



**Biocides Solutions**  
for  
**CLP 2015**

**Labeling free solutions to avoid EU H208**

HUNGAROCOAT, Budapest

Ľudmila Mošková

November 25th, 2014

**Ashland Specialty Ingredients**

## Introduction

### 1. CLP 2015 regulation

### 2. IN-CAN preservation

- Solutions to avoid EU H208

### 3. Dry film protection

- Solutions to avoid EU H208

# Three main businesses

			
<p><b>Commercial Unit</b></p>	<p><b>Ashland Specialty Ingredients</b></p>	<p><b>Ashland Performance Materials</b></p>	<p><b>Valvoline</b></p>
<p><b>Leading Products &amp; Services</b></p>	<p><b>#1</b> cellulose ethers, global leader in vinyl pyrrolidones</p>	<p><b>#1</b> unsaturated polyester resins and vinyl ester resins</p>	<p><b>#2</b> quick-lube chain, <b>#3</b> passenger-car motor oil in the U.S.</p>
<p><b>Sales<sup>1</sup></b></p>	<p><b>\$2.4 billion</b></p>	<p><b>\$1.8 billion</b></p>	<p><b>\$2.0 billion</b></p>

1 For 12 months ended June 30, 2014

2 Ashland Water Technologies was sold on July 31, 2014.

# Ashland Specialty Ingredients

## Key Markets and Applications

### Consumer Specialties

#### Pharmaceutical

- Oral solid & oral liquid dosage forms
- Film coatings
- Solubilization enhancement
- Pharmaceutical services

#### Care

- Oral, hair & skin care ingredients
- Biofunctionals
- Preservatives
- Advanced materials for medical care
- Home care (cleaning & household cleaning, fabric care, detergents, dishwashing)

#### Nutrition

- Food & beverage ingredients
- Beer & wine stabilizers
- Agriculture

### Industrial Specialties

#### Coatings

- Paint and coatings
- Waterborne architectural & industrial coatings
- Emulsion polymerization

#### Construction

- Dry mortar
- Gypsum plasters
- Joint compounds
- Renders
- Tile adhesives
- Exterior insulation finishing systems

