

DATA SHEET
URETHANE RESIN SYSTEMS

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STRAIGHT TALK ABOUT URETHANE FOAM AND CASTING RESINS

TWO-COMPONENT SYSTEMS.

Warning bells should go off in your head anytime you mix two or more chemicals together (not just add water) and the resulting mixture “sets up.” This means you have a plastic resin system. It could be epoxy, polyester, silicone, RTV rubber, urethane or a number of other systems. The most dangerous of these are the urethane resins.

Products that consist of two-component urethane resin and curing agents include auto paints, floor paints, molding products, insulation foams, bathtub and porcelain refinishes, water proofing coatings. Some products I see in almost every shop are Great Stuff™ in spray cans and Smooth On™.

In addition, many shops have large containers of two-component urethane mold materials. Some of these also contain highly toxic mercury preservatives paints.

PART A. The resin part of a urethane product usually is not very hazardous. This is because it is not actually a “urethane resin” yet. Instead, it is any of several types of resins such as polyesters, polyethers, polyols, epoxies, and so on. These resins do not become “polyurethane” until they are reacted (cured, hardened, etc.) with Part B.

PART B. The curing agent is a diisocyanate. It is the diisocyanates that are the problem. These isocyanate hardeners are capable of causing severe respiratory allergies and lung damage. Most notably, they cause a debilitating incurable occupational illness called “isocyanate asthma.” Sudden respiratory spasms and anaphylactic shock on exposure to diisocyanates also have resulted in deaths among workers using urethanes. There have been cases in which deaths occurred suddenly and without warning in people with no prior history of allergies.

SINGLE-COMPONENT URETHANES.

Urethane paints and varnishes that are single component products usually consist of the finished resin dissolved in solvents. These products are not as hazardous. Usually, their only hazards are the solvents and preservatives in the product.

But there are some urethane systems that only appear to be a single component product. For example, Great Stuff™ looks like a single product, but the two components are mixed in the long nozzle. So any time you purchase a urethane product, read the label and Material Safety Data Sheet (MSDS) carefully. If the label or MSDS indicates that the substance releases diisocyanates, is it highly hazardous.

IF THEY'RE SO BAD, WHY AIN'T I DEAD?

Not everyone exposed to isocyanates becomes seriously ill, just as not everyone is allergic to poison ivy. Although the isocyanates are irritating to all people at high levels, the allergic effects can manifest themselves at very low levels in only some people.

To protect people from these effects, the American Conference of Governmental Industrial Hygienists set an extremely restrictive workplace air quality limit (Threshold Limit Value or TLV) for diisocyanates. To see just how incredibly restrictive (low) the TLV for diisocyanate is, the table below compares it with TLVs for other substances.

TLVs: CHEMICALS COMPARED TO DIISOCYANATES

SOME DIISOCYANATES FOR WHICH THE 0.005 ppm TLV IS SET

Substance	Threshold Limit Values (TLVs) in parts per million (ppm)	Name	CAS #
Ethyl Alcohol	1000.	TDI (toluene diisocyanate)**	584-84-9
Acetone	500.	MDI (methylene bisphenyl isocyanate)	101-68-8
Mineral Spirits	100.	HDI (hexamethylene diisocyanate)	82-06-0
Toluene	50.	isophorone diisocyanate	4098-71-9
Carbon Tetrachloride	5.	methylene bis (4-cyclohexylisocyanate)	5124-30-1
Phosgene (war gas)	0.1		
Methyl Isocyanate*	0.02		
Diisocyanates	0.005**		

* This chemical killed thousands in an accident in Bhopal, India

** The ACGIH has proposed a TLV for TDI of 0.001 ppm! It is not yet adopted.

HOW DO I KNOW DIISOCYANATES ARE IN MY STUFF?

Read the product's MSDS. Look for the words "diisocyanate" or "isocyanate" listed under "chemical family" or as part of a chemical name under the "hazardous ingredients" section. The Table above lists five of the names you may encounter.

Some of the MSDSs and product labels will provide stern warnings about the dangers of the diisocyanates. Others will not. The products without strong warnings usually contain one of the

forty or more isocyanates for which no standards exist. This does not mean that these diisocyanates are safe. It means they have not been tested and proved toxic. It also means that the manufacturer is taking advantage of a flaw in the labeling law that allows untested chemicals to be considered “innocent until proven guilty.”

