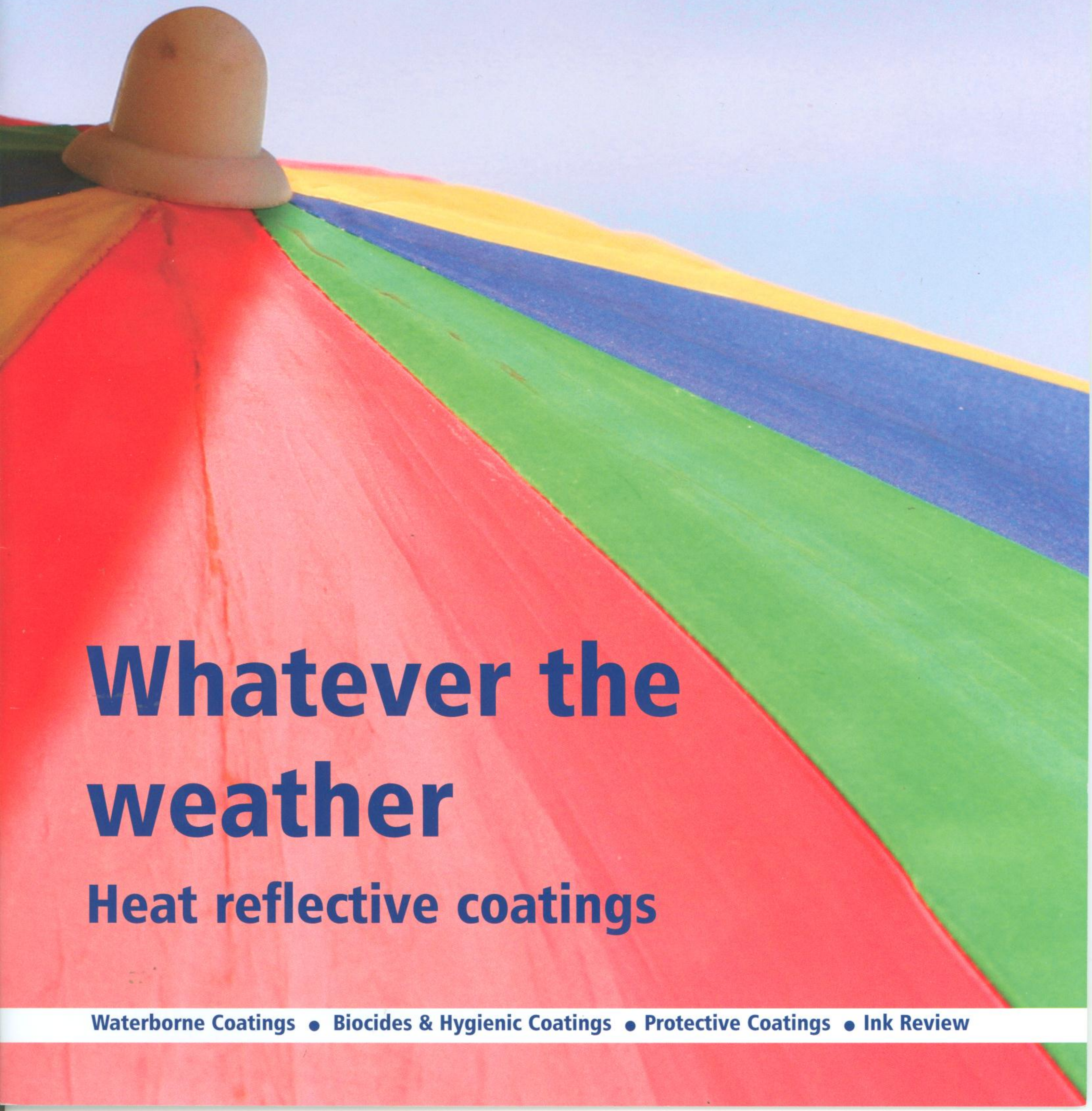
Leading Journal for the Coatings Industry in Europe and the Middle East

Vol 201 No 4563
August 2011

POLYMERS PAINT COLOUR JOURNAL

PPCJ

MIDDLE EAST COATINGS SHOW 2012



Whatever the weather

Heat reflective coatings

Waterborne Coatings • Biocides & Hygienic Coatings • Protective Coatings • Ink Review

Thomas Köhler, Anders Carlsen and **Gerhard Tiedtke**, Dow Microbial Control discuss the development and notified 2-Methyl-1,2-benzisothiazole-3(2H)-one (Methyl-BIT, BIOBAN MBIT), a new active substance, which is a building block for powerful in-can preservation

Breakthrough innovation for in-can preservation

Due to increasing restrictions on many traditional active ingredients used as in-can preservatives (BPD[a], ecolabels, label limits) the number of viable choices had decreased. At the same time, the global development towards environmentally more acceptable products (VOC[b]) regulations, residual monomer restrictions, natural ingredients) results in a higher susceptibility of commercial products towards microbial spoilage. The few most frequently used active ingredients are limited in efficacy spectrum, speed-of-kill and/or chemical stability. Therefore, it gets increasingly difficult to achieve robust preservation given developing consumer preferences and increasing regulatory and ecolabel restrictions.

