Nomination for the 2012 Annual Presidential Green Chemistry Challenge Award

Project: Successful FIFRA Registration of a slow formaldehyde release bactericide resulting in significantly reduced exposure to formaldehyde in the US metalworking industry.

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The EPA Decision for Registration of a Pesticide Product Containing the New Active Ingredient N,N'-Methylenebismorpholine in Metalworking, Cutting, Cooling and Lubricating Fluid Concentrates was issued November 7, 2011.

This nominated technology is not eligible for the small business award or an academic award.

The focus area is the design of greener chemicals.

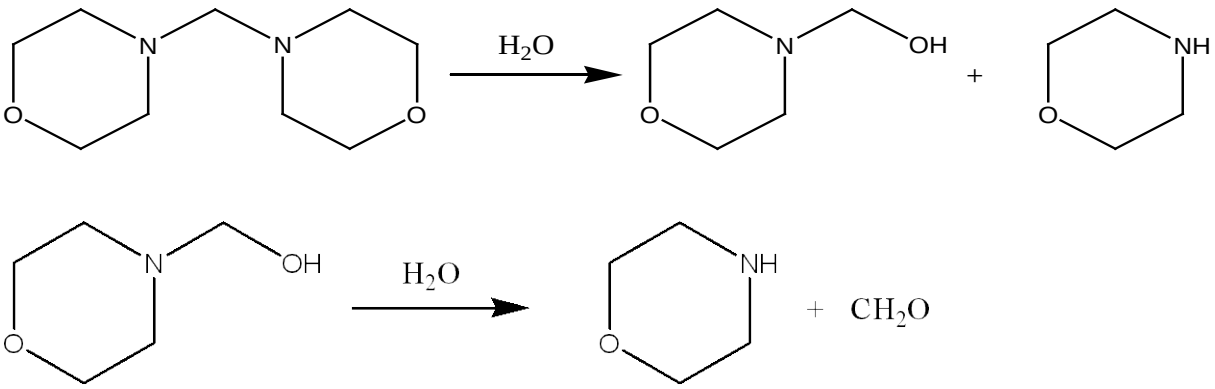
The R&D for this technology was divided between the US and Europe. The exposure study was done in the UK since the product was already in compliance in that country, enabling an observational study. Human Subjects Review Board criteria were met for this study. All of the analytical work establishing the mechanism was done in the USA.

Abstract:

Formaldehyde release bactericides have been the predominant type of chemistry used to preserve metalworking fluids over the last 4 or more decades. Concerns regarding exposure to formaldehyde in the metalworking and many other industries have arisen over the last 10 to 15 years. In exploring the apparent dichotomy of the rapid hydrolysis of N,N'-Methylenebismorpholine (MBM) in water, which occurs at low concentration in water in under six seconds, and a half-life of several months in a metalworking fluid, Lubrizol discovered that the MBM has sufficient oil solubility to be incorporated into the oil micelles formed in metalworking fluid emulsions. This not only provides stability in the metalworking fluid, but also provides slow release of formaldehyde and therefore a very low airborne concentration in metalworking production plants. One study conducted in the UK[(1)] found 1.1 to 3.3 parts per billion formaldehyde, which is lower than the concentration found in human breath[(2,3)] and well below the EPA occupational level of concern of 100 ppb. Although formaldehyde is a chemical of concern, EPA concluded that MBM is a reduced risk alternative to formaldehyde releasers currently on the market and a viable option for users to move away from products with higher formaldehyde release rates. EPA further states that the metalworking fluid use pattern is expected to pose little to no environmental concern[(4)]. Since the product is very compatible with most metalworking fluid concentrates, the registration applied for was intentionally limited to use solely in concentrates in order to minimize exposure to US workers. Many bactericides are added to the diluted fluids "tankside", which results in many more workers being exposed to the highly concentrated antimicrobial.