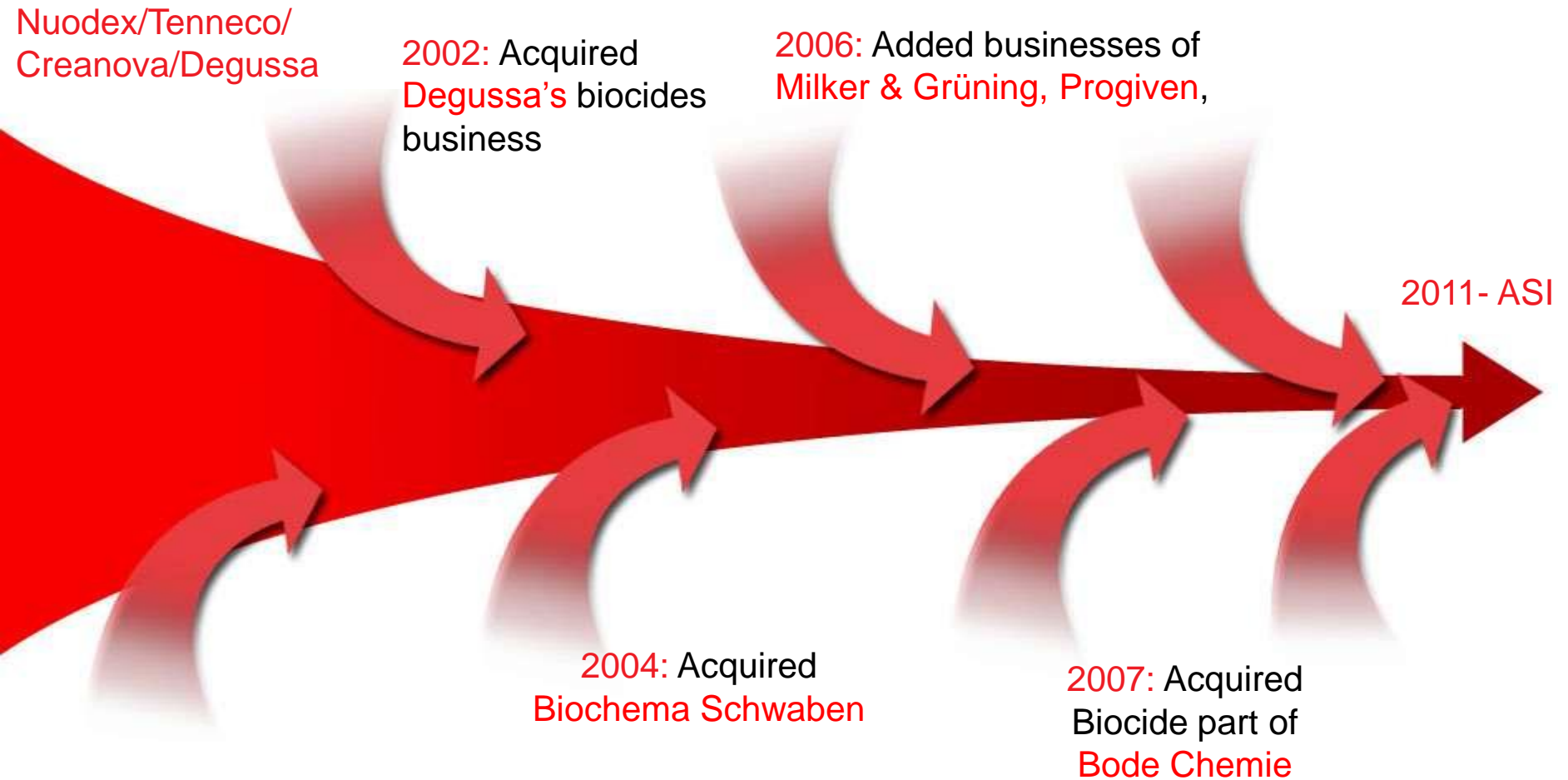
#### Adhesives

- Structural assembly
- Flexible packaging and converting
- Pressure-sensitive adhesives
- Labels

#### Energy

- Drilling fluids
- Cement slurries
- Completion/workover fluids
- Production & fracturing fluids
- Kinetic inhibitors
- Fluidized polymer suspensions
- Gel pigs

# History



# EU Biocides manufacturing facilities



*Memmingen, Germany*



*Horhausen, Germany*

# 1. CLP 2015 Regulation

# CLP 2015 labeling Regulation

- **CLP : Classification Labeling Packaging**

EU adaptation of GHS (Globally Harmonized System) which regulates the classification of mixtures

- Labeling rules for mixtures will change from **1st June 2015** (manufacturing date)

- Commission Regulation 286/2011 amended **Annex II of Regulation 1272/2008** for mixtures

# What is changing for end-products label?

- **New regulation affects the skin sensitizing substances :**
- **Current status:**  
**Xi R43 label** for end-products containing skin sensitizing substances with concentrations above skin sensitization thresholds (15ppm CMIT/MIT, 500ppm BIT, 1000ppm MIT, 500ppm OIT, 1000ppm HHT, 1% EDDM...)
- **New regulation:**  
**New EU H208 info statement for end-products** containing skin sensitizing substances at  **$\geq 1/10$  tenth of the current labeling limits**

For mixtures containing substances with a current R43/H317 threshold of 1% - 0.1% a corresponding “statement” at 0.1% on the product label!

For mixtures containing substances with a current R43/H317 threshold  $<0.1\%$  a corresponding “statement” at one tenth of the R43/H317 threshold on the product label!

# New labeling limits EU H208

Substances	NEW EU H208 triggers	Current Xi R43 / EU H317 triggers
CMIT/MIT	1,5 ppm	15 ppm
OIT	50 ppm	500 ppm
BIT	50 ppm	500 ppm
MIT	100 ppm/0,01% *	1000 ppm /0,1% *
FH donors(HHT/EDDM/TMAD)	1000 ppm/0,1%	1%
Formaldehyde	1000 ppm/0,1%	2000 ppm/0.2%
IPBC	1000 ppm	1%
BRONOPOL	No skin sensitization	No skin sensitization
ZnPt	No skin sensitization	No skin sensitization
Phenoxy Ethanol	No skin sensitization	No skin sensitization

