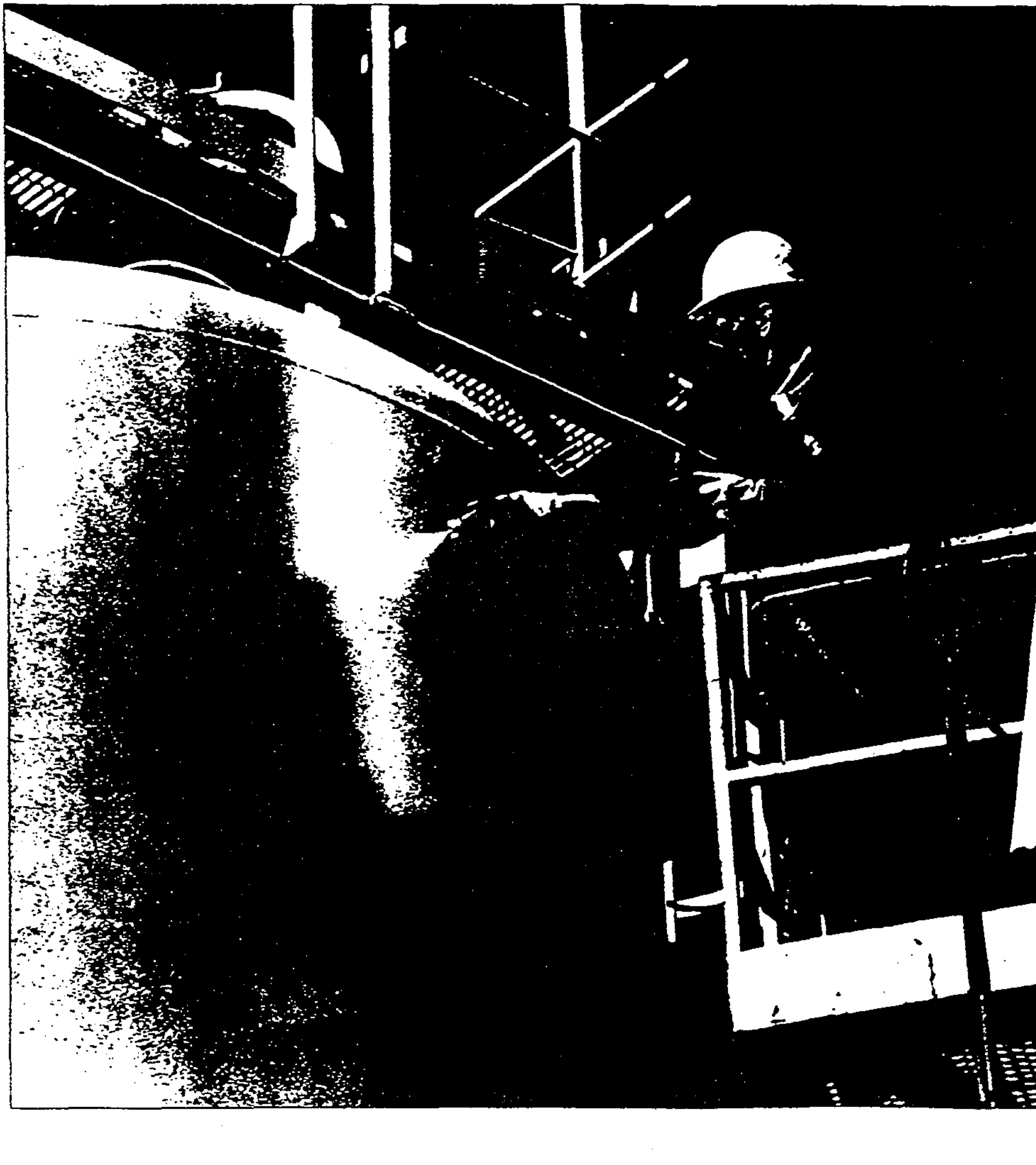
Polyurethane Coatings

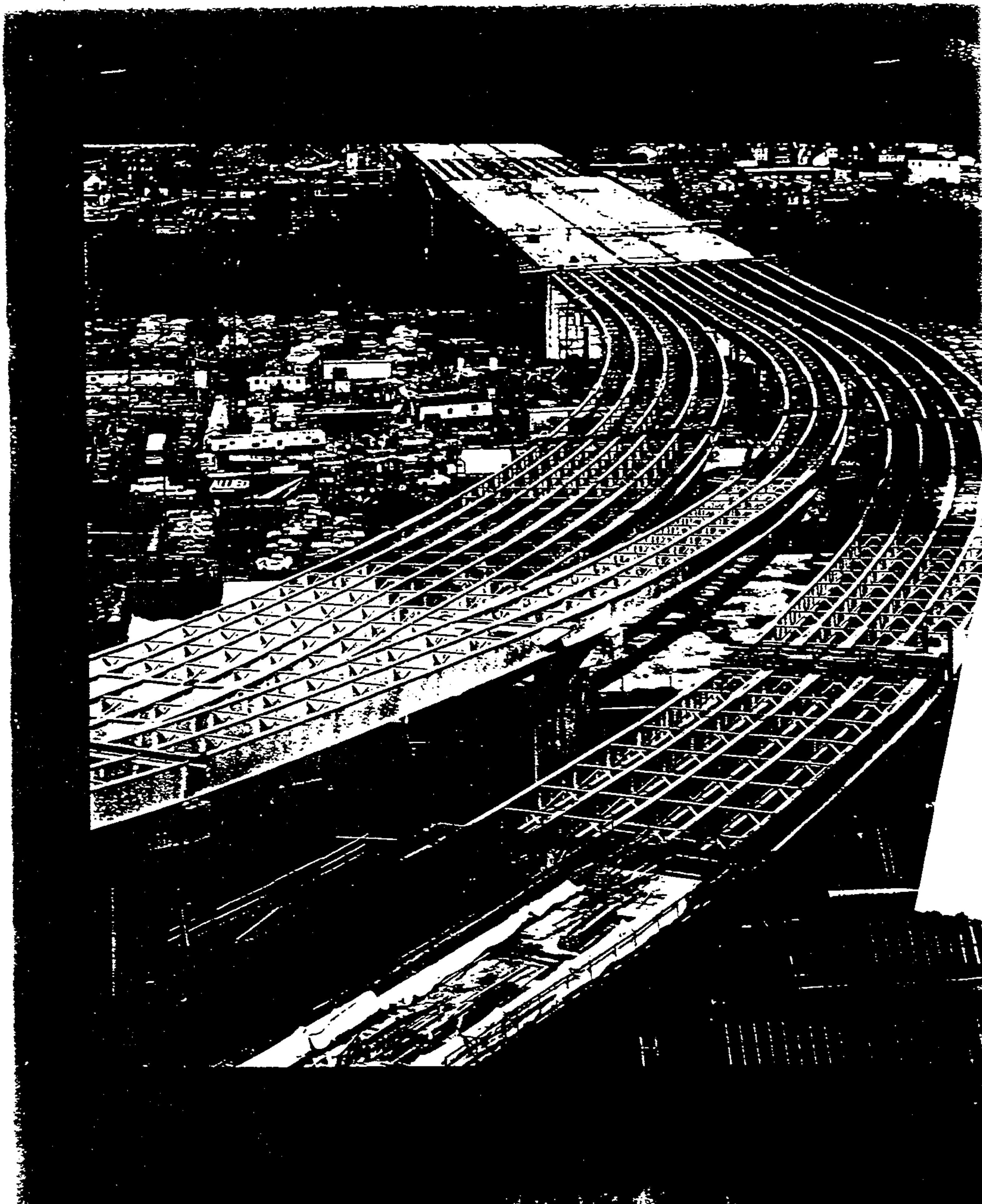
Performance, Quality, Safety

Bayer

Mobay

Professional Answers To Questions About Safe Application Of High-Performance Polyurethane Maintenance Coatings




ALLIED

Polyurethane Coatings

Needed by industries throughout the world.