Details of the Technology:

One critical component of product registration for the European Union (Biocide Products Directive) and EPA (FIFRA) is the determination of product stability and hydrolysis rates. MBM is the reaction product of morpholine and paraformaldehyde. Via NMR studies, the hydrolysis is a two step process:



The initial hydrolysis study for the BPD registration, using a gas chromatography method, showed that hydrolysis occurred in less than one day[5]. Additional hydrolysis experiments using HPLC with post column derivitization were conducted in water and in modified Gamble's solution. Results showed that at a concentration of 1500 ppm, which is the typical concentration in metalworking fluid compositions, complete hydrolysis occurred is less than 6 seconds[6,9]. These data would imply that the product is quite hydrolytically unstable and unsuitable for use in aqueous metalworking fluids. However, practical field experience contradicted this hypothesis.

Therefore, a stability test in aqueous metalworking fluid emulsions was undertaken using HPLC as the analytical tool. This proved to be a quite challenging project since most analytical techniques for the determination of formaldehyde are destructive in nature and prohibit distinguishing between free and bound formaldehyde. Methodology using normal phase HPLC with post column derivitization was successful in determining that the half-life of the MBM molecule in an aqueous metalworking fluid is 5-8 months[7,8] (95% confidence limit). Since this was not a GLP study, EPA discounted the half-life by 50%.

Based on the large difference between the hydrolysis rate in water versus in the metalworking fluid, it was hypothesized that the MBM is likely incorporated in the oil micelle and therefore protected from rapid hydrolysis by the oil. To circumstantially prove that this is the likely mechanism, a solubility study was conducted comparing MBM to other formaldehyde release bactericides. Since there is significant variability in

oil compositions, the study was conducted in a very non-polar solvent for consistency. Heptane was chosen as the solvent, and a tubidimetric technique using Hach Method 8195, based on USEPA Method 180.1, was adopted for determination of the solubility range. Data obtained is shown below:

Concentration	Ntu reading	Ntu Corrected for blank
Heptane blank	0.10	-
10500 mg/L	0.63	0.53
4192 mg/L	0.23	0.13
2380 mg/L	0.11	0.01
564 mg/L	0.11	0.01
0.1 ntu std	0.11	-

Based on this data, the solubility range of MBM in n-heptane is estimated to be between 2000 and 2500 mg/L at $20.5 \pm 0.5^{o}C$.

Using the same methodology, MBM was compared with other related chemistry:

Chemistry	CAS#	Solubility (mg/L in heptane)
1,3,5-Triazine-1,3,5(2H,4H,6H)-triethanol	4719-04-4	0
N,N'-methylenebismorpholine	5625-90-1	2000-2500
Oxazolidine, 3,3'-methylenebis[5-methyl-	66204-44-2	500-1000
1,3,5-Triazine-1,3,5(2H,4H,6H)-triethanol,α1,α3,α5-trimethyl-	25254-50-6	200-280
(ethylenedioxy)dimethanol	3586-55-8	20-50

This data shows that MBM is significantly more soluble in non-polar solvents than other related chemistry and likely explains its longer half-life in metalworking fluid emulsions.

Additional benefits to its very rapid decomposition in water include minimization of pesticide residues remaining in packaging materials after rinsing the container, and reduced concern in the event of a spill into the environment, particularly into waterways. Rapid hydrolysis in Gamble's solution indicates a lower concern regarding absorption through the skin and upon inhalation since at low concentration the parent MBM molecule is rapidly destroyed.

However, the key benefit is the minimal exposure to formaldehyde in the machining environment. There are three possible sources of exposure to formaldehyde in the machine shop: 1) background exposure from sources extraneous to the antimicrobial

agent in the metalworking fluid (e.g., formaldehyde: in outdoor air, human breath, released from other materials in a production facility such as plywood and insulation materials, as well as facility operations such as welding processes or fork lifts) (Ross et al., 2004)[10], 2) volatilization of unbound formaldehyde liberated from the formaldehyde condensate antimicrobial in metalworking fluid sumps or machining streams, and 3) formaldehyde liberated from the antimicrobial in the aerosols generated during the machining process.