\*lower values under authority discussion but not confirmed

# What does « EU H208 Statement » means ?

**EU H208** informs about the presence of skin sensitizing substances as follows :

**EUH208** — “Contains (name of sensitizing substance).

May produce an allergic reaction”

→ **EU H208 is an issue for all ready mix products which are often handle by hand and/or are designed for DIY market**

→ **General interest for wet-products with a high risk of exposure for end-users (indoor paints, ready mix adhesives & joint compounds, ceramic grouts...)**

→ **Raw materials like Polymer emulsions and slurries are also under pressure due to their own content of biocide (s) and significant contribution to EU H208 labeling**

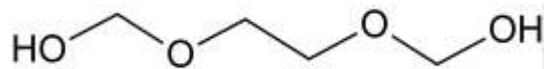
## 2. IN-CAN PRESERVATION

# IN-CAN PRESERVATION/ Actives review

## F-DONORS

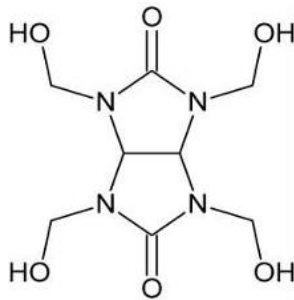
### • O-FORMAL

→ **EDDM or EG-formal**



### • N-FORMAL

→ **TMAD, HHT**

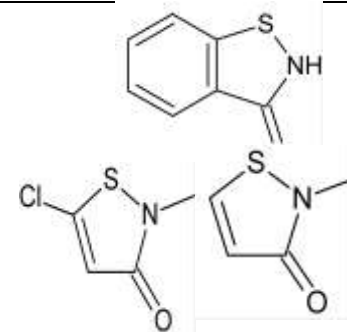


## NON F-DONORS

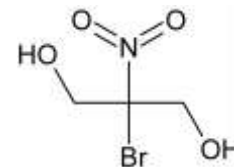
→ **BIT**

→ **CMIT/MIT**

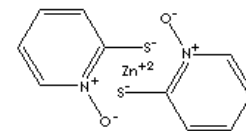
→ **MIT**



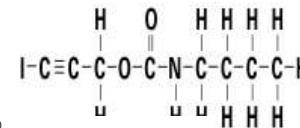
→ **Bronopol**



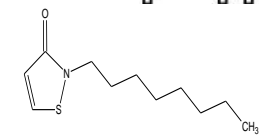
→ **ZnPt**



→ **IPBC**



→ **OIT**



13

# Why is it a challenge to avoid EU H208 ?

- The challenge for customers is to keep a high level of performances (fast speed of kill to avoid the formation of Biofilm ) **without CMIT/MIT and less %BIT & MIT**
- Example of FH-free preservation system to be replaced :  
**15 ppm CMIT/MIT+ 100ppm BIT+ 100ppm MIT**
- Example of labeling free solution :  
**50ppm BIT+ 100ppm MIT+ Others actives**  
Other actives are needed to compensate the loss of CMIT/MIT and half reduction of BIT

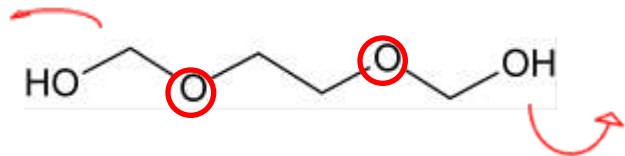
**a. Formaldehyde-donors biocides**

**b. Bronopol-Biocides**

**c. Formaldehyde-free Biocides**

# a. Formaldehyde-donors

# Formaldehyde donors



## EDDM

- (Ethylenedioxy)dimethanol  
EGF(EthyleneGlycol-Formal)
- CAS N°3586-55-8
- **49% FH**
- **O-Formal**

