Manuscript received July 31, 2011, accepted for publication September 2, 2011

A third criterion was that the carrier system would not only deliver the fungicide to the leather but without the use of solvents that are unfriendly to people and the environment. Not only do solvents possess their own inherent toxicity, but they can also contribute to greater absorption of the fungicide product into the human skin, thereby aggravating skin irritation potential and negatively impacting overall toxicological properties. In addition to the toxicity considerations, solvents also contribute volatile organic components into the atmosphere, which is to be minimized or avoided, and they can also be problematic for the effluent treatment plant.

Finally, the formulation meeting all these criteria should have a reasonably low cost so that the treatment cost at the tannery level would be no higher than currently used products.

This research initiative led to the development of a series of new products. One candidate in particular met all the project criteria. This product is described as an azole-based antifungal agent in an odorless, low toxicity eco-friendly carrier system. It will be referred to in this paper as Azole 388*. This paper discusses the results and conclusions from extensive performance tests conducted in overseas markets on leathers produced under full-scale tannery conditions during a five-year period from 2006 through 2011.

## Materials and Method

The fungicide that is the subject of this paper was tested over a period of nearly five years. The performance data were developed by application of the product under full-scale tannery conditions at numerous tanneries in several different countries. In each case the product was applied under identical conditions as the commercial fungicide in use at the tannery and at the same use level or at equal cost. The tanneries provided leather cuttings taken from the production runs treated with the new fungicide and with the commercial fungicide in use. These were evaluated using the "tropical chamber" mold resistance test. This is an accelerated test based on ASTM testing standards (American Society for Testing and Materials).[1] These chambers are maintained at a temperature of approximately 30 degrees Celsius and a relative humidity level of 95 to 98%, and they are inoculated with the spores of fungal species that commonly attack leather, including Aspergillus and Penicillium species. The environment created in the tropical chamber is highly conductive to fungal growth and this method is used for the accelerated evaluation of mold resistance.

At least 3 replicate test pieces measuring 7 cm by 10 cm are cut from each leather and exposed in the tropical chamber for a total of 4 weeks. The leather pieces are inspected weekly and rated for fungal growth. The mold growth ratings are based on the percentage of the leather surface covered with mold growth. The scale is from 0 to 100. 0 means 0% of the leather sample is covered with mold growth and 100 means 100% of the surface is covered. The average rating of the 3 replicate pieces tested is taken as the result for that leather.

Interpretation of the tropical chamber mold growth ratings is as follows:

- Long-term mold resistance: a rating of 0 to 20 in week 4
- Medium-term mold resistance: a rating of 0 to 20 in week 3
- Short-term mold resistance: a rating of 0 to 20 in week 2
- Limited mold resistance: a rating of 0 to 20 in week 1
- No mold resistance: a rating greater than 20 in week 1

## Results and Discussion

Using the standard 4-week tropical chamber test, numerous mold resistance tests were carried out on leathers produced at many different tanneries under full-scale tannery conditions. For each individual comparison of Azole 388 against the reference product, the raw material used, the leather production recipe and processing conditions were all identical so that the only variable was the fungicide. Leather containing no fungicide was included in each test as negative control. Representative results from these numerous real-world tests are presented here.

Tables I through III show the results of tropical chamber mold resistance studies done on wet blue leathers produced in different tanneries. Azole 388 was compared to the fungicide in use at the tannery (in some cases the tannery did not disclose the identity of the fungicide in use) and compared to a negative control with no fungicide. Azole 388 consistently provided good mold resistance for the 4-week period indicating it provide long-term mold resistance to the treated leather. Figures 1 through 3 provide photographs showing the condition of the test pieces after completion of the 4-week tropical chamber tests. In all the tests it can be seen that the negative controls failed during the first week in the tropical chamber illustrating the viability of the fungi in the chamber and the severity of the test. These examples are typical of the results obtained from the numerous full-scale trials conducted.

Table IV shows the results from a study which was run for longer than the standard 4 weeks. After the 4-week test period was completed, all the leathers passed with zero growth, except the negative control without fungicide which failed in the first week. To see how long the fungicides would continue

*This product will be made commercially available in the United States under the trade name Zenith 388.