Bridges, industrial plants and other structures of all kinds are exposed to temperature extremes, radiation from the sun, chemical attack, abrasion, fumes, marine atmospheres, and other sources of corrosive damage. Left unchecked, these hostile factors inflict serious damage that can result in the losses that are associated with collapsed structures and the need to repair or replace them.

Throughout the world, heavy duty polyurethane maintenance coatings are used to protect bridges and the buildings and structures of chemical plants, petroleum refineries, pulp and paper mills and other industrial facilities. In the U.S.A. alone, millions of gallons a year are used because polyurethane paints and coatings are recognized as the cost-effective leaders in providing long-lasting protection and long-term durability.

Chemistry Makes Polyurethanes Work

Polyurethanes are reaction products. The material of the protective film is formed by a *chemical reaction* between a polyisocyanate curing agent and either a resin (two-component system) or water in the atmosphere (moisture-cure system). The reaction results in a polymer—a material with extremely large molecules crosslinked into a dense barrier against corrosive elements.

Polyurethanes Can Be Tailor Made

The polyisocyanate can react with resin types such as polyesters, acrylics and polyethers. As a result, polyurethane coatings are unsurpassed in the ability to be formulated to meet specific environmental and performance requirements.

Polyurethanes Can Be Applied by Standard Methods, Safely

Although polyurethane paints and coatings provide an unusual degree of superior performance, they can be applied by conventional methods: conventional-air, airless and electrostatic spraying, brushing, and rolling. Since polyisocyanates, like other paint and coating ingredients, involve potential health hazards, they require protective measures during application.

Mobay Supplies Polyisocyanates for Polyurethane Coatings

Mobay Corporation does not make paints or coatings. The company manufactures and supplies polyisocyanate chemicals used by the manufacturers of polyurethane paints and coatings.

Choosing a paint or coating involves two fundamental concerns: performance and safety in application. The following pages provide information about both concerns with expert testimony, explanatory information and supporting data. This information relates only to Mobay products; information about specific paints or coatings should be obtained from the paint or coatings manufacturer.

Performance and Quality

Polyurethanes are among the lowest cost coatings with durability and long life.

Corrosion Resistance

Testing and experience have demonstrated the superiority of polyurethane coatings in their resistance to attack from weathering, abrasion, acids, alkalis, solvents, and marine atmosphere. Documented case histories show that polyurethane coatings made with Mobay polyisocyanate products have outperformed other types of coatings in a sulfuric acid plant in Louisiana, a wastewater plant that treats seawater, trans-Alaska pipeline pumping stations, chemical and fertilizer plants, tanks for holding carbon tetrachloride and other solvents, and a wide range of other facilities.

Long-Term Service and Low Life-Cycle Costs

Polyurethane's protection lasts a long time with minimum maintenance. Life expectancy of polyurethane coatings in some applications is as high as 10 to 12 years.

Appearance

Although polyurethanes are used primarily for corrosion protection, appearance is also a consideration. Light-stable aliphatic polyurethanes provide retention of color and gloss where surface appearance is important.

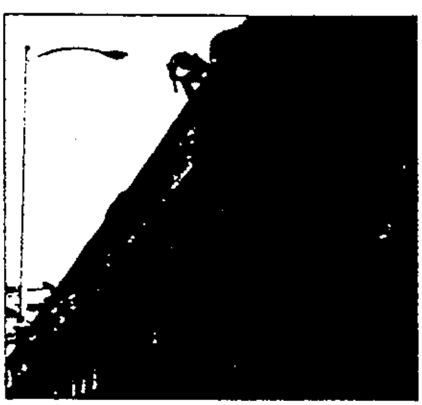


Figure 1.

Over the course of his career, Dr. Roebuck has had considerable experience in specifying maintenance coating materials of all types. A recipient of the Steel Structures Painting Council's John D. Keene Award, he is known world-wide for his expertise in corrosion control. He has authored over 100 publications, teaches a graduate level course at the University of Southern California on corrosion control in petroleum processing, and is active in the National Association of Corrosion Engineers and the Steel Structures Painting Council.

Dr. Albert H. Roebuck discusses high-performance coatings.

Q. *How many different maintenance coating materials are currently in use?*

A. A wide variety of coatings are currently being specified. These include alkyds, chlorinated rubbers, vinyls, the inorganic zincs, the epoxies, the acrylics and the polyurethanes.

Q. *What considerations go into specifying a maintenance coating system?*

A. Corrosion resistance is, of course, one of the prime considerations. Corrosion resistance relates to the ability to protect the structure. And it's also related to the resistance of a coating to abrasion—it's toughness—and also the film thinning. The better a film resists chalking, the longer its life and the greater its corrosion resistance for that reason.

Q. *What about longevity of the coating?*

A. Longevity is extremely important. For example, if two coating systems cost roughly the same thing initially but one lasts twice as long as the other, then the coating which lasts twice as long is roughly one-half the cost of the other coating system in terms of service life.

Q. *On what basis are coating costs estimated?*

A. Costs are estimated today, many times, on the basis of cost per square foot per year of service life. And again, it is seen that service life is critical in order to obtain low-cost coating systems for a plant.

Q. *What about appearance?*

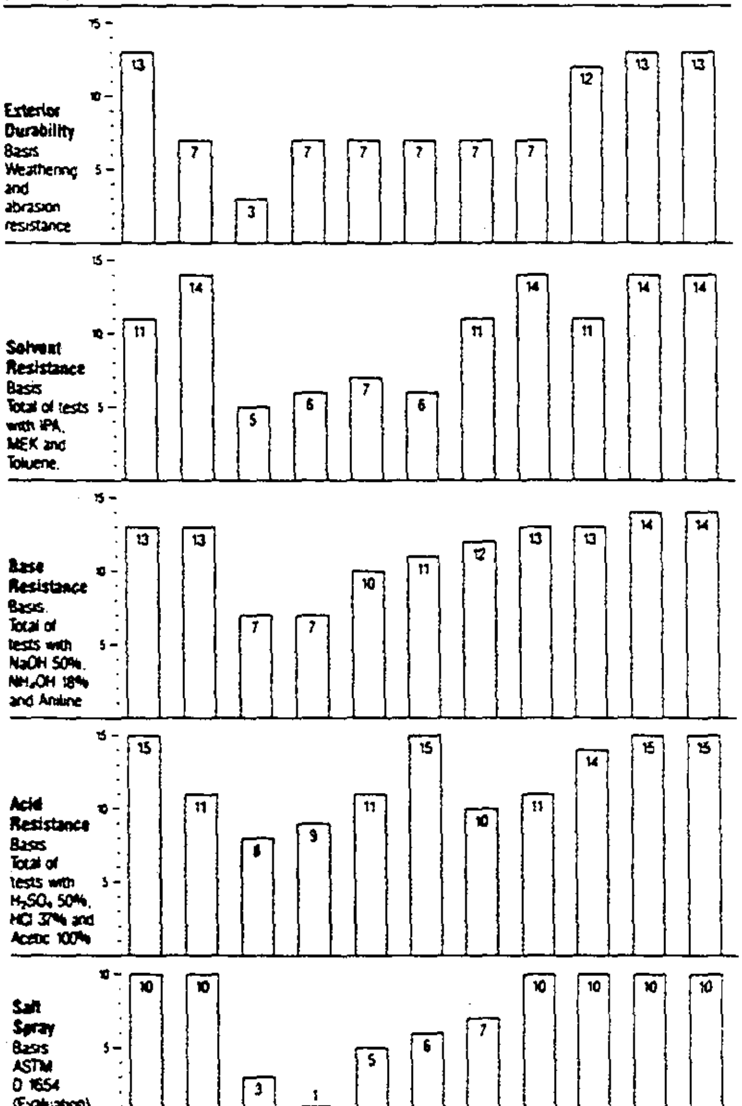
A. Appearance is critical also. Certain areas in a plant requiring highlighting need the resistance to chalking and fading and the color retention offered by the polyurethane type coatings—the aliphatic polyurethanes. Either, the acrylics or the polyesters, is excellent and must be rated highly.