- **Main features :**

Cost effective

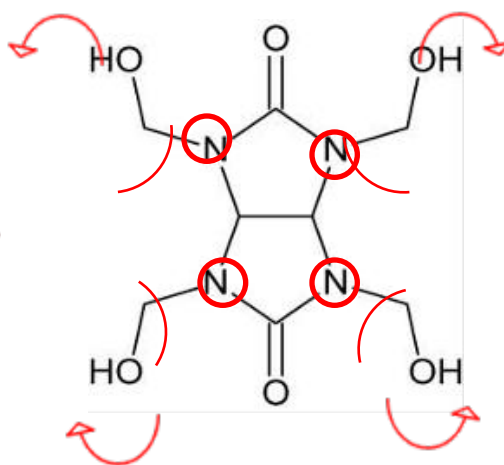
Quick kill (fast FA release)

Head space

Stable in various Ph

Skin sensitization > 1%,

Info statement EUH208 : 1000ppm



## TMAD

- Tetrahydro-1,3,4,6 tetrakis  
(hydroxymethyl)
- CAS N°5395-50-6
- **40% FH**
- **N-Formal**

- **Main features :**

High performances

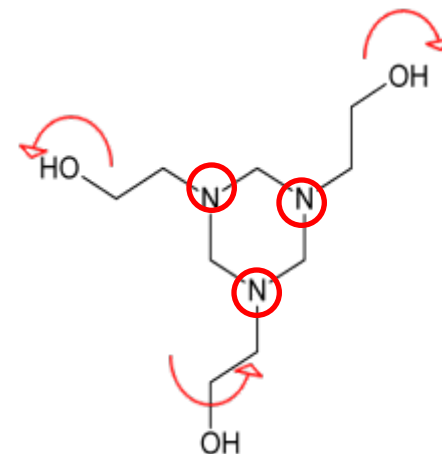
Odor free

Long term efficacy

(Slow FA release)

Skin sensitization > 1%

Info statement EUH208 : 1000ppm



## HHT

- 1,3,5-tris(2-hydroxyethyl)  
Hexahydro-1,3,5-triazine
- CAS N° 4719-04-4
- **41%FH**
- **N-Formal**

- **Main features :**

Stability at high pH

Long term efficacy

(slow FA release)

Quick kill

Skin sensitization > 0.1%

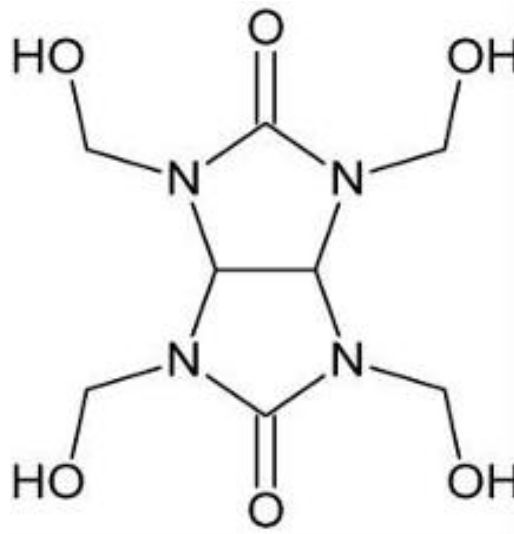
Info statement EUH208: 1000ppm

# a. Labeling free solutions/**O-FORMAL Donors**

O-Formal	Actives	Limits of use triggering EU H208
Bodoxin AE	EDDM	0,1%
Bodoxin AO	EDDM + OIT	0,1%

- **Keep using EDDM as fast speed of kill biocide in combination with BIT/MIT**
- **Advantage : flexibility to adjust % EDDM and BIT/MIT**
- **0,1% Bodoxin AE + 0,1% Nuosept BM22 :**  
→ maxi (1000 ppm EDDM + 50ppm BIT+ 50ppmMIT)
- **0,1% Bodoxin AO + 0,1% Nuosept BM22**  
→maxi (1000ppmEDDM + 50ppm BIT+ 50ppmMIT+ 50 ppm OIT)

- **TMAD (Bacillat range)**
- **40%FH/100% dissociation as worse case scenario**  
**EU H208 trigger = 0,1% TMAD**  
**(potential release of 1000ppm free FH)**
- **Ashland produces a premium quality TMAD (< 0,1% Free FH)**
- **ASI 's TMAD products will not get classified as CMR Cat 1B**