**TABLE I**
**Tropical chamber mold growth ratings of wet blue leather treated with the fungicides Azole 388 and TCMTB 30[a]**

| Sample Identification | Mold Growth Ratings | | | |
|---|---|---|---|---|
| | 1 Week | 2 Weeks | 3 Weeks | 4 Weeks |
| Buffalo Wet Blue1 — 0.1% Azole 388 | 0 | 0 | 0 | 0 |
| Buffalo Wet Blue1 — 0.1% Azole 388 | 0 | 0 | 0 | 0 |
| Buffalo Wet Blue1 — 0.1% Azole 388 | 0 | 0 | 0 | 0 |
| **Average** | **0** | **0** | **0** | **0** |
| Buffalo Wet Blue2 — 0.1% TCMTB 30 | 0 | 0 | 0 | 0 |
| Buffalo Wet Blue2 — 0.1% TCMTB 30 | 0 | 0 | 0 | 0 |
| Buffalo Wet Blue2 — 0.1% TCMTB 30 | 0 | 0 | 0 | 0 |
| **Average** | **0** | **0** | **0** | **0** |
| Negative Control | 90 | 100 | 100 | 100 |

[a]Commercial solvent-based formulation containing 30% 2-(thiocyanomethylthio) benzothiazole

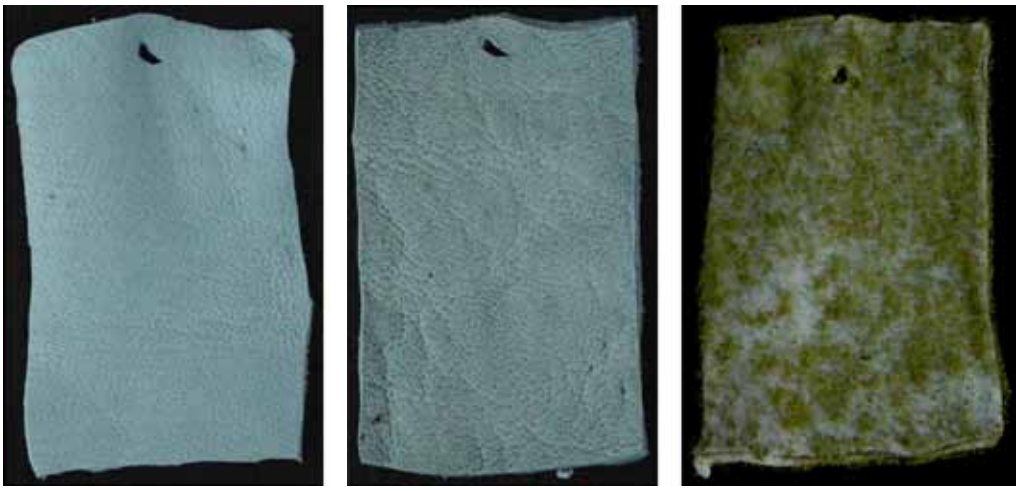

Figure 1: Wet blue test pieces with 0.1% Azole 388 (left), 0.1% TCMTB 30 (center) and no fungicide (right) after 4 weeks of tropical chamber testing. The leathers treated with Azole 388 and TCMTB 30 had no mold growth after 4 weeks and are therefore considered to possess long-term mold resistance while the leather without fungicide failed during the first week and was completely over grown with mold after 4 weeks and exhibits no mold resistance.

to provide fungal protection, we decided to continue the tropical chamber test beyond the normal exposure period until failure, namely until the leathers show a mold growth rating higher than 20 (ratings of 0 up to 20 are considered passing). The test was run for a total of 16 weeks, which is four times the normal length. This allowed for differentiation between the different fungicides used. It was seen that the wet blue with 0.1% TCMTB 30 passed 11 weeks in the chamber. The wet blue with 0.08% Azole 388 passed 13 weeks in the chamber. The wet blue with 0.1% Azole 388 passed 16 weeks in the chamber, and the test was discontinued before this leather actually failed.

Table V shows the results of another mold resistance study that was also extended beyond the standard 4 week period. In this case the positive control was an OIT based fungicide. This test was run for 16 weeks. The wet blue with 0.35% OIT passed 3 weeks in the chamber and failed in the fourth week. The wet blue with 0.1% Azole 388 passed 16 weeks, far exceeding the 4 weeks required to be considered possessing long-term mold resistance. The negative control without any fungicide failed in the first week.

