April 1, 2012

Working Safely with Isocyanates and MOCA in Polyurethane Casting Shops

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Introduction

The purpose of this manual is to explain how to work safely with Isocyanates and MOCA (also known as MbOCA). It covers both hand and machine casting operations.

The focus of this document is on how to minimize skin exposures to these chemicals as this is a primary way workers can get exposed. It also describes ways to test for isocyanates and MOCA in the shop. This manual provides information on how to know whether or not employees are being exposed to MOCA and Isocyanates.

This manual will explain the following topics:

- How employees can be exposed
- What are potential health concerns
- How Personal Protective Equipment can help control exposure
- How the company can help control the spread of contamination

This manual will also explain the following testing methods for MOCA and Isocyanates:

- Urinalysis Testing
- PERMEA-TEC Testing
- MOCA SWYPE Testing

Who this Guide is for

This guide is for PMA member companies and their employees who use Isocyanates and/or MOCA. You can also use this guide when planning to use Isocyanates and/or MOCA for the first time or when reviewing risk assessments for your current use of these chemicals. It is not intended to cover all federal, state and local regulatory requirements as it is primarily intended to address skin exposures to these chemicals.

NOTE: Each workplace is different. There are a wide variety of chemicals used in the shops, so it is not possible to provide specific guidance that will apply in each work area.

What are Isocyanates and MOCA?

Isocyanates

Isocyanates are compounds used to form polyurethanes. Two common Isocyanates used are TDI and MDI. These compounds are combined with other materials to form prepolymers.

Toluene diisocyanate (TDI) is a colorless to pale yellow liquid with a sharp, pungent odor. Polymeric methylene diisocyanate (MDI) is a dark brown liquid and pure methylene diisocyanate (MDI) is a white to light yellow liquid.

Note there are other isocyanates that are used in casting operations. No matter what the type of isocyanate is in your shop, they can still cause a skin exposure.

MOCA is a compound with the chemical name 4,4'- methylenebis(2-choloroaniline). This material is used as a curing agent during castable polyurethane manufacturing. MOCA (or MBOCA) is a cross-linking agent which reacts with the Isocyanate based prepolymers to create urethane products. MOCA is supplied in pellet form. The pellets are amber or yellow in color and may have a slight odor. MOCA is also sold in other forms, but the pellet form helps to minimize dusting

There are other curatives than MOCA that may have different health risks than MOCA. However, it is good practice to try and keep all production chemicals off of the skin.

Why are special casting work practices needed to control skin exposures?

- Polyurethane (POLY) casting often requires a lot of close-up handwork
- Casting chemicals can be absorbed through your skin without proper personal protective equipment
- Like most chemicals, casting chemicals could cause serious health problems if mishandled
- You can work safely with POLY chemicals by using some basic work practices
- One rule to keep in mind:

Keep chemicals off your skin

What is the basic production process and how can it affect skin exposures?

- The way exposures occur differ between each step of the process
- Understanding how exposure occurs will allow you to use your work skills and experience to help reduce exposures
- The POLY products are made from “raw” chemicals (INGREDIENTS).
- You can be exposed to chemicals during each one of these steps
    - INGREDIENTS are combined together to make a MIX
    - The MIX is poured into a mold and hardens. The piece is only partially cured (PARTCURE) when demolded
    - The PARTCURE piece is put into an oven for a post-cure
- Once fully cured (FULLCURE), the piece is safe to handle
    - The fully cured (FULLCURE) piece is trimmed and processed

Note: Hot work on FULLCURE pieces can release chemicals to the air that may be breathed in, and to the surface of pieces that may cause skin exposure

How can employees be exposed to unmixed INGREDIENTS?

- Isocyanates (ISO) and a CURATIVE are the main chemicals
- Other chemicals are added to give the POLY special properties such as flexibility, durability, heat resistance
- You can be exposed to INGREDIENTS by transfer of pour materials to the mix machine or melter by:
    - Direct skin contact
    - Splashes onto clothing
    - Spills on work surfaces and floors (some unmixed INGREDIENTS can stick around for years so pay special attention to cleaning and decontaminating raw material spills)
    - Tools contaminated with ISO and CURATIVE during maintenance
    - Coming in contact with flushing and cleaning solvents used with ISO and CURATIVE
- Heating INGREDIENTS may also release ISO and CURATIVE vapors into the air. To reduce air exposures to these chemicals:
    - Cover containers
    - Cover purge containers
    - Cover used mix containers
- Maintenance workers can also be exposed when maintaining ISO and CURATIVE equipment, including melters, tanks, lines, and mixers

How can employees be exposed to MIXED chemicals?