Yet ALL the diisocyanates are hazardous as EPA made clear in 1994:

...EPA believes that it is reasonable to anticipate that all members of the diisocyanate category will exhibit chronic pulmonary toxicity...¹

Only one of the diisocyanates (toluene diisocyanate - TDI) has been studied for long term hazards. It caused cancer in test animals.² The other diisocyanates have not been tested so manufacturers are not required to warn users about cancer hazards either. If the MSDS says that OSHA, IARC, and NTP do not consider the chemicals carcinogens, it means that there is not enough data for these three agencies to evaluate!

SALESPEOPLE TELL ME THAT THEIR PRODUCT IS “DIFFERENT.”

Manufacturers can change regulated diisocyanates into unregulated ones by linking several of them together (prepolymerizing) or by modifying them with other chemical groups. In fact, many isocyanates in products used today have been altered so that regulated monomers are only a small fraction (frequently less than 1%) of the isocyanates present. These altered diisocyanates are often not even listed on MSDSs and sometimes touted as “safe.” Some of the altered diisocyanate molecules are heavier so less of them get into the air where they can be breathed. However, all of these isocyanates should be considered similarly toxic.

The assumption that isocyanates are equally toxic is accepted in the United Kingdom. The UK workplace standards only consider the total number of isocyanate groups present in the chemical, not the species to which the isocyanate groups are attached.³ The U.S. should adopt this standard.

WHAT STEPS SHOULD I TAKE WITH URETHANE PRODUCTS?

If you are using a resin product that might contain an isocyanate, take the following steps:

- 1) Find out if the product is a resin system consisting of two or more components. Consult product literature to determine if the product requires mixing either by hand or that mixing occurs when the product is extruded by the container. (Single-component urethane varnishes and paints are not without hazard, but the amounts of isocyanates they contain as impurities are usually much smaller.)
- 2) Look on the MSDS for the words “isocyanate” or “diisocyanate.”
- 3) If the product contains an iso- or diisocyanate, ignore any claims that it is “prepolymerized,” modified, or safe in any way. If you need additional advice or data on the chemicals in the product, call your Health and Safety Officer.

- 4) Try to find a safer substitute for the product.
- 5) If the product must be used, work in a local exhaust system such as a spray booth. If the exhaust system cannot provide 100 % protection, use air-supplied respiratory protection as back-up. Airline or SCBA equipment is required unless air sampling has been done and a change-out schedule has been calculated for the air-purifying respirator cartridges. Air-purifying respirators with organic vapor cartridges are appropriate only with a change-out schedule because the isocyanate does not provide odor warning when cartridges are spent.
- 6) Leave freshly cast, painted or foamed objects in the exhaust system for several hours or overnight until they have completely set up and have finished off-gassing before taking them into the general workspace. If possible, wash the product's surface. Tests have shown that isocyanate curing agents can remain on surfaces for days or months after they are fully cured.
- 7) Never burn or heat finished urethane objects until they begin to discolor, smoke, or decompose except in local exhaust ventilation. Heat releases many toxic gases and vapors including various species of isocyanates.

Footnotes:

1. 59 FR 61454, Nov. 30, 1994, EPA: Addition of Certain Chemicals; Toxic Chemical Release Reporting: Community Right-to-Know; Final Rule.
2. NIOSH, Current Intelligence Bulletin 53, "Toluene Diisocyanate (TDI) and Toluenediamine (TDA): Evidence of Carcinogenicity, December 1989.
3. United Kingdom Health and Safety Executive Total Reactive Isocyanate Group (TRIG) standard.

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REPRINTS:

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AIR-PURIFYING RESPIRATORS: ARE THEY OK FOR URETHANE?

www.osha.gov, letter of interpretation, July 18, 2000

Many artists have told ACTS that sellers of two-component urethane products suggest using ordinary air-purifying respirators for protection from the diisocyanates released by these foams, paints, and casting systems. Salesmen say that the Occupational Safety and Health Administration (OSHA) now approves using these respirators for diisocyanates. Such statements are dangerous and misleading unless OSHA's limits on using these respirators are explained.

OSHA'S RULES do not allow respirators for any substance unless the employer first has a written respiratory protection program, medical certification for each person wearing one, professional fit testing, and documented worker training. If this program is in place, then OSHA allows cartridge respirators for substances such as the diisocyanates whose warning properties do not enable workers to reliably sense their presence—but only under two conditions.

