Arch Chemicals, Inc.

Innovative In-Can Preservation

Scott Brown
Technology Manager
Arch Chemicals, Inc.

Arch Chemicals, Inc.

Overview

- Market requirements
- Historical trends
- Regulatory/VOC/IAQ pressures
- Current Options: In-Can Preservation
- Future product innovation

  - Non-formaldehyde, Zero VOC, Global approvals

  - Benzisothiazolinone (BIT) and Zinc Pyrithione (ZPT)

  blend for In-Can Preservation

Market Requirements for Biocides

- Broad spectrum antimicrobial activity
- Temperature and pH stability
- Aqueous based solutions or dispersions
- Compatibility with formulation
- Low environmental impact
- Low toxicity e.g. skin irritancy
- Relevant regulatory compliance (EPA, FDA, BPD, BfR, REACH)
- Cost effective

Arch Chemicals, Inc.

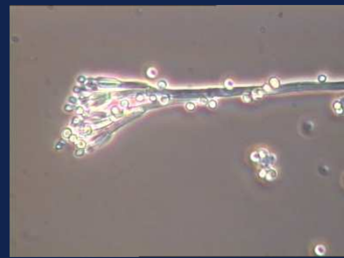
The Facts

- Water based coatings can be highly susceptible to bacterial and fungal degradation during production or after application
- Microbial attack can result in discoloration, reduced viscosity, malodors and impaired technical performance
- Effective preservatives are required for water based coatings

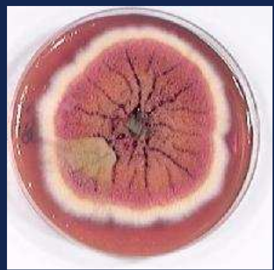
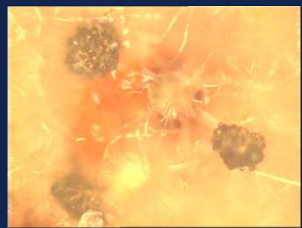
Arch Chemicals, Inc.

The Usual Suspects: Typical spoilage organisms

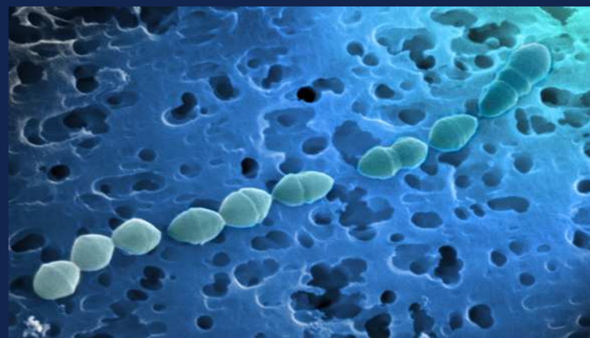

Rhodotorula glutinis

Penicillium s

Epicoccum sp



Streptococcus sp on Filter


Alternaria alternata

Spoilage Symptoms

Organisms can grow on the surface or dispersed within the product

Fungal growth on surface of emulsion polymer

Container bulging from buildup of microbial CO_2

Arch Chemicals, Inc.

Global Historical Trends

- Pre 1970 organometallics & formaldehyde widely used
  - Mercury based biocides (ex. PMA) regulated out of use
  - Regulatory pressure on organo-tin (ex. TBT) and organo-arsenic (ex. OBPA) compounds due to persistence and toxicity
  - Formaldehyde (and donors) under increasing pressure
- Since 1980 use of Isothiazolones (IT) has grown, and now a major share of industrial preservation
- New generation of non-metallic active molecules are more susceptible to chemical degradation
- Combinations of actives now prevalent
- Balance between efficacy and toxicity

Arch Chemicals, Inc.

Global Regulatory Landscape

"Globalization"

Common Formulations

Common Biocides

Global Purchasing

Export/Import of Products

IARC

EPA/ FDA

BPD

AOX

15ppm CMIT/MIT Labelling Limit

→ Fewer Preservative Choices

Common Trends

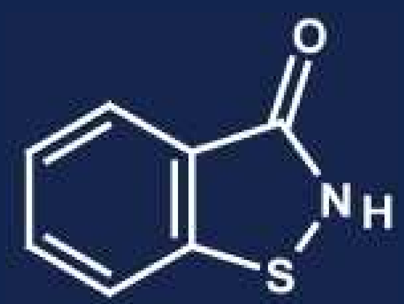
- Decreased Use of Solvents / More Aqueous Products
- Lower VOC
- CMIT/MIT Labelling Limitations
- Formaldehyde Pressure (IARC)