- The CURATIVE (MOCA) binds together the ISO. This changes the MIX from a liquid to a solid
- You can be exposed to the MIX in the same ways as INGREDIENTS. Exposures can occur by:
    - Direct hand contact and splashes onto arms
    - Splashes onto clothing
    - Spills on work surfaces and floors
    - Tools contaminated with ISO and CURATIVE
- You can still be exposed to hardened spills and splashes because the INGREDIENTS are not completely reacted. This exposure can happen days after the spill.
- It can take many days to reach full cure at room temperature. Room temp cure time is related to pot life. Long pot life = Slow cure rate.
- Hot MIX can also release ISO and CURATIVE vapors into the air

How can employees be exposed to PARTCURE?

- The MIX solidifies in a few minutes

But the reaction between ISO and CURATIVE still continues. So PARTCURE pieces are put in an oven for a POSTCURE

- That's why you can still be exposed to ISO and CURATIVE until POSTCURE is complete. For example, exposures can occur:
    - During demolding
    - During flashing cut-off
    - Wiping out mold between pours
- Mold release saturation of gloves can increase skin exposure to chemicals on the surface of PARTCURE pieces because the mold release can help chemicals pass through gloves
- "Flaming" of bubbles that sometimes are present on castings during the initial cure may also release ISO vapors into the air

How can employees be exposed to chemicals POSTCURE?

- Hot finishing processes can release ISO materials into the air. This can be an important source of exposure even to ISO materials that do not normally vaporize
- Examples of hot finishing work include:
    - Grinding (without coolant)
    - Hot wire cutting
    - Hot trimming tools
    - Sawing (without coolant)
    - Flaming and heat gun
    - Hot iron branding
- Exposure can still occur even if you do not see smoke coming off the POSTCURE piece

Review the document: "Handling the Heat" for more information about hot processing of POLY materials. It is available at www.polyurethanes.org, Doc # AX-396

How do surfaces outside work area get contaminated and then cause exposure?

- Chemicals can get outside of your work area by:
    - Touching a tool with a contaminated gloved hand, and then someone touching the tool with bare hands
    - Touching other surfaces with gloved hand, including door knobs, drinking fountains, phones or other commonly handled items.
    - Dust accumulating on tops of equipment and surfaces in the shop
    - Walking with contaminated shoes of a controlled work area
    - Taking equipment out of the work area without decontamination
    - Accumulating inside exhaust ducts

What are potential health concerns?

- This is a general summary of potential hazards of ISO's and one CURATIVE called MOCA
- Some of the hazards below may not apply to the chemicals in your workplace. For example, many shops do not use MOCA.
- Read the MSDS and talk with your supervisor to learn about each of the specific chemicals you work with
- Cuts, burns and other damage to your skin can increase potential for skin exposure
- Isocyanates have both short-term and long-term health effects. Short-term effects occur immediately or within a few days of the exposure. Long-term effects occur months or even years after the exposure.

Isocyanates

Short-Term Effects

The Short-term health effects of Isocyanates include skin, eye and respiratory irritation.

Skin Symptoms to be aware of are:

- Redness
- Swelling
- Blistering

Eye Symptoms to watch for include:

- Pain and burning
- Reddening
- Tearing

Respiratory symptoms to note are:

- Coughing
- Tightness of the chest and chest pain
- Shortness of breath

Other symptoms that may indicate a short-term health effect include:

- Nausea, vomiting and abdominal pain
- Headache
- Insomnia

Long-Term Effects

The long-term health effects which may result from Isocyanate exposure include skin and respiratory sensitization. A sensitization is an allergic response which occurs over a period of time. TDI is also a suspect cancer-causing agent.

A respiratory sensitization to Isocyanates causes an asthma-like condition with:

- Tightness of the chest
- Coughing
- Shortness of breath

Respiratory sensitization can occur just from skin contact. So keep isocyanates off your skin!

