



The Andur Report



November 2013

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Urethane R&D Staff

Dr. Steve Seneker

Senior Scientist
P:517-438-5259

Robert Czeiszperger

Senior Chemist
P:517-438-5283

Jordan Duckett

Technical Service Rep.
P:517-438-5277

Sales Staff

Howard Cox

Business Director
P:517-438-5222

Joe Bell

Southern U.S.
P:704-263-3731

Phil Green

Midwestern U.S.
P:517-266-8822

Richard Ingraham

Eastern U.S. & Canada
P:517-563-2322

Aurora Rubber

West Coast
P:714-894-1520

Customer Service

Donna Schlotman

P:517-438-5203

Lindsay Stratton

P:517-438-5253

Anderson Development Company

REACH and the Use of MBOCA for Articles Going Into the EU

With the situation of MBOCA being banned in the EU, US processors may be wondering whether their cast articles that contain MBOCA in a cured state can be exported into Europe.

As long as the article contains less than 0.1% residual or unreacted MBOCA, they are okay to be imported into Europe per the regulations.

So, knowing that this type of thing might be coming, we decided to have some elastomers tested for residual MBOCA. We found an independent lab, Smithers Rapra, that had developed a very good method for determining the level using a solvent extraction and running the extract in HPLC.

We put together various samples, testing the effect of stoichiometry, backbone, postcure, and hardness. Since higher hardness materials use more MBOCA, most of the focus was on a 75D material. We used the typical casting conditions

for the temperatures and demold times. (see page 3) The results are below. Basically, most of the elastomers had less than 0.1% unreacted MBOCA. However, two of the samples were very close to the 0.1% limit. The two high samples were

Prepolymer	Description	Stoic. (NH2/NCO)	Post Cure Conditions	Unreacted MBOCA Content (wt %)
Andur 95 APLF	LFTDI/PTMEG	0.95	16 hours @ 212 F	0.01
Andur 2-95 AP	TDI/PTMEG	0.95	16 hours @ 212 F	0.02
Andur 7201 DPLF	LFTDI/PPG	0.95	16 hours @ 212 F	0.01
Andur 7 DPLM	TDI/Ester	0.95	16 hours @ 212 F	0.01
Andur 75 DPLF	LFTDI/PTMEG	0.95	16 hours @ 212 F	0.01
Andur 75 DPLF	LFTDI/PTMEG	0.98	16 hours @ 212 F	0.02
Andur 75 DPLF	LFTDI/PTMEG	1.00	16 hours @ 212 F	0.02
Andur 75 DPLF	LFTDI/PTMEG	1.02	16 hours @ 212 F	0.03
Andur 75 DPLF	LFTDI/PTMEG	1.05	16 hours @ 212 F	0.08
Andur 75 DPLF	LFTDI/PTMEG	0.95	no postcure	0.07
Andur 75 DPLF	LFTDI/PTMEG	0.95	4 hours @ 212 F	0.02
Andur 75 DPLF	LFTDI/PTMEG	0.95	8 hours @ 212 F	0.01

Continued on page 3

New Product: Andur 73 DPLF (FDA)

Andur 73 DPLF (FDA) is a prepolymer intended for parts that need to have approvable dry food contact status, according to FDA Code of Federal Regulations 21CFR 177.1680. It is a low free TDI PTMEG-based material. It can be cured with any typical diamine curative such as Curene 442 (MBOCA) or Curene 107, but it's primarily intended to be cured with Versalink® 740M. The Ver-

salink® 740M is a diamine that is approved for dry food contact in a urethane formulation and yields a durometer similar to MBOCA in many cases. The 73 DPLF (FDA) was specifically designed to provide excellent green strength and dimensional stability at demold time and during the post-cure process with the Versalink® 740M. This means that parts come out of the oven with good rigidity, re-

moving the need for any type of fixture to keep the part from deforming. The prepolymer has a low viscosity, 8.4%-8.8% NCO range, less than 0.1% free TDI, and results in a 70-75D elastomer when cast with either the Versalink® 740M or Curene 442.