These data show that Azole 388 is very effective in inhibiting fungal growth in leather. Even at a level of 0.08%, Azole 388 far exceeds the requirement to pass 4 weeks tropical chamber exposure in order to qualify as possessing long-term mold resistance and it actually passed more than 16 weeks. As a rough rule of thumb, 1 week in the tropical chamber equates to 3 months in the average outside world, which can range from warm moist tropical climates to cold climates. Therefore, passing 16 weeks in the chamber is indicative of real-world

**TABLE II**
**Tropical chamber mold growth ratings of wet blue leather treated with the fungicide Azole 388 and an unidentified fungicide**

| Sample Identification | Mold Growth Ratings | | | |
|---|---|---|---|---|
| | 1 Week | 2 Weeks | 3 Weeks | 4 Weeks |
| Wet Blue Leather A — 0.1% Azole 388 | 0 | 0 | 0 | 0 |
| Wet Blue Leather A — 0.1% Azole 388 | 0 | 0 | 0 | 0 |
| Wet Blue Leather A — 0.1% Azole 388 | 0 | 0 | 0 | 0 |
| **Average** | **0** | **0** | **0** | **0** |
| Wet Blue Leather B — Unidentified | 0 | 10 | 20 | 35 |
| Wet Blue Leather B — Unidentified | 0 | 0 | 10 | 25 |
| Wet Blue Leather B — Unidentified | 0 | 5 | 15 | 30 |
| **Average** | **0** | **5** | **15** | **30** |
| Negative Control | 45 | 85 | 100 | 100 |

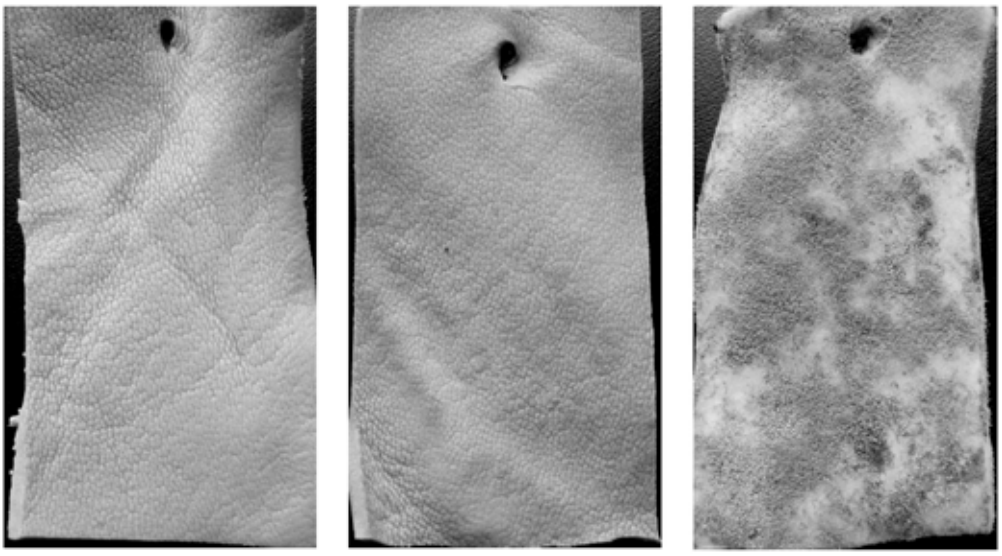

Figure 2: Wet blue test pieces with 0.1% Azole 388 (left), unidentified fungicide (center) and no fungicide (right) after 4 weeks of tropical chamber testing. The leather treated with Azole 388 had no mold growth after 4 weeks and exhibits long-term mold resistance. The leather in the center passed 3 weeks but failed in week 4. It exhibits medium-term mold resistance. The leather without fungicide failed during the first week was completely over grown with mold after 4 weeks and exhibits no mold resistance.

protection periods of over 2 years. After fine-tuning the dosage level, a number of tanneries already using Azole 388 and requiring minimum 2 years mold protection under warm and humid conditions, have adopted use levels of Azole 388 in the 0.06 to 0.08% range, while some have opted to use 0.1%.