A skin sensitization to Isocyanates may also cause a skin allergy with:

- A rash
- Itching
- Irritation

Once your body develops a sensitization you may have skin or lung symptoms even when you are exposed to very low concentrations of Isocyanates. If you develop either a skin or respiratory sensitization, avoid further exposures to Isocyanates.

MOCA

Routine workplace MOCA exposure does not cause short-term health effects. MOCA is suspected to cause bladder cancer. Bladder cancer has a long latency period. The latency period is the time between exposure and the development of the disease. Bladder cancer usually takes at least twenty years to show noticeable symptoms.

MOCA has been proven to cause cancer in laboratory animals and is regulated in some countries as a confirmed human carcinogen.

You must review the Material Safety Data Sheets for additional safety and health information about the materials used.

What about other CURATIVES and the other chemicals used in the shop?

- All chemicals need to be handled with care
- Review the MSDS and talk with your supervisor about ways to safely handle these chemicals
- Complete hazard communication training and learn about the specific hazards of the shop chemicals
- Many POLY-related chemicals can be absorbed through the skin and cause health problems
- Treat them all with respect
- Following the work practices will help reduce exposure to all chemicals in the shop

How can PPE help control exposure?

- Exposure usually occurs on hands, arms, and the front of the body.
- Wear the Personal Protective Equipment (PPE) required for your particular job. This may include:
    - Gloves for handling hot molds
    - Chemically-resistant gloves (need to be chosen for the specific chemicals in your workplace). Chemicals on the outside of gloves will seep through the gloves
    - Long-sleeved clothing and/or disposable sleeves to cover arms. Contamination of unprotected arms is a common source of MOCA exposure.
    - Chemically-resistant apron
    - Safety glasses, splash resistant goggles and other eye protection as needed (Note: safety and regular glasses are easily contaminated with CURATIVE and ISO by gloved hands
- Wear chemically resistant coveralls, shoe covers, and appropriate respirators for high exposure situations (for example, large spill response)
- Consult the OSHA regulations that apply to proper selection and use of personal protective equipment and respirators

Change Gloves Frequently When Handling Chemicals!

- This has been found to be one of the best ways to reduce MOCA exposure in research conducted at polyurethane casting shops
- The study found that most important and effective control was the use of thin inner liner vinyl gloves that were worn under fabric heat protection gloves.
- Frequent changing of inner liner gloves throughout the workday (especially when visually contaminated) kept MOCA urinalysis results to a minimum
- Note that liner vinyl gloves will not be the best choice in all shops or for all chemicals. See testing procedures at the end of this document on how to verify proper glove selection

How can workers help to control exposure?

- Covering work surfaces with materials that can frequently be changed
- Using separate tools for CURATIVE work (for example, repairs on CURATIVE melters). These can be marked with red paint to designate restricted use to CURATIVE area
- If using automatic dispensers, pour carefully under local exhaust (if available) with a drip tray
- Pouring molten materials carefully. Stirrer must not be placed onto surface liner. Allow liquid from stirrer to drain back into the mixture
- Covering heated mixture for transporting
- Promptly cleaning up spills during casting. Use special CURATIVE and ISO decontamination solution. (Note: before cleaning up large spills you may require special training and extra Personal Protective Equipment)
- Changing clothing contaminated with any significant splash of ISO, CURATIVE, or PARTCURE
- Avoiding contamination of your PPE by not leaving gloves on potentially contaminated work surfaces
- Carefully using mold release. Excessive mold release on surfaces can contribute to the spread of chemicals through the plant
- Changing out gloves wet with mold release (mold release will help the chemicals get through your gloves)
- Do not eat, drink, or smoke in work areas to avoid ingesting chemicals. Do not keep cigarettes, gum or other food in your pockets as they can absorb chemicals present in the shop

How can the company help control contamination?