Current In-Can Preservation Options

- Isothiazolins (BIT/MIT/CMIT)
  - 1,2 BenzIsothiazolin-3-one (**BIT**)
  - 2-methyl-4-isothiazolin-3-one (MIT)
  - 5-chloro-2-methyl-4-isothiazolin-3-one (CMIT)
- 1,2-Dibromo-2,4-dicyanobutane (DBDCB)
- 2-Bromo-2-nitro-1,3 propanediol (Bronopol)
- Formaldehyde Donors (various)
  - i.e. 4,4-Dimethyl oxazolidine, 2-(Hydroxymethyl) amino ethanol, etc.
- Phenolics (OPP, PCMC, PCMX)
  - o-Phenylphenol (OPP)
  - p-Chloro-m-cresol (PCMC): p-Chloro-m-xylenol (PCMX)
- Guanidines and Biguanides (various)
  - Polyhexamethylenebiguanide (**PHMB**), etc.

BIT Profile

- Main building block for in-can preservation
- Broad spectrum
- Strong global regulatory package
- FDA/BfR clearances for use in food contact materials
- Non-sensitizer at use levels
- Non-volatile and good thermal stability
- Excellent pH stability



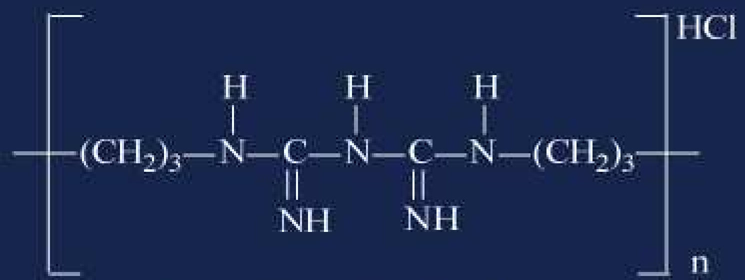
Arch Chemicals, Inc.

Example BIT Formulations and BIT Blends

- BIT Aqueous Solution Formulation
  - 9 % w/w aqueous solution
- BIT Aqueous Dispersion Formulation
  - 20 % w/w aqueous dispersion
- BIT 20 Glycol Solution Formulation
  - 20 % w/w aqueous dipropylene glycol solution
- BIT & ZPT Aqueous Dispersion Formulations
  - Aqueous dispersions of BIT and Zinc Pyrithione
  - 11 % w/w 1:1 ratio and 20 % w/w 1.5:1 ratio
- BIT & Bronopol Aqueous Dispersion Formulations
  - 20 % aqueous dispersion 2:1 ratio

PHMB – Profile

- Poly(hexamethylenebiguanide) hydrochloride (PHMB)
- Strong global regulatory package
- Suitable alternative to CMIT in non-ionic formulations
  - Starch adhesives, Latex adhesives based on PVA, VAE, etc.
  - Effective in low pH systems; good activity against both bacteria and yeast
- Unique non-formaldehyde mechanism
- Water based zero VOC 20% solution
- Excellent thermal stability
- Excellent pH stability
- Excellent redox stability



n = 10 - 13

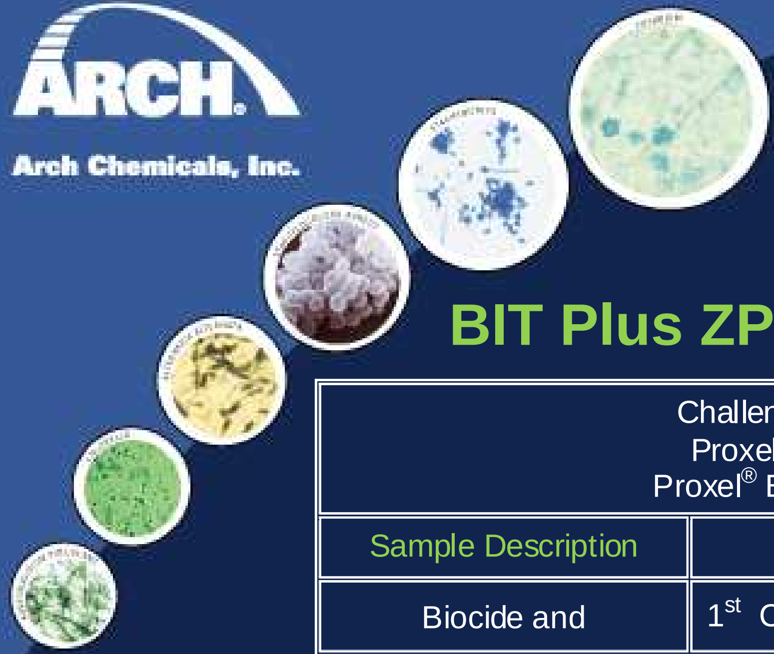
Future Innovation: BIT Plus ZPT Preservatives