It can be seen from these studies that Azole 388 is effective at lower dosage levels than the other commercial fungicides. Compared to TCMTB 30, dosage levels that are 20 to 30% lower can be used and still provide at least the same degree of mold protection. Stated in another way, when used at equal dosage as TCMTB 30, the Azole 388 fungicide gives better mold resistance in terms of longer protection of the leather. Independent studies conducted by the Leather and Shoe Research Association in New Zealand (LASRA), confirmed that in wet blue hides, wet blue pelts and pickled pelts, levels that are 20 to 30% lower can be used to provide reliable long-term protection[2]. The LASRA test uses a mixed fungal culture of at least 14 different fungal species. The test determines the time until the treated leather samples fail, which is when they first show fungal growth. LASRA regards 90 days as the minimum necessary for reliable long-term protection. Azole 388 met this requirement at all application levels. For wet blue hides and wet blue pelts, the lowest level of Azole 388 tested was 0.08%, which passed their stringent 90-day test. For pickled pelts, the lowest level of Azole 388 tested was 0.02%, which passed the 90-day test.

In addition to being effective at lower dosage levels, our work has shown that the product is effective against a wider range

**TABLE III**
**Tropical chamber mold growth ratings of wet blue leather treated with the fungicides Azole 388 and TCMTB 30**

| Sample Identification | Mold Growth Ratings | | | |
|---|---|---|---|---|
| | 1 Week | 2 Weeks | 3 Weeks | 4 Weeks |
| Wet Blue Leather A — 0.1% Azole 388 | 0 | 0 | 0 | 0 |
| Wet Blue Leather A — 0.1% Azole 388 | 0 | 0 | 0 | 0 |
| Wet Blue Leather A — 0.1% Azole 388 | 0 | 0 | 0 | 0 |
| **Average** | **0** | **0** | **0** | **0** |
| Wet Blue Leather B — 0.1% TCMTB 30 | 0 | 0 | 0 | 0 |
| Wet Blue Leather B — 0.1% TCMTB 30 | 0 | 0 | 0 | 0 |
| Wet Blue Leather B — 0.1% TCMTB 30 | 0 | 0 | 0 | 0 |
| **Average** | **0** | **0** | **0** | **0** |
| Negative Control | 35 | 85 | 100 | 100 |

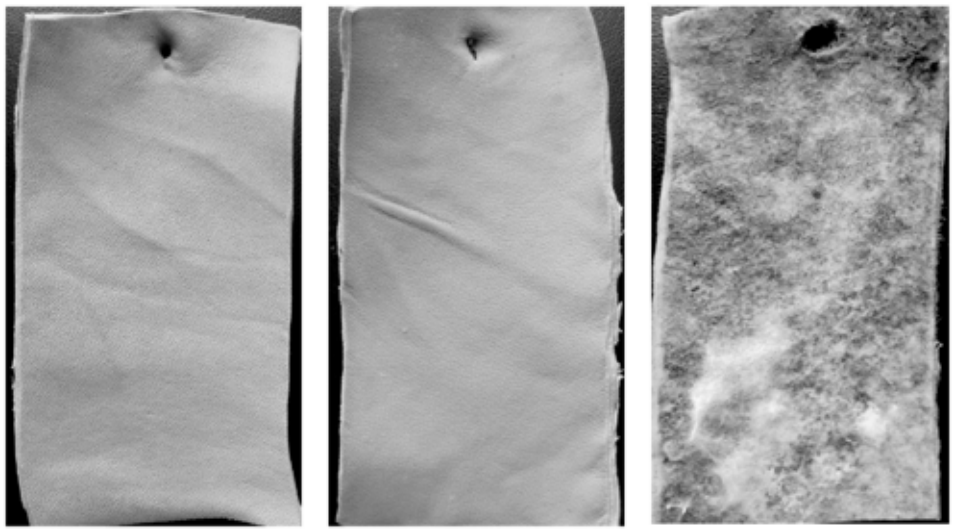

Figure 3: Wet blue test pieces with 0.1% Azole 388 (left), 0.1% TCMTB 30 (center) and no fungicide (right) after 4 weeks of tropical chamber testing. The leathers treated with Azole 388 and TCMTB 30 had no mold growth and exhibit long-term mold resistance while the leather without fungicide failed during the first week was completely over grown with mold after 4 weeks and exhibits no mold resistance.

of different fungal species. This has also been confirmed in full scale tannery work. We have case studies where fungal outbreaks occurred which were caused by uncommon types of fungi that were not controlled by the fungicide being used. In one case the tannery in question was purchasing wet blue from a large wet bluing supplier. Within days of arrival of the wet blue stock at the tannery, the wet blues started molding.