# a. Labeling free solutions/ **N-FORMAL Donors**

N-Formal	Actives ingredients	Limits of use triggering EU H208
<b>Nuosept TBM 40 (NEW)</b>	TMAD + BIT+ MIT	<b>0,20%</b>
<b>Bacillat</b>	TMAD	<b>0,20%</b>
<b>Bacillat TK</b>	TMAD + MIT	<b>0,43%</b>
<b>Bacillat TOK</b>	TMAD + MIT + OIT	<b>0,33%</b>

- **0,1-0,2% Nuosept TBM 40** → <1000ppm TMAD+ 50ppm BIT+ 50ppm MIT  
Ideal solution to replace CMIT/MIT + FH-Donors and BIT+ FH-Donors  
Easy solution but need to **check % BIT coming from raw materials**
- **0.05-0.17% Bacillat + Nuosept BM22** (adjustment in each paint composition)  
**Flex solution** → 1000 ppmTMAD + 50ppmBIT + 50ppmMIT  
Cost effective solution
- **0.15-0.35% Bacillat TK**  
Mainly recommended as booster (replacement CMIT/MIT+ FH donor) in addition to BIT/MIT  
Or when paints get too much BIT from raw materials
- **0.2-0.33% Bacillat TOK** ( 250 ppm TMAD+ 100ppm MIT+ 50ppmOIT)  
Low emission Free FH <100ppm/, Enhanced fungicidal resistance/ Head space  
Also usable as a complement of BIT/MIT (Nuosept BM22)

20

## **Nuosept TBM40**

- Solution of BIT/MIT/TMAD in a non VOC carrier
- No EUH208 to customer end-products
- Liquid solution/easy to pour & handle
- Low odor
- Highly concentrated/High performances
- Broad spectrum of efficacy vs bacteria/yeasts/molds
- Head space protection
- Typical use : 0,1-0,2%

## b. Bronopol solutions

## b. Labeling free solutions/**Bronopol**

PRODUCT name	Actives	Limits of use triggering EU H208
Nuosept KMB (NEW)	BIT/MIT/BNPD	0.2%
Ebotec KB	MIT/BNPD	0.5%

- **Nuosept KMB :**

Broad spectrum of efficacy (Pseudomonas )

Fast speed of kill

Eu Ecolabel compliance

Cost effective

- **Ebotec KB :**

Booster recommended at early stage in production

Ideal replacement of CMIT/MIT+ Bronopol

Recommended in combination with BIT/MIT

for eg **0,1-0,25% Ebotec KB + 0,1% Nuosept BM22**

→ Maximum ( 50ppm BIT+ 100ppm MIT+ 250 ppm BNPD)

# c.FH-Free solutions

# c. Labeling free solutions/**FH-Free biocides**

FA-free products	Actives	Limits of use triggering EU H208
Nuosept BM12 (NEW)	2,5%BIT/5%MIT	0,2%
Nuosept BM22	5%BIT+ 5%MIT	0,1%
Nuosept BMZ1 (NEW)	BIT/MIT/ZnPt	0,2%

- **Nuosept BMZ1**

Broad spectrum of efficacy

Enhanced fungicidal properties

(protection of the interface liquid/head space)

Ideal substitution BIT+ MIT + CMIT/MIT

Eu Ecolabel compliance

Speed of kill

Low risk « Ghost odour »

Cost effective



## 2.DRY FILM PROTECTION

# 3. Dry film protection



**Unprotected** coating



**Protected** coating

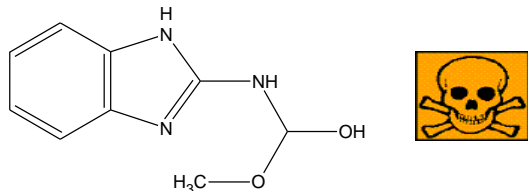
**Fungi & algae** defacements have a negative impact on coatings:

- They affects the decorative function of the coating
- They might degrade the coating itself

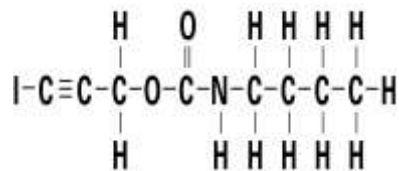
Dry film biocides are used to ensure a protection of the coating surface for 2 to 10 years !