Versalink® is a registered trademark of Air Products and Chemicals, Inc.

OSHA Announces New National Emphasis Program for Occupational Exposure to Isocyanates—Possible Facility Inspections

by Mike Kocak, PMA President/EHS - Regulatory Committee Chair

Following excerpt from OSHA trade News Release, U.S. Dept. of Labor, OSHA Office of Communications: WASHINGTON – The Occupational Safety and Health Administration today announced a new National Emphasis Program to protect workers from the serious health effects from occupational exposure to isocyanates. OSHA develops national emphasis programs to focus outreach efforts and inspections on specific hazards in an industry for a three-year period. Through this NEP, OSHA will focus on workplaces in general, construction and maritime industries that use isocyanate compounds in an effort to reduce occupational illnesses and deaths. “Workers exposed to isocyanates can suffer debilitating health problems for months or even years after exposure,” said Assistant Secretary of Labor for Occupational Safety and Health Dr. David Michaels. “Through this program, OSHA will strengthen protections for workers exposed to isocyanates.” Isocyanates are chemicals that can cause occupational asthma, irritation of the skin, eyes, nose and throat, and cancer. Deaths have occurred due to both asthma and hypersensitivity pneumonitis from isocyanates exposure. Respiratory illnesses also can be caused by isocyanates exposure to the skin. Isocyanates are used in materials including paints, varnishes, auto body repair, and building insulation. Jobs that involve exposure to isocyanates include spray-on polyurethane manufacturing, products such as mattresses and car seats and protective coatings for truck beds, boats, and decks. OSHA’s Web page on Isocyanates provides additional information on recognizing potential hazards, as well as OSHA standards that address isocyanates in the general, construction and maritime industries. Under the Occupational Safety and Health Act of 1970, employers are responsible for providing safe and healthful workplaces for their employees. OSHA’s role is to ensure these conditions for America’s working men and women by setting and enforcing standards, and providing training, education and assistance. For more information, visit <http://www.osha.gov>. June 25, 2013 Contact: OSHA Office of Communications Phone: 202-693-1999.

The isocyanates NEP is effective June 20, 2013 and will be in effect for three (3) years. Now that OSHA has your attention, you might be wondering what is going to happen and how to prepare for it. Fortunately excellent resources are available. The

first place to go is the OSHA Instruction (to its inspectors) concerning the NEP, Directive Number CPL-03-00-017. This tells you how they will perform the inspection, what they will look for and that they expect you to have done. Download the .pdf from: https://www.osha.gov/Osh- Doc/ Directive_pdf/CPL_03-00-017.pdf. Go through it line by line. The next indispensable resource is PMA’s own “Working Safely with Isocyanates and MOCA in Polyurethane Casting Shops”, available on the PMA website. The third resource is an excellent guide from Bayer Material Science, also available on the PMA website. If you can’t wait, we’ve summarized some provisions of the new NEP:

Targeting of General Industry, Maritime, and Construction Companies

Appendix A to the NEP contains a primary list of general industry and maritime sectors (by SIC/NAICS codes) where overexposures to isocyanates are known to occur, and exposures have been demonstrated to be above an OSHA permissible exposure limit (“PEL”) or an occupational exposure limit (“OEL”). Regarding OELs, they are non-regulatory advisory limits, such as RELs or TLVs. A secondary list includes other industries where exposures to isocyanates are also known to occur but where worker overexposures to isocyanates may not have been documented.