Our analysis of the fungal species growing on the wet blue revealed predominantly *Trichoderma sp* and *Penicillium sp*. Some forms of *Trichoderma* can be very resistant to TCMTB so we suspected that the wet blue had been treated with a TCMTB product. This was later confirmed. To control *Trichoderma*, much higher levels of TCMTB may be required. Therefore, leather treated with normal use levels of TCMTB do not provide protection. The tannery in this case had accumulated several containers of wet blues in a short period and all the wet blues were molding. An attempt was made by the tannery to reprocess the moldy wet blues with TCMTB. However, this did not resolve the problem. We recommended the use of Azole 388, and all the wet blues were systematically reprocessed in drums using Azole 388. This stopped the mold problem and all wet blue stock was recovered. The hides reprocessed with TCMTB and with Azole 388 were tested in the tropical chamber. The results are shown in Table VI. The hides reprocessed with Azole 388 exhibited long-term protection with no growth after 4 weeks. The hides reprocessed with TCMTB started molding in the second week.

## TABLE IV
## Extended 16-week tropical chamber mold resistance test of wet blue leathers with the fungicides Azole 388, TCMTB 30 and without fungicide

| Sample Identification | Mold Growth Ratings | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 Week | 2 Weeks | 3 Weeks | 4 Weeks | 5 Weeks | 6 Weeks | 7 Weeks | 8 Weeks |
| 0.1% TCMTB 30 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.1% TCMTB 30 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.1% TCMTB 30 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **Average** | **0** | **0** | **0** | **0** | **0** | **0** | **0** | **0** |
| 0.8% Azole 388 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.8% Azole 388 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.8% Azole 388 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **Average** | **0** | **0** | **0** | **0** | **0** | **0** | **0** | **0** |
| 0.1% Azole 388 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.1% Azole 388 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.1% Azole 388 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **Average** | **0** | **0** | **0** | **0** | **0** | **0** | **0** | **0** |
| Negative Control | 40 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

| Sample Identification | Mold Growth Ratings | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 9 Weeks | 10 Weeks | 11 Weeks | 12 Weeks | 13 Weeks | 14 Weeks | 15 Weeks | 16 Weeks |
| 0.1% TCMTB 30 | 0 | 10 | 20 | 30 | 35 | 40 | 45 | 50 |
| 0.1% TCMTB 30 | 0 | 0 | 10 | 20 | 25 | 30 | 35 | 40 |
| 0.1% TCMTB 30 | 0 | 5 | 15 | 25 | 30 | 35 | 40 | 45 |
| **Average** | **0** | **5** | **15** | **25** | **30** | **35** | **40** | **45** |
| 0.8% Azole 388 | 0 | 10 | 15 | 20 | 25 | 30 | 35 | 40 |
| 0.8% Azole 388 | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 |
| 0.8% Azole 388 | 0 | 0 | 5 | 10 | 15 | 20 | 25 | 30 |
| **Average** | **0** | **5** | **10** | **15** | **20** | **25** | **30** | **35** |
| 0.1% Azole 388 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 |
| 0.1% Azole 388 | 0 | 0 | 0 | 0 | 0 | 0 | 5 | 10 |
| 0.1% Azole 388 | 0 | 0 | 0 | 0 | 0 | 0 | 10 | 15 |
| **Average** | **0** | **0** | **0** | **0** | **0** | **0** | **5** | **10** |
| Negative Control | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