Today, two trends influence the needs and choices for preservatives. First, they need to be 'green'; second, the increasing public awareness about potentially dangerous chemicals is reflected in regulations for relevant preservation (BPD ⇒ BPR[c]).

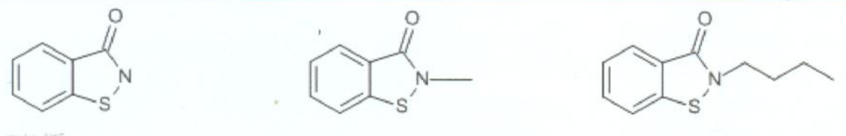
Comparing properties and numbers of originally identified active ingredients (706) to those actually notified actives for in-can-preservation (50) and extrapolating what may be left in 2015 shows a clear trend: the active ingredients surviving are typically more suitable for long-term preservation and have limited efficacy spectra, low speed-of-kill and/or chemical stability.

The slow speed of kill and the selective control of organisms can lead to the adaptation of certain organisms or population shifts. Paints, for instance, never used to have issues with yeast or fungi contamination until slow speed of kill reagents like MIT/BIT combinations were employed over long periods of time.

In search of the maximum understanding of existing 'old' actives, Dow Microbial Control has rediscovered one rather unusual reaction pathway of Dithio-2,2'-bis-benzmethylamide (DTBMA). DTBMA is a well-known biocide that has been on the market for over 30 years. It was recommended for both wet state preservation applications (in-can) and dry-film preservation alike due to its broad spectrum of effectiveness versus moulds, yeasts and bacteria.

It has long been known that DTBMA hydrolyses in alkaline media to N-methylbenzisothiazolinone but be could demonstrated that this conversion is quantitative in solvency moderating matrices.[1]

Table 1 shows conversion rates for DTBMA to MBIT in different acrylic systems. In this experiment, only DTBMA (~200ppm) was added and within two hours about 10 to 15% of DTBMA is converted to MBIT.



BIT bactericide | Methyl-BIT | Bu-BIT fungicide

Fig 1. Structural similarities between isothiazolone-based bactericides and fungicides. On the right are the longer chained Bu-BIT, which are known as fungicides with a modest efficacy against bacteria. On the left side is the typical short-chained isothiazolone bactericide BIT. Methyl-BIT is structurally very similar to both the bacte-ricide BIT and the fungicide Bu-BIT, which could explain why it works better versus fungi than BIT and better versus bacteria than Bu-BIT

Table 1. Conversion rates for DTBMA to MBIT in different systems. Concentrations in ppm

	2 hrs		1 day		3/4 days		14 days	
	DTBMA	MBIT	DTBMA	MBIT	DTBMA	MBIT	DTBMA	MBIT
Masonry paint based on acrylic binder pH 8.00	166	32	102	88	66	124	2	179
styrene-acrylic emulsion on pH 8.05	169	29	101	92	0	184	0	181
Styrene-acrylic paint pH 8.89	155	28	75	97	9	154	0	159

The rapid conversion of DTMBA to MBIT together with the much higher water solubility of MBIT than DTBMA demonstrates that MBIT is the actual biocidal active component in DTBMA. Recently, MBIT has come to be recognised as the biocidal active component in DTBMA and a microbicide on its own.

The isothiazolones are based on the same core, the tendency being that the more traditional bactericides have shorter chains and the fungicides have longer chains. Biological tests in the DMC Labs could show that MBIT is a better fungicide than BIT and a better bactericide than Butyl-BIT (Bu-BIT).[1]

BIT can be de-protonised (pK b ~8.5) and the de-protonised form has much lower efficacy as a bactericide. MBIT does not de-protonise due to the N-methylated hetero-cycle. Non-deprotonised BIT is relatively lipophilic with a low solubility in water (<

Authors:
Thomas Köhler – Tel: +41 817554730; Fax: +41 817554779; Anders Carlsen – Tel: +41 817554776; Fax: +41 817554609; and Gerhard Tiedtke – Tel: +41 817554771; Fax: +41 817554779; Dow Microbial Control, Acima AG fur Chemische, Im Ochsensand, 9471 Buchs, Switzerland. www.dowmicrobialcontrol.com

1K ((+)) (+) + ++ +++

	Conc.	Inoc 1 + 1 wk			Inoc 2 + 1 wk			Inoc 3 + 1 wk			Inoc 4 + 1 wk			Inoc 5 + 1 wk			Inoc 6 + 1 wk			corresponding ai. concentration [ppm ai.]			
	%	B	Y	F	B	Y	F	B	Y	F	B	Y	F	B	Y	F	B	Y	F	BIT	MIT	M-BIT	CMIT
Bioban 551 S	0.1																				50	38	
M-BIT-MIT	0.15																				75	56	
	0.2																				100	75	
	0.4																				200	150	
aged 4 wks, 40°C	0.2																				100	75	
BIT/CMIT-MIT	0.075																			38	31		2
	0.1																			50	41		3
	0.15																			75	62		5
	0.3																			150	123		10
aged 4 wks, 40°C	0.15																			75	62		5
BIT:MIT 2:1 form.	0.1																			50	25		
	0.25																			125	63		
	0.4																			200	100		
	0.6																			300	150		
aged 4 wks, 40°C	0.4																			200	100		
BIT:MIT 1:1 form.	0.1																			50	50		
	0.15																			75	75		
	0.2																			100	100		
	0.3																			150	150		
aged 4 wks, 40°C	0.2																			100	100		