- Cartridges can be used if they have an end-of-service life indicator, e.g. they change color or show some visible change when they cease working. This option is excluded since currently there are no such indicators for the diisocyanates.
- Cartridges can be used if the employer has a change out schedule for cartridge replacement based on objective exposure data. This data includes the concentration of airborne contaminant to which employees will be exposed as determined by personal air-monitoring of potentially exposed employees during routine tasks. This is not usually feasible for art and theater shops, since "routine" tasks are rare. The jobs artists do and objects they create are unique.

OTHER FACTORS that OSHA requires employers to consider include:

- Employers must comply with 1910.134(d)(3)(i) which requires them to "provide a respirator that is adequate to protect the health of the employee and ensure compliance with all other OSHA statutory and regulatory requirements under routine and reasonably foreseeable emergency situations." This means that employers must objectively determine the likely exposure during an accidental release, spill, ventilation failure, and so on.

- Employers' programs must account for additional risks during emergency situations due to the fact that air-purifying negative pressure respirators pose a greater risk of leakage than positive pressure respirators.
- Employers must provide eye protection for the workers. Vapors of diisocyanates are corrosive and can cause permanent eye damage. Either full-face respirators must be used or employers are required under 1910.133(a)(1) to select appropriate eye protection with half-face respirators.
- Employers must consider the need for skin protection. Vapors of diisocyanates can cause skin irritation and sensitization. Employers are required under 1910.132(d) to assess the exposure and select appropriate methods to protect the face and neck.
- Employers must take appropriate action if an employee using an air-purifying respirator reports any medical signs or symptoms which could be attributed to diisocyanate exposure and provide additional medical monitoring under 1910.134(e)(7)(i) for that worker. Certain respiratory ailments caused by diisocyanates can affect the worker's ability to use a respirator.

This last rule is particularly important to artists. Overexposure to diisocyanates can cause permanent sensitization and breathing problems. Artists with these problems may no longer be able to wear respirators which can forever compromise their ability to work.

Lastly, OSHA requires that all of the data above be put into writing and included in the employer's respiratory protection program. The program must be regularly reviewed and revised if new data are available or if there are changes in shop conditions, urethane product formulas, production processes, or personnel.

SUMMARY.

In the art and theater world, air-purifying respirators almost never can be used safely or legally as protection against products which release diisocyanates. Shops must either have a local ventilation system (e.g. a spray booth) that air sampling tests show completely capture the diisocyanates, or employers should provide air-supplied full-face respirators with protective clothing for the skin for workers using significant amounts of two-component urethane. For the full OSHA policy, see the July 18, 2000 letter of interpretation at www.osha.gov.

January 1996

CHEMICALLY INJURED PROP MAKER WINS SETTLEMENT

Interviews and expert testimony for the Plaintiff

A non-union Prop Maker employed to repair the costumes for a production of a *Little Shop of Horrors* sued her employer after she developed multiple chemical sensitivity (MCS) allegedly from exposure to the products she used. The suit was settled when the employer's insurance

company agreed to pay the plaintiff all past wages, compensation, and medical bills with interest, and to pay reimbursement for expert witnesses and doctors' testimony.

The Prop Maker's exposures on the job were uniquely excessive. She was literally inside the "Audrey" plant prop rebuilding the infra-structure with urethane foam (Great Stuff™) and spray adhesive. She used these and other products without protective equipment.

Attorney, Elissa Griffith Waldron, Allentown, PA, says the case was difficult because MCS is not as well recognized as other diseases. She feels that success in these cases requires the testimony of at least two doctors with good credentials, and of an industrial hygienist who can quantify the exposures that caused the illness.

Another winning factor was the prop maker herself. While confined to her home, she contacted experts by phone, talked witnesses into testifying, and studied the legal problems presented by her case. Her advice to others suing for MCS damages is "never give up."

May 1997

INJURED PROP MAKER: SETTLEMENT UPDATE

Interviews, e-mail, and expert testimony for the Plaintiff

In January, 1996, ACTS FACTS reported on a suit brought by the resident artist at Jeannie Costumes, Macungie, PA, against her employer. The artist alleged that she was chemically injured while repairing Ninja Turtle costumes and props for a *Little Shop of Horrors*. She literally worked inside the "Audrey" rebuilding the plant's infra-structure with urethane foam (Great Stuff™) and spray adhesive. She used these and other products without protective gear for about two weeks before succumbing to illness.