Q. *Is there anything else you would like to add, Dr. Roebuck?*

A. I'd like to add one additional factor, which we have not discussed, and that would be the cleanability of polyurethanes which they offer because of their tightness and ability to resist chalking. Excellent cleanability. They can be readily washed and for this reason are widely used by certain industries requiring this characteristic.

Table I.
Test Data: Comparative Cumulative Resistance/Durability Ratings

System	A	B*	C	D	E	F	G	H	I*	J**	K*
Top Coat	High-Build Urethane	High-Build Epoxy	Alkyd	30% Silicone Alkyd	High-Build Vinyl	Chlorinated Rubber	Epoxy Mastic	Two-Component			
								High-Build Epoxy Mastic	Aliphatic Acrylic Urethane	Aliphatic Polyester Urethane	Aliphatic Polyester Urethane
Primer	Inorganic Zinc	Inorganic Zinc	Alkyd	Alkyd	Vinyl	Chlorinated Rubber		Zinc-Rich Epoxy	Zinc-Rich Epoxy	Urethane Moisture-Cure	Zinc-Rich Epoxy
Total Rating (70 max.)	62	55	26	30	40	45	47	55	60	66	66



*Intermediate Coat: Two-component epoxy/polyamide
**Intermediate Coat: Urethane moisture-cure based on Mobay's Desmodur E-21 resin

Test Procedures: To measure solvent, base, and acid resistance, eleven different paint systems were subjected to four-hour spot tests. Test reagents were placed in a concave pocket in steel panels painted with one of the test coatings, applied in accordance with manufacturers' instructions. After four hours, the effects of the corrosive fluid on the painted panel were rated. Each reagent was evaluated on a scale of 1-5 (5 = no effect, 1 = complete failure). A rating of 15 is the maximum obtainable for each class of reagents. Salt spray testing was conducted according to ASTM B 117. Exterior durability ratings were based on empirical observations. The results of the tests are shown in the chart above. The tests were conducted in Mobay laboratories.

Coatings Cost Guide

The basic objective of the coatings specifier is to achieve maximum protection and appearance at the least possible cost. As Table II shows, urethane coating systems are among the most cost-effective systems when compared on a long-term basis.

Table II.
Comparative Costs of Eleven Coating Systems

System	Coating	Dry Mils	Cost $/ft²/Mil	Total Applied Cost $/ft²	Life Expectancy (years)	Life-Cycle Cost $/ft²/yr.
A High-Build Urethane	Top Coat	6.5	0.027	1.23	10	0.12
Inorganic Zinc	Primer	2.5	0.025			
B High-Build Epoxy	Top Coat	5.0	0.019	1.38	6	0.23
2-Component Epoxy	Intermediate	1.8	0.019			
Inorganic Zinc	Primer	2.5	0.025			
C Alkyd	Top Coat	3.0	0.021	0.71	2	0.35
Alkyd	Primer	1.5	0.018			
D 30% Silicone Alkyd	Top Coat	1.8	0.033	0.70	2	0.35
Alkyd	Primer	1.3	0.018			
E High-Build Vinyl	Top Coat	5.0	0.04	0.89	6	0.15
Vinyl	Primer	2.0	0.031			
F Chlorinated Rubber	Top Coat	4.0	0.031	0.80	6	0.13
Chlorinated Rubber	Primer	2.0	0.028			
G Epoxy Mastic	1-Coat	6.0	0.02	0.599	6	0.10
H 2-Component High-Build Epoxy Mastic	Top Coat	6.0	0.019	1.11	6	0.19
Zinc-Rich Epoxy	Primer	2.5	0.032			
I 2-Component Aliphatic Acrylic Urethane	Top Coat	1.5	0.295	1.44	10	0.14
2-Component High-Build Epoxy	Intermediate	4.0	0.019			
Zinc-Rich Epoxy	Primer	2.5	0.032			
J 2-Component Aliphatic Polyester Urethane	Top Coat	1.5	0.036	1.219	10	0.12
Urethane Moisture-Cure	Intermediate	2.5	0.027			
Urethane Moisture-Cure	Primer	2.5	0.027			
K 2-Component Aliphatic Polyester Urethane	Top Coat	1.5	0.036	1.45	10	0.14
2-Component High-Build Epoxy	Intermediate	4.0	0.019			
Zinc-Rich Epoxy	Primer	2.5	0.032			

Note: Total applied cost in $/ft² includes the total paint millage cost, surface preparation, and application costs. Surface preparation and primer coats are shop applied. Intermediate and top coats are field applied. These costs were taken from NACE paper No. 183, "*1988 Paint and Coatings Selection and Cost Guide*". Polyurethane coatings show an additional cost of $0.05/ft²/coat to reflect cost of fresh-air-supplied respirators. Although application costs for polyurethanes initially appear higher, many contractors have found actual costs to be lower due to increased productivity, fewer application problems, and less rework.

Application Safety

All chemicals, including isocyanates, can be used safely by limiting exposure.

Health Effects

There are four types of ingredients in industrial coatings: resins, pigments, volatile solvents, and additives. Substances within each of these groups can affect the body through one or more of four routes: inhalation, skin contact/absorption, eye contact or ingestion. Substances vary considerably in the seriousness of their effects and the concentration levels that present a hazard.

With respect to polyisocyanates, in general, overexposure can irritate eyes, nose, throat, skin and lungs. An exposed person may experience skin sensitization and/or respiratory sensitization resulting in asthmatic symptoms which could be permanent. Overexposure may cause lung damage and a reduction in lung function which could also be permanent. Overexposure can also result in flu-like symptoms such as fever, chills, or an achy feeling. But the key to avoiding adverse health effects lies in applying one simple rule: prevent overexposure. (For a more detailed discussion of health effects, consult the Mobay Material Safety Data Sheet for the specific product involved.)

By and large, ingestion is not a common route of exposure in the workplace. Skin contact or absorption as well as eye contact can be prevented by wearing proper work apparel and eye protection, and by careful handling to prevent spills and splashes. Inhalation is the most prevalent route of exposure and requires the most skill, caution, knowledge and equipment.

Vapor Pressure

The concentration of a substance in the air a painter may breathe is of critical importance in preventing overexposure through inhalation. The concentration depends upon the application technique (i.e. spray vs. non-spray) and the material's vapor pressure—the ability of a liquid to evaporate into the air. The higher the vapor pressure, the more easily the liquid evaporates; the lower the vapor pressure, the less readily it evaporates.

Table III on page 5 shows the room-temperature vapor pressure (measured in millimeters of mercury) of a few pertinent chemicals. For comparison purposes, the table also lists the chemicals in order of their relative vapor pressures with MDI having the base value of 1.

Monitoring Surveys Determine Polyisocyanate Exposure Levels

The monitoring surveys reported here involved solvent-borne polyurethane paints containing Mobay polyisocyanate products that are based on HDI (hexamethylene diisocyanate) (i.e. Desmodur N-75) and MDI (diphenylmethane diisocyanate) (i.e. Desmodur E-21). In addition to the polyisocyanate products in the systems evaluated here, the two-component paint systems contained traces of HDI monomer while the one-component moisture-cure system contained significant amounts of MDI monomer. Furthermore, as previously indicated, these systems contain organic solvents. All these contaminants should always be included in a monitoring program.

Exposure criteria for evaluating monitoring results

HDI and HDI Polyisocyanate Exposure Limits

To protect the worker against airborne exposures to chemicals, the Occupational Safety and Health Administration (OSHA) and the American Conference of Governmental Industrial Hygienists (ACGIH) have established, respectively, Permissible Exposure Limits (PELs) or Threshold Limit Values (TLVs) for a number of chemicals. According to ACGIH: TLVs "...refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse health effects."