**TABLE V**
**Extended 16-week tropical chamber mold resistance test of wet blue leathers with the fungicides Azole 388, OIT 9[a] and without fungicide**

| Sample Identification | Mold Growth Ratings | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 Week | 2 Weeks | 3 Weeks | 4 Weeks | 5 Weeks | 6 Weeks | 7 Weeks | 8 Weeks |
| 0.35% OIT 9 | 0 | 0 | 0 | 15 | 25 | 30 | 40 | 55 |
| 0.35% OIT 9 | 0 | 0 | 5 | 25 | 35 | 40 | 50 | 65 |
| 0.35% OIT 9 | 0 | 0 | 10 | 35 | 45 | 50 | 60 | 75 |
| **Average** | **0** | **0** | **5** | **25** | **35** | **40** | **50** | **65** |
| 0.1% Azole 388 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.1% Azole 388 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.1% Azole 388 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **Average** | **0** | **0** | **0** | **0** | **0** | **0** | **0** | **0** |
| Negative Control | 40 | 85 | 100 | 100 | 100 | 100 | 100 | 100 |

| Sample Identification | Mold Growth Ratings | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 9 Weeks | 10 Weeks | 11 Weeks | 12 Weeks | 13 Weeks | 14 Weeks | 15 Weeks | 16 Weeks |
| 0.35% OIT 9 | 60 | 75 | 85 | 100 | 100 | 100 | 100 | 100 |
| 0.35% OIT 9 | 70 | 80 | 90 | 100 | 100 | 100 | 100 | 100 |
| 0.35% OIT 9 | 80 | 85 | 95 | 100 | 100 | 100 | 100 | 100 |
| **Average** | **70** | **80** | **90** | **100** | **100** | **100** | **100** | **100** |
| 0.1% Azole 388 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5 |
| 0.1% Azole 388 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 0.1% Azole 388 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 10 |
| **Average** | **0** | **0** | **0** | **0** | **0** | **0** | **0** | **5** |
| Negative Control | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

[a]Commercial water-based fungicide formulation containing 9.3% 2-n-Octyl-4-isothiazolin-3-one

Table VII and Figures 4 and 5 show the results of mold resistance studies conducted with crust and finished leathers. These types of leather are more susceptible to mold growth than wet blue leather since they contain more organic materials that can serve as nutrients for fungi. Consequently, higher levels of fungicide are typically required to provide extended protection of crust and finished leathers. Our tests show that for Azole 388, depending on the nature of the crust or finished leather, levels as low as 0.1% can provide long-term protection. By comparison, for other fungicides like TCMTB 30, higher levels are required. This is illustrated in the data shown in Tables VII and Figure 4 and 5.

It should be noted that during the course of using this new fungicide over a 5-year period it was found to be user friendly in terms of handling. Short-term accidental exposure of the skin to the concentrated fungicide produced no irritant effects during the exposure and left no irritation or observable effects after removal of the product by rinsing with water. Nevertheless, it is recommended to always wear proper personal protective equipment such as rubber gloves and goggles when handling this and other chemicals. The product also does not have a strong irritating or lachrymating odor and is user-friendly in terms of its near odorless character for tannery staff that may work in proximity of open containers of the chemical.

As the product was found to be relatively mild to the skin, leather containing a very high dosage level of 0.45% Azole 388 was submitted to BLC Leather Technology Centre, an

## TABLE VI
## Tropical chamber mold growth ratings of molded wet blues reprocessed with the fungicides Azole 388 and TCMTB 30 and tested for 8 weeks

| Sample Identification | Mold Growth Ratings | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 Week | 2 Weeks | 3 Weeks | 4 Weeks | 5 Weeks | 6 Weeks | 7 Weeks | 8 Weeks |
| Wet Blue Marked as "1" (Azole 388) | 0 | 0 | 0 | 0 | 5 | 10 | 15 | 20 |
| Wet Blue Marked as "1" (Azole 388) | 0 | 0 | 0 | 0 | 5 | 10 | 15 | 20 |
| Wet Blue Marked as "1" (Azole 388) | 0 | 0 | 0 | 0 | 5 | 10 | 15 | 20 |
| **Average** | **0** | **0** | **0** | **0** | **5** | **10** | **15** | **20** |
| Wet Blue Marked as "2" (TCMTB 30) | 0 | 10 | 15 | 20 | 30 | 45 | 55 | 65 |
| Wet Blue Marked as "2" (TCMTB 30) | 0 | 10 | 15 | 20 | 35 | 50 | 65 | 85 |
| Wet Blue Marked as "2" (TCMTB 30) | 0 | 10 | 15 | 20 | 25 | 40 | 60 | 75 |
| **Average** | **0** | **10** | **15** | **20** | **30** | **45** | **60** | **75** |
| Negative Control | 35 | 85 | 100 | 100 | 100 | 100 | 100 | 100 |