In view of the concern surrounding exposure to formaldehyde a field study was conducted at a machining site that exclusively used MBM in the metalworking fluids it was supplied. The site was selected by a Lubrizol customer since Lubrizol does not supply finished metalworking fluids. All field data were collected at one site, a manufacturer of automotive components located in the UK. Atmospheric sampling of formaldehyde was conducted over a three-day period during the day shift. This study was observational in nature. Worksite air samples were taken in fixed positions in proximity (within 2 meters) of metalworking machines which utilized MBM as the machining fluid antimicrobial agent in semi-synthetic (water-based) type coolants. Personal samples were also taken. Results of this airborne monitoring were in the range of 1.1 to 3.3 parts per billion formaldehyde.

To put this data in perspective, the chart below shows a comparison of our data with other published monitoring data that used different antimicrobial biocides. It should be noted that while Lillienberg did not identify the biocides in her publication, she did verify, when contacted, that the data identified as Company 3 utilized MBM. It is my opinion that this corroborates the data we obtained.

Study Source	Biocide	Biocide Concentration	Airborne FA (ppb)
Cohen 1995[11]	HHT	1,500 ppm	Range <100 up to 500
Linnainmaa 2003[12]	HHT/Carbamate	Mean 470 ppm Range <0.5 - 3,500	Mean 42 Range 8 - 179
Lubrizol/Outside Lab (analysis)	MBM	Mean 1,493 ppm	Mean 1.97 Range 1 - 6
Lillienberg 2008[13] Lillienberg 2008	Unknown Unknown	Unknown Unknown	2 - 34 (Company 2) 1 - 6 (Company 3)

Conclusion: Although CONTRAM™ ST-1 contains and releases formaldehyde, the amount released during use in the industrial machine shop environment is negligible and even below the amount exhaled in human breath. Introduction of this chemistry to the US market represents a significant decrease in exposure to formaldehyde compared

with other formaldehyde release chemistry currently on the market, and may even pose a lower overall risk than “formaldehyde free” products on the market today.

References:

Ref #	Title	MRID#
1	UK Industrial Hygiene Monitoring Study	47555831
2	Mass spectrometric profile of exhaled breath—field study by PTR-MS, Moser et al, Respiratory Physiology & Neurobiology, Volume 145, Issues 2-3, February 2005, Pages 295-300	
3	Compounds enhanced in a mass spectrometric profile of smokers' exhaled breath versus non-smokers as determined in a pilot study using PTR-MS, Kushch et al, *J Breath Res 026002 (26 pp)* 2008;2(2):026002	
4	Decision for Registration of a Pesticide Product Containing the New Active Ingredient N,N’-Methylenebismorpholine in Metalworking, Cutting, Cooling and Lubricating Fluid Concentrates (can be accessed at www.regulations.gov)	Docket No: EPA-HQ-OPP-2009-0254
5	Determination of General Physico-Chemical Properties (pp. 47-57)	47755830
6	Determination of Hydrolysis Time for CONTRAM ST-1 by HPLC	48064803
7	Half Life of CONTRAM ST-1 in Aqueous-Soluble Oil Metalworking Fluid	47555821
8	Supplemental Information for MRID 47555821: Half Life of CONTRAM ST-1 in Aqueous Soluble Oil Metalworking Fluid	48064802
9	Determination of Hydrolysis Time for CONTRAM ST-1 by HPLC in Water and Modified Gamble’s Solution, a Pseudo-Alveolar Fluid	48064804
10	Ross, A. S., el al., Determinants of Exposure to Metalworking Fluid Aerosol in Small Machine Shops, 2004, Hyg., Vol 48, No. 5, pp 383-391(British Occupational Hygiene Society, Oxford University Press, pub)	
11	Cohen, H., A study of formaldehyde exposures from metalworking fluid operations using hexahydro-1,3,5-tris (2-hydroxyethyl)-S-triazine, 1995, In: *Proceedings of the Industrial Metalworking Environment: Assessment and Control.* American Automobile Manufacturer's Association, Dearborn, MI	
12	Linnainmaa et al., Control of Workers’ Exposure to Airborne Endotoxins and Formaldehyde During the Use of Metalwoking Fluids, AIHA Journal, Vol. 64, pp 496-500, July/August 2003	
13	Lillienberg et al, Exposure to Metalworking Fluid Aerosols and Determinants of Exposure, Am. Occup. Hyg, Vol. 52, No.7, pp 597-605, 2008	