The ACGIH has established a TLV for hexamethylene diisocyanate (HDI) monomer of 0.005 ppm as an eight-hour time-weighted average (TWA). Although PELs have been established for several of the diisocyanates, federal OSHA has not established one for HDI. Mobay endorses the ACGIH TLV-TWA, and recommends a Ceiling level (C) for HDI of 0.02 ppm (Mobay Guideline Level, MGL). This concentration should not be exceeded even for brief periods.

ACGIH and federal OSHA have not established a TLV or PEL for the HDI-based polyisocyanates. However, the recommended Mobay Guideline Level (MGL) for the HDI-based polyisocyanates is 0.5 mg/m^3 (TWA—averaged over 8 hours) and a 1.0 mg/m^3 Short-Term Exposure Limit (STEL—averaged over 15 minutes). On Tables V through X, the 1.0 mg/m^3 STEL is used as the most appropriate guideline since samples were taken only during spraying or mixing and large unsampled parts of the workshift involved no potential for isocyanate exposure.

MDI Exposure Limits

The current ACGIH TLV-TWA for MDI is 0.051 mg/m^3. Currently, the OSHA PEL is 0.2 mg/m^3 as a ceiling value (29 CFR 1910.1000). At present, no allowable limit has been established for the Desmodur E-21 polyisocyanate, which is based on MDI.

Solvent Exposure Limits

PELs and/or TLVs have been established for most solvents used in paints. These limits, or manufacturer's guidelines, were used for the organic solvents associated with the coating systems evaluated at the time of these surveys.

When substances present together in the workplace air have different health effects, they should be considered *separately* with respect to their TLVs.

When they have similar effects (as with the organic solvents associated with the coating systems evaluated in these surveys) their *combined* effect should be given primary consideration. TLVs can be substituted in the following formula for this purpose:

$$\%TLV\ (mixture) = 100 \times \frac{Conc_1}{TLV_1} + \frac{Conc_2}{TLV_2} + \ldots + \frac{conc_n}{TLV_n}$$

Survey of Painting of a Bridge Superstructure and Deck

Throughout the summer of 1988, Mobay's Occupational and Product Safety Department, Coatings Product Safety group, conducted a series of industrial hygiene surveys during the painting of the Fleming Park bridge, Neville Island, Pennsylvania. The purpose was to determine airborne isocyanate and solvent vapor concentrations during brush-and-roll application of a Desmodur E-21 based polyurethane primer and during airless spray of Desmodur N-75 based two-part polyurethane intermediate and top coats. The results appear in Tables IV, V, and VI.

Table III.
Vapor Pressure Comparison

Chemical	VP, mm Hg	Relative VP
MDI (Monomer and Polymer)	0.00001	1
Polyisocyanate (Desmodur N)	0.000075	7.5
HMDI (Desmodur W)	0.001	100
HDI	0.025	2,500
TDI	0.025	2,500
Xylene (Xylol)	8	800,000
Water	18.0	1,800,000
MEK (Methyl Ethyl Ketone)	91	9,100,000

Table IV.
Brush-Roll Application of One-Part, Moisture-Cure Polyurethane Primer (Desmodur E-21)

	Airborne Concentrations		
Sample Site	Monomeric MDI (mg/m³)	Polymeric MDI (Desmodur E-21) (mg/m³)	Solvent Index (%)
Painter #1	0.011	0.07	118
Painter #2	0.005	0.03	69
Painter #3	0.001	<0.01	–
Deck	<0.011	<0.06	–
Onshore	<0.013	<0.07	–
Above Open Paint Can	<0.013	<0.07	–
Threshold Limit Value (TLV) or Guideline	**0.051**	–	**100%**

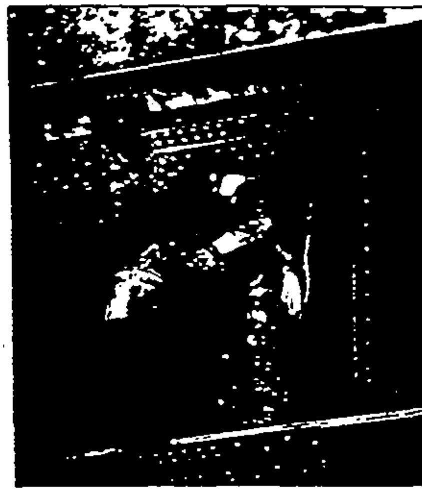


Figure 2.

Figure 3.

Table V.
Spraying Two-Part Polyurethane Intermediate Coat (Desmodur N-75)

	Airborne Concentrations		
Sample Site	Monomeric HDI (ppb)	HDI Poly-isocyanate (Desmodur N) (mg/m³)	Solvent Index 100%
Painter #1	2.4	2.5	151
Painter #2	1.9	2.2	117
Painter #3	4.1	5.2	151
Downwind 50 ft.*	0.5	<0.02	<14
Deck	0.6	0.09	26
Under Bridge	<0.4	0.02	–
Threshold Limit Value (TLV) or Guideline	**5.0**	**1.0†**	**100%**

* Distances are average number of feet from spray gun

† STEL, see page 4 "Exposure criteria for evaluating monitoring results"

Table VI.
Spraying Two-Part Polyurethane Top Coat (Desmodur N-75)

	Airborne Concentrations		
Sample Site	Monomeric HDI (ppb)	HDI Poly-isocyanate (Desmodur N) (mg/m³)	Solvent Index 100%
Painter #1	4.6	1.65	133
Painter #2	4.0	1.81	224
Mixer/Supervisor	0.7	0.03	<20
Deck	<0.6	<0.03	–
In Truck	<0.6	<0.03	–
Under Bridge 25 ft.*	<0.7	<0.03	–
Under Bridge 25 ft.*	<0.7	<0.07	–
Under Bridge 15 ft.*	1.6	0.80	–
Downwind, 50 ft.*	1.3	0.8	–
Mixing Area	0.8	0.04	–
Threshold Limit Value (TLV) or Guideline	**5.0**	**1.0†**	**100%**

* Distances are average number of feet from spray gun

† STEL, see page 4 "Exposure criteria for evaluating monitoring results"

Dr. Doull, a medical doctor, is a professor at the University of Kansas Medical Center. He is a world renowned toxicologist who has co-authored a standard textbook on toxicology. He is a charter member of the Society of Toxicology and served as its president from 1986 to 1987. He is a consultant to the National Academy of Sciences, the U.S. Environmental Protection Agency and many other health related organizations.

Dr. John Doull answers questions about application safety.

Q. *With all the stories about toxicity lately, it seems that everything is hazardous, everything is toxic. Is that true?*

A. Well, it's true in a sense that every chemical is capable of producing injury if the dose is sufficiently high.

Too many vitamins can cause poisoning. Paracelsus, who is the patron saint of toxicology, said over 400 years ago, "All substances are poisonous. There are no exceptions. It is only the dose that distinguishes between the poison and the remedy." Now, the good news from that is that every chemical, including the isocyanates, can be used safely by limiting exposure.

Q. *Some painters are concerned about the hazards associated with isocyanates. For example, can isocyanates cause asthma?*

A. Yes, overexposure to isocyanates can cause sensitization, which in turn can produce asthma. In addition, there are certain individuals who are more susceptible to this effect than others. Also, people who have been repeatedly overexposed or who have been exposed to a single large dose, such individuals may develop isocyanate sensitization and this in turn may cause them to react to future exposures to very low levels, even below the levels that might be considered safe for other individuals.

Q. *Are the effects of overexposure permanent?*

A. Isocyanates produce several effects. First, the irritation response—burning of the eyes, the nose, the throat, tightness in the chest, difficulty in breathing. These effects are usually temporary and they do not persist once overexposure is discontinued. Now, the second response is the sensitization and this does tend to be permanent. Although in some cases people have recovered from sensitization. Repeated overexposure to isocyanates, above the acceptable exposure levels, can cause eventual lung damage including decreases in lung function and these effects unfortunately can be permanent.