- Providing steel work surfaces where appropriate, so they can easily be decontaminated
- Using a closed transfer system from the shipping drum using vacuum or gravity with a spout
- Setting up weighing, melting, mixing and casting under Local Exhaust hood designed to draw the vapors away from the worker's head
- Storing CURATIVE (MOCA) in a dedicated dry storage area away from the work area
- Providing separate waste bins for chemically contaminated materials (may require special disposal practices-check state and federal regulations)
- Conducting periodic testing for contamination of surfaces, drums, tools and other locations which may become contaminated
- Conducting periodic chemical Hazard Communication training
- Establishing and maintaining a Personal Protective Equipment Program (including selecting task-specific PPE)
- Establishing and maintaining a Respiratory Protection Program
- Conducting periodic surface monitoring.
- Conducting air monitoring as indicated for ISO exposure potential
- Evaluating periodically ventilation effectiveness (ability to capture vapors and keep them away from worker's head)
- Providing adequate wash facilities with special skin decontamination solutions (do not use solvents or petroleum-based hand cleaners)
- Providing separate lockers for work clothing
- Providing for laundering service of contaminated work clothing at the workplace or outside (Note: MOCA is not easily removed by typical alkaline

laundering processes. Adding some vinegar will lower the pH and help to remove the MOCA

- Checking PPE during use for heavy contamination using surface and breakthrough detection monitoring

Regularly Conduct MOCA Urinalysis Testing

- Testing for MOCA in urine is the best way to evaluate the shop's overall control measures
- Recent research sponsored by the PMA clearly showed that periodic urinalysis (measuring MOCA in worker urine) was important to reduce and control worker exposure
- Include both production and maintenance personnel in urinalysis screening
- Periodically check workers away from the main MOCA task to assure MOCA is staying in process area
- Conduct urinalysis testing at least quarterly at end of shift
- Maintain levels below the recommended under 100ug/L MOCA. (Note: recent research sponsored by the PMA showed that companies that test regularly maintain MOCA urine levels less than 20 ug/L)
- Take action if individual MOCA levels are above 100 ug/L (or significantly above company average levels if they are below 100)
    - Talk with worker and investigate work practices going on the day of test (or the day before if urine collected in morning). Urine results are directly related to the test day activities
    - Change work practices or take other actions as needed
    - Retest the workers who had higher levels and verify effectiveness of control actions
- Evaluate overall results and take action. For example:
    - If a large majority workers show MOCA exposure, then contamination is widespread. Closely review overall work and cleaning practices
    - If only a few workers have high MOCA exposures, then review those worker's practices. High individual exposures may be due to unusual work conditions or maintenance tasks

Urinalysis Procedure:

1. Provide forms to workers to document work activities the day before urinalysis samples are collected. Do not collect samples from workers who were off work the day before samples collected
2. The workers will then fill out the sheet during their shift to document their work activities. This helps to explain how exposures may have occurred or been prevented
3. Next day, the workers need to pick up the sample container at the beginning of the shift
4. The workers must deposit a sample as soon as possible and return the container to be frozen, and write down the number on the individual container on the provided sheet
5. After all samples have been collected, all the container numbers must be accounted for and the samples must remain in the freezer for 24 hours prior to being shipped to the analytical lab

*Individual results must be shared within one week of testing.

*Results from previous testing will drive the next testing schedules

*Testing should be done quarterly

PERMEA-TEC™ MOCA Glove Breakthrough Testing Procedure

PERMEA-TEC sensors detect shop chemicals passing through gloves. This helps determine how often gloves need to be changed. PERMEA-TECs are available for aliphatic and aromatic isocyanates, MOCA and other aromatic amine curatives, and solvents. Consult the specific instructions for each type of PERMEA-TEC sensor

*Procedure copied directly from CLI test kit instruction

1. Affix PERMEA-TEC sensors to the thumb, middle finger and palm of the outside of the glove currently being worn. Don the glove to be evaluated over the first glove.
2. After one hour, remove the outside glove and the underlying PERMEA-TEC sensors.
3. Develop the sensor by slowly adding ten drops of clean tap water to the white border strip. A positive indication of break-through results in a color change characteristic to the specific aromatic amine being used
4. If no break-through is indicated, apply fresh PERMEA-TEC sensors and continue to wear the outside glove for another hour. Follow step 3 to determine if breakthrough has occurred.
5. By repeating steps 3 and 4, you can determine a user-safe time period for gloves.

Results from previous testing will drive the next testing schedule

Surface SWYPE™ Testing Procedure

Surface SWYPES detect chemical contamination on workplace benches, controls, door handles, and other work surfaces. This helps evaluate work practice controls and the effectiveness of cleaning procedures. Surface SWYPES are available for MOCA and for aromatic and aliphatic isocyanates. Consult the specific instructions for each type of Surface SWYPE

* Procedure copied directly from CLI test kit instruction

Gloves must be worn when using the Surface SWYPE detectors.