## TABLE VII
## Tropical chamber mold growth ratings of crust and finished leathers treated with the fungicides Azole 388 and TCMTB 30

| Sample Identification | Mold Growth Ratings | | | |
|---|---|---|---|---|
| | 1 Week | 2 Weeks | 3 Weeks | 4 Weeks |
| Wet Crust A — 0.1% Azole 388 | 0 | 0 | 0 | 10 |
| Wet Crust A — 0.1% Azole 388 | 0 | 0 | 0 | 5 |
| Wet Crust A — 0.1% Azole 388 | 0 | 0 | 0 | 0 |
| **Average** | **0** | **0** | **0** | **5** |
| Wet Crust B — 0.1% TCMTB 30 | 0 | 10 | 25 | 45 |
| Wet Crust B — 0.1% TCMTB 30 | 0 | 15 | 35 | 55 |
| Wet Crust B — 0.1% TCMTB 30 | 0 | 5 | 15 | 35 |
| **Average** | **0** | **10** | **25** | **45** |
| Finished Leather A — Azole 388 | 0 | 0 | 0 | 0 |
| Finished Leather A — Azole 388 | 0 | 0 | 0 | 10 |
| Finished Leather A — Azole 388 | 0 | 0 | 0 | 5 |
| **Average** | **0** | **0** | **0** | **5** |
| Finished Leather B — TCMTB 30 | 0 | 0 | 0 | 10 |
| Finished Leather B — TCMTB 30 | 0 | 0 | 5 | 15 |
| Finished Leather B — TCMTB 30 | 0 | 0 | 10 | 20 |
| **Average** | **0** | **0** | **5** | **15** |
| Negative Control | 30 | 75 | 100 | 100 |

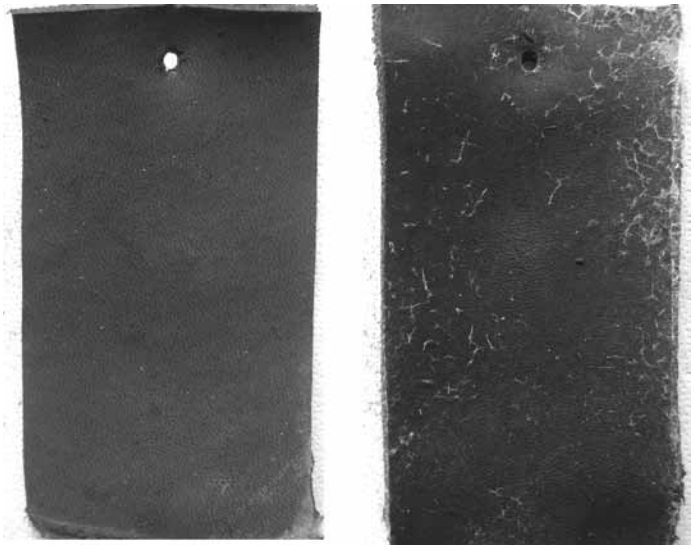

Figure 4: Wet crust cuttings after 4 weeks tropical chamber testing. The crust on the left treated with 0.1% Azole 388 only shows traces of mold (mold growth rating of 5), which means the leather possesses long-term mold resistance. The crust on the right with 0.1% TCMTB 30 shows considerable mold growth after 4 weeks (mold growth rating of 45) and possesses only short-term mold resistance.