Q. *Do isocyanates cause cancer?*

A. Well, they are not known to cause cancer in humans. In one lifetime animal study in which rats and mice were exposed by inhalation to toluene diisocyanate or TDI, they did not cause cancer. However, in another lifetime study in which the rats were given massive doses of TDI by tube directly into the stomach, there was an increase in tumors. We don't really have comparable studies with all of the other isocyanates or at least they have not yet been reported.

Q. *Do isocyanates cause sterility, birth defects or reproductive problems?*

A. I'm not aware of any scientific evidence, either human or animal evidence, that isocyanates cause sterility or birth defects or reproductive problems.

Q. *Can you always tell when you are being overexposed?*

A. Unfortunately you can't because you can't smell or you can't detect isocyanates at concentrations which in fact may be harmful. This is why you must always wear proper respiratory protective equipment unless you have actual monitoring data which indicates that the contaminant levels are well within the acceptable limits.

Q. *Why can polyurethane paints be used safely?*

A. There are several reasons. First, most of these coatings are made with the polyisocyanates which are the less hazardous form. The amount of monomers is kept quite low. In fact, some of these polyisocyanates were deliberately prepared for use in paints.

Second, if you have good ventilation and you use good work practices, then the contaminant level in the air will be reasonably low. And third, and most important, your protective equipment and your respirator can protect you.

Q. *What is proper protection against isocyanate-containing paints?*

A. The kind of respiratory protection that you need really depends on the concentration of isocyanate in the air. In some cases, a vapor particulate or cartridge respirator may be adequate. In other cases, you may need to have a full air-supplied respirator. You should consult the paint manufacturer's labels, the MSDS—the Material Safety Data Sheet—for advice in this regard. However, it is important to remember that if you don't know what the concentration of isocyanate is, then you have to use the air supplied respirator to be sure that you're getting enough protection.

Q. *How great is the danger of overexposure to isocyanate from an open can of polyurethane paint?*

A. Oh, I would way that it's minimal, assuming that the person is not sensitized to the isocyanates in which case the risk would be small. However, skin contact with the mixed paint or with the activator can cause dermatitis. The painter should also wear safety glasses and should wear recommended gloves when handling the mixed paint.

Q. *At what point in the use of paints containing polyisocyanates is there the greatest danger of overexposure?*

A. Certainly during spray paint application, particularly in confined spaces where the ventilation is poor. This certainly would be the worst case.

Monitoring Survey of Painting of Chemical Plant Facilities

The Mobay Occupational and Product Safety Department also monitored spray painting of chemical process tanks and brush-and-roller painting of handrails at the Mobay New Martinsville, WV plant. The results are presented in Tables VII, VIII, and IX.

Table VII.
Air Spraying of Desmodur N-75 Based Top Coat on Chemical Storage Tank

	Airborne Concentrations		
Sample Site	**Monomeric HDI (ppb)**	**HDI Poly-isocyanate (Desmodur N) (mg/m³)**	**Solvent Index Cumulative % TLV**
Spray Painter	0.9	0.14	<22
Painter Helper	<0.2	<0.02	<22
Downwind (North) 25 ft.*	<0.2	<0.02	<22
Above Painters	<0.2	<0.02	<24
East 25 ft.	<0.2	<0.02	<22
Downwind 50 ft.	<0.2	<0.02	<25
West 15 ft.	<0.2	<0.02	<24
Upwind 15 ft.	<0.3	<0.03	–
Threshold Limit Value (TLV) or Guideline	**5.0**	**1.0†**	**100%**

* Average distances from spray gun
† STEL, see page 4, "Exposure criteria for evaluating monitoring results"

Table VIII.
Brush-and-Roll Application of Desmodur N-75 Based Top Coat on Handrails

	Airborne Concentrations		
Sample Site	**Monomeric HDI (ppb)**	**HDI Poly-isocyanate (Desmodur N) (mg/m³)**	**Solvent Index Cumulative % TLV**
Painter	<0.3	<0.03	<25
Top Staircase	<0.3	<0.03	<25
2nd Landing	1.3	0.05	<25
1st Landing	<0.3	<0.03	<25
Threshold Limit Value (TLV) or Guideline	**5.0**	**1.0***	**100%**

* STEL, see page 4, "Exposure criteria for evaluating monitoring results"

Table IX.
Air Spray Application of Desmodur N-75 Based Top Coat on Waste Treatment Tank

	Airborne Concentrations		
Sample Site	**Monomeric HDI (ppb)**	**HDI Poly-isocyanate (Desmodur N) (mg/m³)**	**Solvent Index Cumulative % TLV**
Painter	0.9	0.16	<28
Upwind 15 ft.*	0.9	<0.04	<28
Downwind 15 ft.*	1.4	0.24	<28
Downwind 35 ft.*	<0.4	<0.04	<28
Threshold Limit Value (TLV) or Guideline	**5.0**	**1.0***	**100%**

Figure 4.

Monitoring Survey of Paint Mixing in a Laboratory

Controlled laboratory monitoring while paint was mixed showed that air concentrations of HDI monomer, polyisocyanate, and solvents were not detectable. The limits of detection were 0.7 ppb, 0.01 mg/m³, and 23% of the cumulative TLV, respectively.

Table X.
Mixing of Desmodur N-75 Based Paint in a Laboratory

	Airborne Concentrations		
Sample Site	**Monomeric HDI (ppb)**	**HDI Poly-isocyanate (Desmodur N) (mg/m³)**	**Solvent Index Cumulative % TLV**
At Mixer	<0.7	<0.01	<23
Point A*	<0.7	<0.01	<23
Point B*	<0.7	<0.01	<23
Point C*	<0.7	<0.01	<23
Point D*	<0.7	<0.01	<23
Threshold Limit Value (TLV) or Guideline	**5.0**	**1.0†**	**100%**

* Distances varied from 1½ to 3 feet from mixer
† STEL, see page 4, "Exposure criteria for evaluating monitoring results"

Monitoring Considerations

The monitoring surveys reported here involved polyurethane paints containing Mobay polyisocyanate products based on HDI (hexamethylene diisocyanate) and MDI (diphenylmethane diisocyanate). As the tables at left show, it is important to measure both the airborne isocyanate monomers and the polyisocyanates. IT MUST BE REMEMBERED HOWEVER, THAT CONDITIONS VARY WIDELY FROM JOB TO JOB, AND PAINT SPECIFIERS, PAINTING CONTRACTORS, OR FACILITY OWNERS MUST OBTAIN SUFFICIENT MONITORING DATA FOR MAKING THEIR OWN INFORMED JUDGMENT AS TO RESPIRATORY PROTECTION REQUIREMENTS FOR A GIVEN APPLICATION.

All paints are potentially hazardous during application because they contain four classes of chemicals—pigments, solvents, resins, and miscellaneous additives. To one extent or another, these materials present potential health hazards when a painter is overexposed to them. That is why it is necessary to employ all reasonable precautions and protective equipment to prevent overexposure during application.

Painters must use protective equipment when spraying any reactive coating system. Particularly important, they must read the paint-can label and applicable Material Safety Data Sheet and carefully follow the paint manufacturer's recommendations printed there.

Monitoring should be done so that levels of exposure are known; when exposure levels are not known, hazardous levels must be assumed and the maximum protective equipment must be employed. In Mobay's monitoring experience, cases have been observed in which contamination levels greatly exceeded permissible limits, making supplied-air respiratory equipment mandatory.

Monitoring the Exposure Area

In the Fleming Park bridge study, the outdoor space potentially exceeding permissible limits of air contamination had an ellipsoidal shape (see Figure 5). The dimensions of the ellipsoid, in this case, were 20 feet upwind, 20 feet to each side, and 50 feet downwind from the spray gun. These dimensions corresponded well to the area where spray mist could be seen depositing on surfaces and solvents could be smelled.