Table 2. Challenge test of an acrylic exterior paint, pH >8 using a mixed in-oculum of bacteria (B), fungi (F) and yeast (Y). The ratings are given in a graphical evaluation, (1K) abbreviated for one colony per plate

0.1%) whereas MBIT is more hydrophilic with a higher solubility in water (~2%). In essence, MBIT is a more potent biocide at alkaline pH and has higher availability in the aqueous phase than BIT, which is essential for contact with micro-organisms.

MIC studies and synergism studies of MBIT (DTBMA) combinations have been carried out and published by Dow Microbial Control [1]. In the following, a deeper look is taken at the comparison between MBIT/MIT and BIT formulations in an application scenario.

Many waterborne systems including paints are susceptible to microbiological contamination and spoilage, and require the use of an in-can preservative to provide protection during manufacture and to guarantee the desired shelf life [2]. Biocidal active ingredients (ais) possess a range of both physicochemical and biological properties that will affect their applicability in certain types of formulations and/or manufacturing processes [3]. The selection of an appropriate in-can preservative is an important factor in the development of a paint formulation and failure to prevent spoilage due to microbiological growth can result in the development of foul odours, discolouration, loss of structure and the generation of gasses that might distort/damage the final packaging.

The susceptibility of a coating formulation to microbiological spoilage and the potential efficacy of an in-can preservation system are usually determined using a micro-biological challenge test.[4] Amongst others the International Biodeterioration Research Group (IBRG) has been developing a test protocol for testing the in-can preservation of paints and varnishes.[5]

The following study compares a synergistic MBIT/MIT formulation to traditional in-can formulations in an acrylic paint system (six cycle/week challenge test for not aged and the same conditions after heat ageing of paint for four weeks at 40°C).

The results in **Table 2** show how well the combination of 50ppm MIT and 38ppm MBIT is preserving a material in wet state – in this case an acrylic exterior paint; pH >8. The combination of MBIT/MIT is the only formulation that withstands six inoculations against a mixed bacteria/yeast/fungi inoculum at the lowest concentration. It can be concluded that MBIT formulations work very well in synergistic combination with other actives – in this case MIT.

SUMMARY

MBIT is a proven, effective bactericide and fungicide for wet state preservation applications. Dow Microbial Control demonstrates a well-balanced synergistic combination of MBIT (DTBMA) and MIT that is effective against several common spoilage organisms outperforming common BIT blends.

Due to better water solubility, MBIT is more bio-available in the aqueous phase than BIT, which is critical for contact with micro-organisms. At alkaline pH the impossible salt formation of MBIT leads to a more potent biocide than BIT.

Compared to DTBMA, MBIT can be much more easily formulated. Due to its solubility in water, MBIT formulations are available as stable, VOC-free liquids rather than the viscous, sometimes more difficult to handle, aqueous dispersions of DTBMA.

Authors:
Thomas Koehler, Associate Scientist, Dow Microbial Control, Acima AG fur Chemische, Im Ochsensand
9471 Buchs, Switzerland
Tel: +41 817554730; Fax: +41 817554779

Anders Carlsen, Sr Technical Sales Rep
Acima AG fur Chemische
Im Ochsensand
9471 Buchs, Switzerland
Tel: +41 817554776; Fax: +41 817554609

Gerhard Tiedtke - R&D Leader
Acima AG fur Chemische
Im Ochsensand
9471 Buchs, Switzerland
Tel: +41 817554771; Fax: +41 817554779;
www.dowmicrobialcontrol.com

References
1. Köhler, T, Carlsen A, Tiedtke G (2011), New solutions for in-can preservation in the making for Europe. European Coatings Conference, Novel Biocide Technology V, Proceedings 65-75.
2. Downey, A (1995), The Use of Biocides in Paint Preservation, Handbook of Biocide and Preservative Use, Ed. Rossmore H W, Blackie Academic and Professional, London.
3. Paulus, W (2005) Directory of Microbicides for the Protection of Materials: A Handbook, Kluwer Academic Publishers.
4. Askew P D (2006) Coatings and Coatings Materials in Springer Handbook of Materials Measurement Methods Eds Czichos H, Saito T, Smith L, Springer Science and Business Media.
5. Lunenberg-Duindam J, Lindner W (2000). In-Can Preservation. European Coating Journal. 03, 66 -73.

Glossary
a) BPD: Biocidal Product Directive
b) VOC: Volatile Organic Compound
c) BPR: Biocidal Product Regulations