1. First, lightly spray the area to be tested with Developing Solution.
2. Wait approximately 30 seconds and then wipe with a Surface SWYPE pad.
3. Allow 2 – 3 minutes for the color change reaction to occur.
4. Do not reuse the Surface SWYPE after activation.

The sensitivity of the Surface SWYPE is 3-5 µg for aromatic amines and isocyanates. SWYPE™ testing should be done twice a month by a trained individual, and the results must be documented. SWYPE™ testing must also be done after a spill that requires the spill kit to be used, and the results must also be recorded.

Skin SWYPE™ Testing

Skin SWYPES detect chemical contamination on worker's skin. This helps identify work practices that may cause exposures. It can also help check skin cleaning practices. Skin SWYPES are available for MOCA and for aromatic and aliphatic isocyanates. Consult the specific instructions for each type of Surface SWYPE

***Procedure taken directly from CLI Labs website**

Skin SWYPES™ Procedure

1. Using moderate pressure, wipe the suspected exposed skin area (behind the ear, pencil; bridge of nose, safety glasses, etc.) with the cloth pad portion of the Skin SWYPE.
2. Use a separate SWYPE for each area to be checked.
3. To process, add ¼" of Developing Solution to the small plastic cup provided.
4. Place the Skin SWYPE in the cup with the cloth pad portion in the solution and the color detection strip up at the top.
5. The solution will wick up, carrying any contaminant, to the detector pad.
6. Remove the SWYPE from solution cup when the detector pad is saturated.

The test takes approximately 5 minutes for the color change reaction to occur.

The sensitivity of the Skin SWYPE is 3-5 µg for aromatic amines and isocyanates.

Isocyanate Air Monitoring Procedures

- Measurement of Isocyanates is complicated, and a detailed explanation will not be provided in this document.
- Industrial Hygiene laboratories (accredited by the American Industrial Hygiene Association) can provide detailed sampling guidance. Some provide “free” rentals of sampling equipment
- Some insurance providers will conduct air monitoring for their customers
- Some suppliers will conduct air monitoring for their customers
- The Alliance for the Polyurethane Industry has an explanation of Isocyanate sampling methods at http://polyurethane.americanchemistry.com/Resources-and-Document-Library/3822.pdf

Urinalysis Result Form

Name:	
Date:	
Date of Testing:	
Result:	
Action Taken:	

PERMEA-TEC Form

Name:	
Date of Testing:	
Tested By:	
Result after 1hr:	
Result after 2hr:	
Action Taken:	

MOCA SWYPE™ Form

Name:	
Area:	
Date of Testing	
Test Result:	
Action Taken:	

SWYPE™ Results Chart

0

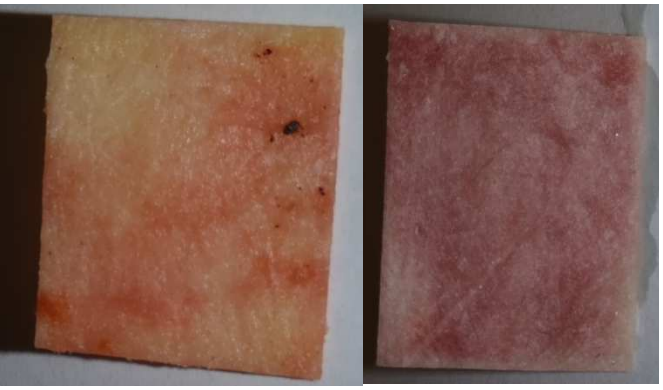
- This result indicated there is no contamination on the surface

- Any red tinge coloring indicated on the SWYPE from level 0, is considered a 1 or higher. A level 0 must show no indication of any red color

1

- This reading includes any “tinge” of red

- This indicates there is MOCA present, but does not require immediate decontamination



2

- If a level 2 reading has been observed, it must be reported to supervisor and be decontaminated.

- After decontamination, a reading of 0 or 1 is acceptable

3

- A level 3 SWYPE is indicated by heavy red coloring

- If a level 3 reading has been observed, it must be reported to a supervisor and be decontaminated.

- After decontamination, a reading of 0 or 1 is acceptable