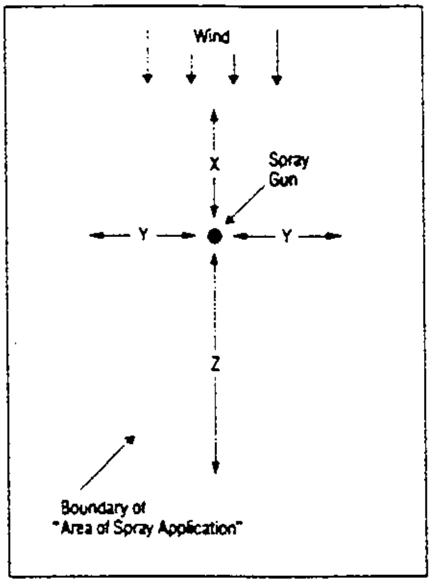


Figure 5.

Mobay industrial hygienists refer to this as the *area of spray application*—the space inside which all workers needed to have the same respiratory protection as the painters themselves. The shape and dimensions of this *area of spray application* depend on several factors: number and nearness of painters, wind speed and direction, type of paint application, spraying rate and amount of misting and bounce back caused by the various surface shapes being painted, and degree of enclosure. The great variability of these factors makes it impossible to generalize or develop a standard size and shape of the *area of spray application* and therefore this area must be determined in the field on a case-by-case basis. Monitoring should always be carried out by properly trained personnel employing the appropriate measuring instruments, accurately calibrated.

John B. Conomos
President, John B. Conomos, Inc.
Bridgeville, Pennsylvania

Painting contractor discusses protection on the job.

Q. ***What measures do you impose to protect your workers from the potential hazards involved in using polyurethanes?***

A. Well, basically you have two choices. One is the air-fed mask and the second is the cartridge type. Your choice is based on where you're going to use it and how you're going to apply the material. If we are involved in spraying materials indoors or outdoors, we use the air-fed. If we're doing work in enclosed areas such as buildings, tanks, and so forth, we use the air-fed whether we are brushing or spraying. And if we're just mixing material or brushing in open areas, then we use just the plain cartridge type mask.

Q. ***Are there situations where you require fresh-air-supply respirators when spraying other solvent-based paints?***

A. Yes. When we get involved in doing tank linings or painting in enclosed areas, especially when we're spraying. We have found that a fresh air respirator is the way to go. It provides the proper atmosphere for a man to do his job efficiently.

Q. ***Since you deal with potential hazards in applying polyurethanes as well as other materials, what do you think your industry needs to increase worker safety?***

A. I believe that the more knowledge our workers are given relative to the hazards and how to deal with those hazards, the better off we are. We believe that we need more training information. We need more information relative to types of protective devices, types of clothing, salves, etc. And we want to take this information and transmit it efficiently to our people. If we do that, we can handle these hazards in a manner that will provide safety to the worker and a quality job to the owner.

Respiratory Protection

Mobay fully endorses use of respirators not only for protection from polyisocyanates, but also for protection from solvent vapors and other paint ingredients.

A wide variety of respirators is available from industrial safety equipment suppliers. They are available in two general types: air-purifying respirators and supplied-air respirators. The selection depends upon the level of airborne exposure, the type of isocyanate involved, and the application conditions. Here too, painters must consult paint-can labels and Material Safety Data Sheets from the paint manufacturer for assistance. In addition, product safety literature, including Material Safety Data Sheets, is published by Mobay for each of its products.

Respirators should be used strictly in accordance with the manufacturer's instructions and the OSHA respiratory protection standard § 1910.134, (see Appendix B, page 12). Air-purifying respirators must be properly fitted. Respirator users must be medically approved to wear respirators. Filters and organic-vapor cartridges must be changed as frequently as recommended by the respirator manufacturer.

The concentration at which the odor of diisocyanates is detectable is higher than allowable limits. Therefore the sense of smell does not provide a suitable warning. Breakthrough could occur during use of an air-purifying respirator without immediate detection, and an individual could be exposed in excess of allowable limits. However, solvent-vapor breakthrough will be detectable by odor well before isocyanates break through in concentrations above their TLVs.

With supplied-air respirators, it is essential that the blower or other air source draw the air from outside the contaminated area so the painter is supplied with clean respirable air. If compressor air is used, it must be properly filtered and monitored to ensure a continuous supply of grade D breathing air to the respirator.

Figure 6.

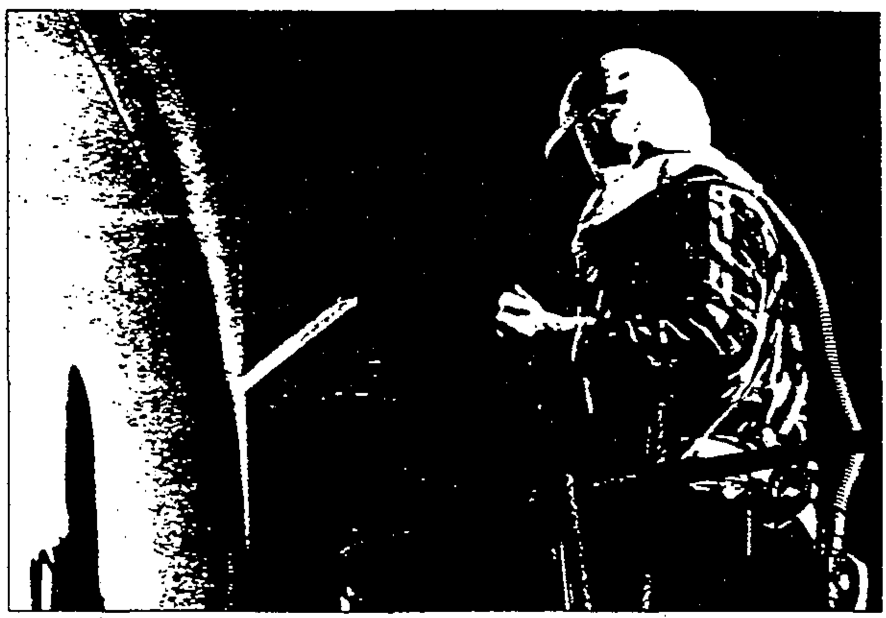


Figure 7.

The spray painter in Figure 6, applying a Desmodur N-75 based coating, used an air-supplied respirator because contaminant levels of paint ingredients were unknown at the time.

In Figure 7, the spray painter, applying a Desmodur N-75 based top coat, has fresh-air protection through an air-supplied hood. Because hoods cover the head and shoulders, they can provide added protection from eye and skin contact with paint mist.

In the application of a Desmodur N-75 based top coat, shown in Figure 8, monitoring results during both brush and roller use indicated airborne levels of paint ingredients at that time (see Table VIII) to be such that an air-purifying respirator afforded adequate protection. This type of respirator, commonly called a vapor-particulate respirator, has a cartridge that absorbs organic vapors and a prefilter that removes particulates from the air.

Contact Protection

Because isocyanates and the other ingredients in polyurethane paints can cause dermatitis and eye irritation, painters should wear chemical goggles or glasses with side shields and chemical-resistant gloves (butyl rubber is recommended). Barrier creams for application to the skin are available; these offer limited protection and should be used only to supplement the coverage afforded by protective clothing.

Other Sources of Information

Other sources of information are Mobay's product data sheets, Material Safety Data Sheets, and labels. If you need any of this literature or further information, contact your Mobay representative or call Mobay's Corporate Occupational and Product Safety Department at (412) 777-2867.

Figure 8.

Appendix A

Glossary

Airless Spraying
Spray application of paint with equipment that uses direct pump pressure instead of compressed air to atomize the paint.

Asthma
A condition of continuous or intermittent labored breathing accompanied by wheezing, a sense of constriction in the chest, and often attacks of coughing or gasping.