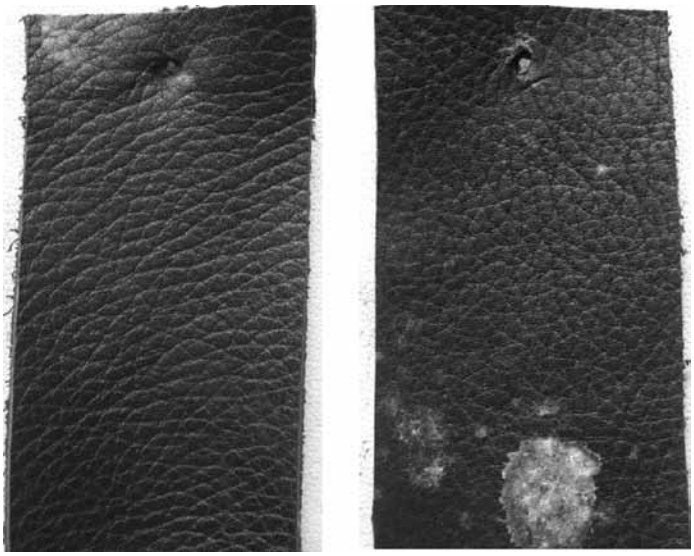

Figure 5: Finished leathers made from crust with 0.1% Azole 388 (left) and 0.1% TCMTB 30 (right) after 4 weeks of tropical chamber mold resistance testing. The finished leather on the left has only minor traces of mold growth (mold growth rating of 5) after 4 weeks, which indicates the leather possesses long-term mold resistance. The finished leather on the right has moderate mold growth after 4 weeks in the tropical chamber (mold growth rating of 15).

## TABLE VIII
## Tropical chamber mold growth ratings of crust leathers treated with the fungicides Azole 388 and TCMTB 30

| Sample Identification | Mold Growth Ratings | | | |
|---|---|---|---|---|
| | 1 Week | 2 Weeks | 3 Weeks | 4 Weeks |
| Tanned Goat Leather I — 0.1% Azole 388 | 0 | 0 | 0 | 0 |
| Tanned Goat Leather I — 0.1% Azole 388 | 0 | 0 | 0 | 0 |
| **Average** | **0** | **0** | **0** | **0** |
| Tanned Goat Leather II — 0.1% TCMTB 30 | 0 | 0 | 10 | 20 |
| Tanned Goat Leather II — 0.1% TCMTB 30 | 0 | 0 | 0 | 10 |
| **Average** | **0** | **0** | **5** | **15** |
| Negative Control | 35 | 75 | 100 | 100 |

Figure 6: Crust leathers with 0.1% Azole 388 (left), 0.1% TCMTB 30 (center) and no fungicide (right) after 4 weeks of tropical chamber mold resistance testing. The crust leather on the left has no mold growth (mold rating of 0), which indicates the leather possesses long-term mold resistance. The leather in the center has a very moderate degree of mold growth (mold growth rating of 15). The leather on the right is fully covered with mold growth (mold growth rating of 100).

independent laboratory in the UK, to test skin irritation potential and to evaluate the fungicide's suitability for skin contact applications. The tests included analyzing for TCMTB, OIT, PCP, formaldehyde, NPEO, VOC, and other components that cause irritation potential. The leather treated with Azole 388 passed all of the tests and complied with BLC requirements.[3] Due to its low skin irritation potential, use of the product in the crust and finished leather has been adopted by several upholstery leather producers, in addition to its use in wet blue.

## Conclusion

The new fungicide that is the subject of this paper was extensively tested in industrially produced leathers for fungicidal efficacy. The results of these tests over a period of nearly 5 years show that this product consistently performed well, providing long-term mold resistance to the treated leathers. It was further found that the product is more effective at lower dosage levels than the commercial fungicides used and which served as positive controls in these studies. This fungicide is formulated using a non-toxic, eco-neutral liquid carrier, which renders a product that is more eco-friendly than traditional solvent-based fungicide products that generate volatile organic compounds (VOC). During the course of applying and using the product by numerous tanneries it also emerged that the product is user friendly in terms of its near odorless character and its easy handling. The conclusion of this work is that with the development and introduction of this new leather fungicide, the industry now has a viable new alternative for fungal control in leather making.

## Acknowledgment

We would like to express our thanks to LASRA for allowing us to cite from their report.

## References

1. Zenith Industrial Chemicals Pte Ltd, Zenith Official Testing Standard - Tropical Chamber Mold Resistance Test.
3. Allsop, T.; Evaluation of Fungicide, LASRA Annual Conference, October 2009.
4. BLC Leather Technology Centre, Technical Report, June 2008.