In 1996, the employer's insurance company paid the Claimant compensation of over \$60,000 plus all back wages, medical bills with interest, and reimbursement for lawyers' fees, expert witness, and doctors' testimony. This year, her disability status changed. On March 17, she was awarded another \$80,000 for commutation of wages and medical expenses. The defendants also must continue to pay her medical bills—even for natural remedies that she purchases at a health food store on recommendation of her physician. Asked how other injured artists can get good settlements, she said:

"...you need to find your own witnesses, experts and physicians...don't wait for someone else to do it! It took me over three years to find my physician...even if you don't have a specialist, make sure you are seeing a family doctor or any physician who is recording your health [problems]! Record ALL your efforts...they will come in handy when testifying in your case. DON'T let people tell you what is true—you tell them! It is your body!"

August 1998

THEATRICAL SCENE SHOP CITED BY OSHA

BNA-OSHR, 28(6), July 8, 1998, pp. 170

Mystic Scenic Studios Inc., Dedham, MA, is contesting a serious citation and a \$3,000 penalty for the alleged violations of three items, including failure to establish written standard operating procedures governing the selection and use of respirators (1910.134(b)(1)); failure to use locking and/or fastening devices on the exit door which do not prevent free escape from inside the building (1910.37(b)(4)); and for employee(s) exposure to an airborne concentration of methylene bisphenyl isocyanate (MDI) listed in Table Z-1 in excess of 0.20 milligrams per cubic meter of air (mg/m³) as a ceiling concentration (1910.1000(a)(1)).

To put it more clearly, it is alleged that the employer:

- 1) Did not have a proper respiratory protection program;
- 2) Had locks on exit doors that prevented rapid escape;
- 3) Over-exposed employees to MDI, one of the most toxic of the foam urethane diisocyanates.

These violations are common in many scene shops I have inspected.

June 2007

URETHANE PAINTS HAZARDOUS LONG AFTER DRYING

Journal of Occupational & Environmental Hygiene, June 2006, 4:406-411

Two-component urethane paints (i.e., composed of a Part A and a Part B) are widely used. They are commonly used for school gymnasium floors, stage and scenery decks (floor surfaces), or for resurfacing bathtubs and other porcelain fixtures. They are also a common auto body spray paint. The primary hazard of these paints are the curing agents—the highly toxic isocyanates. A recent study in the Journal of Occupational and Environmental Hygiene reported that isocyanate curing agents remain on the surfaces of auto body paints for prolonged periods (days to weeks) after they are fully cured. To study this phenomenon, workers spray painted 23 scrap sections of auto bodies using methods they regularly use to paint cars. The paints were cured either by putting them in a spray booth under a heat lamp, or by air drying in the shop. Geometric mean curing time of 23 painted surfaces was 56.4 hours (range 0.8 hours to 32 days).

After they were cured, the 23 sprayed surfaces were tested at regular time intervals using a semi-quantitative SWYPE technique.* Quantitative isocyanate analysis was also performed on two sprayed parts.**

It was found that unbound isocyanates like those found in the original bulk material remained on the majority of sampled painted surfaces for up to 120 hours for typical paint formulations and for 1 month for others, showing that the complete curing of polyurethane paints in auto body

refinishing can be a very slow process. Such surfaces are probably an under-recognized potential source of skin exposure to auto body workers.

COMMENT.

I assumed that once two-component urethanes were completely dry and cured, they were safe to handle and use. I was obviously wrong. And if auto body paints can be a source of exposure to isocyanates for weeks after curing, I now must assume that other two-component urethane products may pose similar risks. Included would be all types of two-component urethane foams, mold making materials, roof coatings, weather proofing, and more.

Another well-documented hazard occurs when the A and B parts are not properly mixed. In this case, the material can outgas significant amounts of isocyanates forever, rendering them an inhalation hazard. Isocyanates can cause life-threatening asthma, anaphylactic shock, and allergic dermatitis. Highly sensitive individuals can react to tiny amounts of these chemicals. Air-purifying respirators cannot be used for protection unless air monitoring is done to determine the cartridge change out schedule. Send an SASE for ACTS' Urethane data sheet for additional information.

* SWYPE surface pads from CLI in Des Plaines, IL, are impregnated with a proprietary reagent that changes color on contact with aliphatic isocyanates. Product directions call for spraying mineral oil on test surfaces because it will dissolve unbound isocyanates and increase their recovery on porous surfaces. However, these were very nonporous surfaces and mineral oil was not used.

** National Institute for Occupational Safety & Health method 5525.