Dermatitis
Inflammation, irritation or reddening of the skin.

Electrostatic Spraying
A system of applying paint by spray in which the paint and the painted object have opposite electrical charges, causing the paint to be attracted to the object.

HDI
Hexamethylene diisocyanate.

MDI
Diphenylmethane diisocyanate.

Monomer
The smallest, simplest molecule of an organic chemical compound that is capable of conversion to polymers by combination with itself or other similar molecules or compounds.

OSHA
Occupational Safety and Health Administration

Pigment
A substance that imparts black, white or color to paint.

PEL
Permissible Exposure Limit; an exposure limit established by OSHA's regulatory authority. May be a Time-Weighted Average (TWA) limit or a maximum-concentration exposure limit.

Polymer
A large-molecule chemical compound consisting of repeating structural units (monomers).

ppb
Parts per billion.

ppm
Parts per million.

Resin
A semisolid or solid flowable organic material used as a binder in a coating.

Sensitization
The body's hyperactive (allergy-like) response to a substance that has been touched or inhaled by a susceptible individual.

STEL
Short-Term Exposure Limit (an OSHA standard), the maximum contaminant concentration to which a worker may be exposed for 15 minutes.

TLV
Threshold Limit Value (published by the American Conference of Governmental Industrial Hygienists), the airborne-contaminant concentration below which nearly all workers may be repeatedly exposed day-after-day without adverse effects.

TWA
Time Weighted Average, the arithmetical mean concentration over an 8-hour period.

Vapor Pressure
The pressure that causes a liquid to evaporate. It is measured when the liquid and vapor are in equilibrium and is expressed in millimeters of mercury.

Appendix B

OSHA Regulations

Parts of OSHA regulations relevant to respiratory protection are printed below as they appear in 29 CFR Ch. XVII, § 1910.134. These regulations were in effect on the date of publication of this booklet (June 1989). Since subsequent revisions may have occurred, the reader is cautioned to follow current regulations.

§ 1910.134 Respiratory protection.

(a) *Permissible practice.* (1) In the control of those occupational diseases caused by breathing air contaminated with harmful dusts, fogs, fumes, mists, gases, smokes, sprays, or vapors, the primary objective shall be to prevent atmospheric contamination. This shall be accomplished as far as feasible by accepted engineering control measures (for example, enclosure or confinement of the operation, general and local ventilation, and substitution of less toxic materials). When effective engineering controls are not feasible, or while they are being instituted, appropriate respirators shall be used pursuant to the following requirements.

(2) Respirators shall be provided by the employer when such equipment is necessary to protect the health of the employee. The employer shall provide the respirators which are applicable and suitable for the purpose intended. The employer shall be responsible for the establishment and maintenance of a respiratory protective program which shall include the requirements outlined in paragraph (b) of this section.

(3) The employee shall use the provided respiratory protection in accordance with instructions and training received.

(b) *Requirements for a minimal acceptable program.* (1) Written standard operating procedures governing the selection and use of respirators shall be established.

(2) Respirators shall be selected on the basis of hazards to which the worker is exposed.

(3) The user shall be instructed and trained in the proper use of respirators and their limitations.

(4) [Reserved]

(5) Respirators shall be regularly cleaned and disinfected. Those used by more than one worker shall be thoroughly cleaned and disinfected after each use.

(6) Respirators shall be stored in a convenient, clean, and sanitary location.

(7) Respirators used routinely shall be inspected during cleaning. Worn or deteriorated parts shall be replaced. Respirators for emergency use such as self-contained devices shall be thoroughly inspected at least once a month and after each use.

(8) Appropriate surveillance of work area conditions and degree of employee exposure or stress shall be maintained.

(9) There shall be regular inspection and evaluation to determine the continued effectiveness of the program.

(10) Persons should not be assigned to tasks requiring use of respirators unless it has been determined that they are physically able to perform the work and use the equipment. The local physician shall determine what health and physical conditions are pertinent. The respirator user's medical status should be reviewed periodically (for instance, annually).

(11) Approved or accepted respirators shall be used when they are available. The respirator furnished shall provide adequate respiratory protection against the particular hazard for which it is designed in accordance with standards established by competent authorities. The U.S. Department of Interior, Bureau of Mines, and the U.S. Department of Agriculture are recognized as such authorities. Although respirators listed by the U.S. Department of Agriculture continue to be acceptable for protection against specified pesticides, the U.S. Department of the Interior, Bureau of Mines is the agency now responsible for issuing and approving pesticide respirators.

(c) *Selection of respirators.* Proper selection of respirators shall be made according to the guidance of American National Standard Practices for Respiratory Protection Z88.2-1969.

(d) *Air quality.* (1) Compressed air, compressed oxygen, liquid air, and liquid oxygen used for respiration shall be of high purity. Oxygen shall meet the requirements of the United States Pharmacopoeia for medical or breathing oxygen. Breathing air shall meet at least the requirements of the specification for Grade D breathing air as described in Compressed Gas Association Commodity Specification G-7.1-1966. Compressed oxygen shall not be used in supplied-air respirators or in open circuit self-contained breathing apparatus that have previously used compressed air. Oxygen must never be used with air line respirators.

(2) Breathing air may be supplied to respirators from cylinders or air compressors.

(i) Cylinders shall be tested and maintained as prescribed in the Shipping Container Specification Regulations of the Department of Transportation (49 CFR Part 178).

(ii) The compressor for supplying air shall be equipped with necessary safety and standby devices. A breathing air-type compressor shall be used. Compressors shall be constructed and situated so as to avoid entry of contaminated air into the system and suitable in-line air purifying sorbent beds and filters installed to further assure breathing air quality. A receiver of sufficient capacity to enable the respirator wearer to escape from a contaminated atmosphere in event of compressor failure and alarms to indicate compressor failure and overheating shall be installed in the system. If an oil-lubricated compressor is used, it shall have a high-temperature or carbon monoxide alarm, or both. If only a high-temperature alarm is used, the air from the compressor shall be frequently tested for carbon monoxide to insure that it meets the specifications in paragraph (d)(1) of this section.

(3) Air line couplings shall be incompatible with outlets for other gas systems to prevent inadvertent servicing of air line respirators with nonrespirable gases or oxygen.

(4) Breathing gas containers shall be marked in accordance with American National Standard Method of Marking Portable Compressed Gas Containers to Identify the Material Contained, Z48.1-1954; Federal Specification BB-A-1034a, June 21, 1968, Air, Compressed for Breathing Purposes; or Interim Federal Specification GG-B-00675b, April 27, 1965, Breathing Apparatus, Self-Contained.

(e) *Use of respirators.* (1) Standard procedures shall be developed for respirator use. These should include all information and guidance necessary for their proper selection, use, and care. Possible emergency and routine uses of respirators should be anticipated and planned for.

(2) The correct respirator shall be specified for each job. The respirator type is usually specified in the work procedures by a qualified individual supervising the respiratory protective program. The individual issuing them shall be adequately instructed to insure that the correct respirator is issued.

(3) Written procedures shall be prepared covering safe use of respirators in dangerous atmospheres that might be encountered in normal operations or in emergencies. Personnel shall be familiar with these procedures and the available respirators.

(i) In areas where the wearer, with failure of the respirator, could be overcome by a toxic or oxygen-deficient atmosphere, at least one additional man shall be present. Communications (visual, voice, or signal line) shall be maintained between both or all individuals present. Planning shall be such that one individual will be unaffected by any likely incident and have the proper rescue equipment to be able to assist the other(s) in case of emergency.

(ii) When self-contained breathing apparatus or hose masks with blowers are used in atmospheres immediately dangerous to life or health, standby men must be present with suitable rescue equipment.