Site Selection

For general industry and maritime inspections, the Directorate of Evaluation and Analysis (“DEA”) of the Office of Statistics will prepare a master inspection list for each OSHA Area Office using the most current employer listing for the SIC/NAICS industries on the primary list in Appendix A. If the area office has inspected all potential establishments in their jurisdiction with SIC/NAICS codes on the primary list, the Area Office may then contact the DEA to generate additional establishments for inspection using the secondary list. The Area Office will create inspection cycles of five (5) or more establishments. Each Area Office must conduct at least three (3) inspections per year. Subsequent cycles will be created in the same manner until the expiration of the NEP or until all establishments on the list have been assigned to a cycle.

Recordkeeping

During the NEP inspection, the employer’s injury and illness records will be reviewed to determine if injuries and illnesses related to isocyanate exposures have been recorded, including any work-related cases of asthma.

Exposure Assessments

Inspections conducted under the NEP will include an evaluation of the employer’s controls (engineering controls, administrative and work

practice controls, and personal protective equipment (PPE)) where potential exposures to isocyanates are present. Personal air samples will be collected during inspections conducted under the NEP. Additionally, wipe samples may also be obtained based on dermal exposure. If wipe sampling reveals surface contamination or dermal exposure, OSHA may issue citations under the housekeeping or PPE standards.

Citation Guidelines

Where inhalation exposure to an isocyanate exceeds the OSHA PEL set forth in 29 CFR 1910.1000(a), Table Z-1, without regard to the use of respiratory protection, the compliance officer shall generally issue a “serious” citation. Where an overexposure exists and feasible engineering and/or administrative controls were not utilized or were ineffective, the compliance officer shall generally issue another citation under 29 CFR 1910.1000(e) and group it with the overexposure citation. Where workers are exposed to a particular isocyanate having an established OEL, but no OSHA PEL, the compliance officer may consider issuing a citation for exposure in excess of the OEL under the General Duty Clause, Section 5(a)(1) of the OSH Act.

Personal Protective Equipment (PPE)

At the opening conference, the OSHA compliance officer shall review the employer’s hazard assessment to determine compliance with the applicable PPE regulations. The PPE evaluation shall include appropriate (i) protective clothing (e.g., coveralls, foot coverings); (ii) eye and/or face protection; (iii) respiratory protection; and (iv) chemical-resistant gloves (e.g., butyl, nitrile).

Hazard Communication

A determination of whether an employer’s hazard communication program complies with 29 CFR 1910.1200 will include consideration by the OSHA compliance officer of the training the employer provides to employees regarding the hazards associated with isocyanates.

Housekeeping

During the inspection, the employer’s methods for ensuring adequate housekeeping will be evaluated and documented.

Taken from PMA’s Polytopics, 2013, 2nd quarter

REACH/MBOCA (cont'd from page 1)

a material cured at 1.05 stoichiometry, which makes sense since it has a 5% excess of MBOCA in it and a material that had not had any postcure.

The conclusion we drew was that if the material is cast and cured properly, the unreacted MBOCA level is well below the 0.1%. At the moment testing is being done to look at aliphatic isocyanate (H₁₂MDI)-based prepolymers cured with MBOCA. Since they are much slower to react with MBOCA, there would be a

greater chance to be over the limit of 0.1%. Catalyzed and uncatalyzed samples were submitted. It is predicted that the uncatalyzed material will be over the limit, but that hopefully the catalyzed specimens will be okay.

For more information and pricing on the test please contact Gary Wyscarver at Smithers Rapra in Akron, OH at:

330-762-7441 ext 1205

or

gwwyscarver@smithers.com

Casting Conditions

TDI Prepolymer Temperature	212 F
MBOCA Temperature	230 to 250 F
Mold Temperature	212 F

Anderson Development Company

1415 E. Michigan St.
Adrian, MI 49221

Phone: 517-438-5283

Fax: 517-263-1000

E-mail: robert.czeiszperger@anddev.com



Mission Statement

Anderson Development will be a global supplier of innovative specialty chemical products, striving for continual improvement in all of our operations. It is our goal to be personal, efficient, and responsive to our customers and employees. We will provide a team-oriented atmosphere while allowing for individual diversity among our employees.

We're on the web!

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