# Active substance review

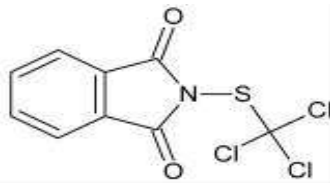
- **CARBENDAZIM**



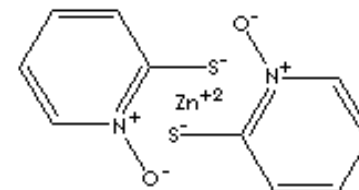
- **IPBC**



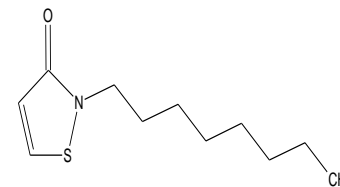
- **FOLPET (SB coatings only)**



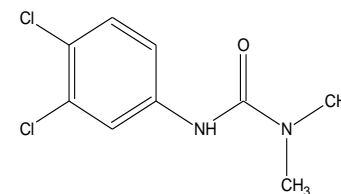
- **ZnPt**



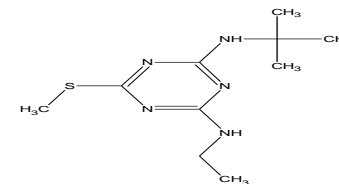
- **OIT**



- **DIURON**



- **TERBUTRYN**



# New labeling limits EU H208

Substances	EU H 208 triggers
OIT	50 ppm
DCOIT	100 ppm
IPBC	1000 ppm
ZnPt	No skin sensitization
ZnO	No skin sensitization
Carbendazim	No skin sensitization
Diuron	No skin sensitization
Folpet	1000 ppm
Terbutryn	1000 ppm

- EU H208 affects paints protected with **OIT & DCOIT**
- No issue when **IPBC** used below 0,1% (Indoor paints)
- **Znpt** is not affected by EUH208 but there is a new limit of 500ppm for Ecolabel

# Incidence of EU H208

- A paint producer claiming fungi and/or algae resistance properties already has to **declare the active substances used onto the label**  
EU H208 Info statement might appear in addition to this declaration
- **No issue for paints positioned as high performance coatings** exhibiting an efficient protection against micro-organisms

# Impact on Ashland dry film biocides

Products	Actives	Main Application	Use levels	EUH208 trigger %	Environment Paint labeling H412 trigger %	EU Ecolabel
Cinon OI	IPBC/OIT	Indoor	0,5-1,6%	>0,16%	N.A	1,6%
Fungitrol ZO2	ZnPt/OIT	Indoor Outdoor	0,2-0,5% 0,4-1%	>0,10%	N.A	0,22% Only indoor
Fungitrol ZO3	ZnPt/OIT	Indoor Outdoor	0,4-0,8% 0,75-1,5%	>0,15%	N.A	0,5% Only indoor
Fungitrol 10W	Carbendazim OIT Diuron	Outdoor	0,5-1%	>0,16%	0,11%	No
Fungitrol OTZ4	ZnPt/OIT /Terbutryn	Outdoor	0,4-1,5%	>0,17%	0,22%	No
Fungitrol TOP 2	Terbutryn/OIT Propiconazole	Outdoor	0,3-1,5%	>0,17%	0,21%	No
Fungitrol 940G	IPBC	Indoor Outdoor	0,1-0,5% 0,25-0,75%	>0,25%	N.A	0,25% Indoor 0,75% Outdoor 1,6% Wood paints
Fongal PZT2	14,9%ZnPt 11%Terbutryn	Indoor Outdoor	0,2-1% 0,5-1,5%	>0,9%	0,21%	No

# Dry film recommendations

- Indoor paints (Ecolabel compliance and No EU H208)  
**0.24% Fungitrol 940G + max. 0,1% Fungitrol ZO2**  
→ maxi ( 1000ppm IPBC + 500 ppm ZnPt + 50 ppm OIT)
- Indoor paints (Ecolabel compliance with EUH208)  
**0.24% Fungitrol 940G + 0,22% Fungitrol ZO2**
- Outdoor paints (H412 without EUH208)  
**0,9% Fongal PZT2 + 0,24% Fungitrol 940G**

**ASHLAND®**

With good chemistry great things happen.™