- Relevant regulatory compliance
  - Formaldehyde free
  - CMIT free
- Zero VOC (solvent free)
- Other Features and Benefits
  - Broad spectrum - bacteria, yeasts and fungi (mold)
  - Complimentary Dual Antimicrobial Mechanisms
  - Excellent heat stability & pH stability (4 to 11)
  - Low cost in use

Arch Chemicals, Inc.

BIT Plus ZPT Preservative Example

- Adhesive – Challenge Test, In-can
- Start with un-contaminated adhesive
- Ladder of increasing biocide dosage
  - One sample with no biocide added
  - Ladder of 1,2-benzisothiazolin-3-one (BIT) alone
  - Ladder of BIT with Zinc Pyrithione (ZPT)
  - All samples receive three microbial challenges
  - Challenge with common spoilage bacteria;
    - » *Pseudomonas aeruginosa (ATCC # 10145), Escherichia coli (ATCC # 11229),*
      Enterobacter cloacae (ATCC # 7256), Acinetobacter calcoaceticus (ATCC # 14987)
- Results
  - Proxel® AQ Preservative BIT alone – passed at 370 ppm ai
  - Proxel® BZ Plus Preservative BIT + ZPT - passed at 24 ppm ai



BIT Plus ZPT Preservative - Example

Challenge Testing Result for Adhesive Proxel® AQ Preservative (BIT alone) Proxel® BZ Plus Preservative (BIT + ZPT)						
Sample Description		Microbial Counts				
Biocide and		1st Challenge 10%		2nd Chal 5%	3rd Challenge 2.5%	
Concentration (ppm)		24 hr	72 hr	72 hr streak	24 hr	72 hr DPC
Control (Unpreserved)		5	5	5	5	$>10^8$
Proxel AQ	1500	3	2	5	5	$>10^8$
Proxel AQ	2000	2	0	5	5	$>10^8$
Proxel AQ	2500	2	0	5	2	3.8×10^4
Proxel AQ	3000	0	0	0	2	1.8×10^3
Proxel AQ	4000	0	0	0	0	<10
Proxel BZ Plus	200	0	0	0	0	<10
Proxel BZ Plus	400	0	0	0	0	<10

Arch Chemicals, Inc.

BIT Plus ZPT Preservative: Further Examples

Substrate: Polymer Emulsions	DS6307 Pass Level
Acrylic Emulsions	0.05 - 0.10%
Acrylic/ Methacrylic Copolymer Emulsions	0.05 - 0.10%
Styrene/Acrylic Copolymer Emulsions	0.10 - 0.20%
Styrene/Butadiene Copolymer Emulsions	0.05 - 0.20%
PVA Emulsions	0.10 - 0.20%

Substrate: Miscellaneous	DS6307 Pass Level
Adhesives	0.05 - 0.20%
Mineral Slurries	0.05 - 0.15%
Pigment Dispersions	0.10 - 0.25%
Inks	0.05 - 0.20%

DS 6307 – Aqueous BIT & ZPT Dispersion Formulation
a.k.a. Proxel ®BZ Plus Preservative

BIT Plus ZPT Preservatives - Dual Mode of Action

Two actives:

- 1,2-Benzisothiazolin-3-one (BIT) is primarily active against bacteria
- Zinc Pyrithione (ZPT) is primarily active against fungi

Two different mechanisms for activity:

- ZPT acts on microbial membranes acting as a chelate and disrupting important ion gradients. Organisms expend energy attempting to restore gradients so increasing their metabolic rate

- BIT is electrophilically active, reacting with microbial enzymes containing thiol groups so disrupting a number of metabolic processes and is more effective against metabolically active organisms

Arch Chemicals, Inc.

Conclusions

- Pressure will continue to increase on formaldehyde, Organotin and Organoarsenic based biocides
- Isothiazolones will continue to be the main building blocks for in-can preservation
- Use of BIT together with other actives can enhance the efficacy and spectrum of activity
- Combination with ZPT enhances in-can activity of BIT and offers improved cost-effect

ARCH

Arch Chemicals, Inc.

Contact us today to learn more about how we can become a part of your solution.

www.archbiocides.com