(iii) Persons using air line respirators in atmospheres immediately hazardous to life or health shall be equipped with safety harnesses and safety lines for lifting or removing persons from hazardous atmospheres or other and equivalent provisions for the rescue of persons from hazardous atmospheres shall be used. A standby man or men with suitable self-contained breathing apparatus shall be at the nearest fresh air base for emergency rescue.

(4) Respiratory protection is no better than the respirator in use, even though it is worn conscientiously. Frequent random inspections shall be conducted by a qualified individual to assure that respirators are properly selected, used, cleaned, and maintained.

(5) For safe use of any respirator, it is essential that the user be properly instructed in its selection, use, and maintenance. Both supervisors and workers shall be so instructed by competent persons. Training shall provide the men an opportunity to handle the respirator, have it fitted properly, test its face-piece-to-face seal, wear it in normal air for a long familiarity period, and, finally, to wear it in a test atmosphere.

(6) Every respirator wearer shall receive fitting instructions including demonstrations and practice in how the respirator should be worn, how to adjust it, and how to determine if it fits properly. Respirators shall not be worn when conditions prevent a good face seal. Such conditions may be a growth of beard, sideburns, a skull cap that projects under the facepiece, or temple pieces on glasses. Also, the absence of one or both dentures can seriously affect the fit of a facepiece. The worker's diligence in observing these factors shall be evaluated by periodic check. To assure proper protection, the facepiece fit shall be checked by the wearer each time he puts on the respirator. This may be done by following the manufacturer's facepiece fitting instructions.

(ii) Providing respiratory protection for individuals wearing corrective glasses is a serious problem. A proper seal cannot be established if the temple bars of eye glasses extend through the sealing edge of the full facepiece. As a temporary measure, glasses with short temple bars or without temple bars may be taped to the wearer's head. Wearing of contact lenses in contaminated atmosphere with a respirator shall not be allowed. Systems have been developed for mounting corrective lenses inside the facepieces. When a workman must wear corrective lenses as part of the facepiece, the facepiece and lenses shall be fitted by qualified individuals to provide good vision, comfort, and gas-tight seal.

(iii) If corrective spectacles or goggles are required, they shall be worn so as not to affect the fit of the facepiece. Proper selection of equipment will minimize or avoid this problem.

(f) *Maintenance and care of respirators.* (1) A program for maintenance and care of respirators shall be adjusted to the type of plant, working conditions, and hazards involved, and shall include the following basic services:

(i) Inspection for defects (including a leak check),

(ii) Cleaning and disinfecting,

(iii) Repair,

(iv) Storage.

Equipment shall be properly maintained to retain its original effectiveness.

(2) (i) All respirators shall be inspected routinely before and after each use. A respirator that is not routinely used but is kept ready for emergency use shall be inspected after each use and at least monthly to assure that it is in satisfactory working condition.

(ii) Self-contained breathing apparatus shall be inspected monthly. Air and oxygen cylinders shall be fully charged according to the manufacturer's instructions. It shall be determined that the regulator and warning devices function properly.

(iii) Respirator inspection shall include a check of the tightness of connections and the condition of the facepiece, headbands, valves, connecting tube, and canisters. Rubber or elastomer parts shall be inspected for pliability and signs of deterioration. Stretching and manipulating rubber or elastomer parts with a massaging action will keep them pliable and flexible and prevent them from taking a set during storage.

(iv) A record shall be kept of inspection dates and findings for respirators maintained for emergency use.

(3) Routinely used respirators shall be collected, cleaned, and disinfected as frequently as necessary to insure that proper protection is provided for the wearer. Respirators maintained for emergency use shall be cleaned and disinfected after each use.

(4) Replacement or repairs shall be done only by experienced persons with parts designed for the respirator. No attempt shall be made to replace components or to make adjustment or repairs beyond the manufacturer's recommendations. Reducing or admission valves or regulators shall be returned to the manufacturer or to a trained technician for adjustment or repair.

(5) (i) After inspection, cleaning, and necessary repair, respirators shall be stored to protect against dust, sunlight, heat, extreme cold, excessive moisture, or damaging chemicals. Respirators placed at stations and work areas for emergency use should be quickly accessible at all times and should be stored in compartments built for the purpose. The compartments should be clearly marked. Routinely used respirators, such as dust respirators, may be placed in plastic bags. Respirators should not be stored in such places as lockers or tool boxes unless they are in carrying cases or cartons.

(ii) Respirators should be packed or stored so that the facepiece and exhalation valve will rest in a normal position and function will not be impaired by the elastomer setting in an abnormal position.

(iii) Instructions for proper storage of emergency respirators, such as gas masks and self-contained breathing apparatus, are found in "use and care" instructions usually mounted inside the carrying case lid.

(g) *Identification of gas mask canisters.* (1) The primary means of identifying a gas mask canister shall be by means of properly worded labels. The secondary means of identifying a gas mask canister shall be by a color code.

(2) All who issue or use gas masks falling within the scope of this section shall see that all gas mask canisters purchased or used by them are properly labeled and colored in accordance with these requirements before they are placed in service and that the labels and colors are properly maintained at all times thereafter until the canisters have completely served their purpose.

(3) On each canister shall appear in bold letters the following:

(i)—

Canister for ________________________

(Name for atmospheric contaminant)

or

Type N Gas Mask Canister

(ii) In addition, essentially the following wording shall appear beneath the appropriate phrase on the canister label: "For respiratory protection in atmospheres containing not more than ____ percent by volume of

____

(Name of atmospheric contaminant)

(4) Canisters having a special high-efficiency filter for protection against radionuclides and other highly toxic particulates shall be labeled with a statement of the type and degree of protection afforded by the filter. The label shall be affixed to the neck end of, or to the gray stripe which is around and near the top of, the canister. The degree of protection shall be marked as the percent of penetration of the canister by a 0.3-micron-diameter dioctyl phthalate (DOP) smoke at a flow rate of 85 liters per minute.

(5) Each canister shall have a label warning that gas masks should be used only in atmospheres containing sufficient oxygen to support life (at least 16 percent by volume), since gas mask canisters are only designed to neutralize or remove contaminants from the air.

(6) Each gas mask canister shall be painted a distinctive color or combination of colors indicated in Table I-1. All colors used shall be such that they are clearly identifiable by the user and clearly distinguishable from one another. The color coating used shall offer a high degree of resistance to chipping, scaling, peeling, blistering, fading, and the effects of the ordinary atmospheres to which they may be exposed under normal conditions of storage and use. Appropriately colored pressure sensitive tape may be used for the stripes.

Table I-1

Atmospheric contaminants to be protected against	Colors assigned[1]
Acid gases	White
Hydrocyanic acid gas	White with ½-inch green stripe completely around the canister near the bottom
Chlorine gas	White with ½-inch yellow stripe completely around the canister near the bottom
Organic vapors	Black
Ammonia gas	Green
Acid gases and ammonia gas	Green with ½-inch white stripe completely around the canister near the bottom
Carbon monoxide	Blue
Acid gases and organic vapors	Yellow
Hydrocyanic acid gas and chloropicrin vapor	Yellow with ½-inch blue stripe completely around the canister near the bottom.
Acid gases, organic vapors, and ammonia gases	Brown
Radioactive materials, excepting tritium and noble gases	Purple (Magenta)
Particulates (dusts, fumes, mists, fogs, or smokes) in combination with any of the above gases or vapors	Canister color for contaminant, as designated above, with ½-inch gray stripe completely around the canister near the top
All of the above atmospheric contaminants	Red with ½-inch gray stripe completely around the canister near the top

[1]Gray shall not be assigned as the main color for a canister designed to remove acids or vapors.

NOTE: Orange shall be used as a complete body, or stripe color to represent gases not included in this table. The user will need to refer to the canister label to determine the degree of protection the canister will afford.

(Approved by the Office of Management and Budget under control number 1218-0099)

(Secs. 4(b)(2), 6(b) and 8(c), 84 Stat. 1592, 1593, 1596, 29 U.S.C. 653, 655, 657; Secretary of Labor's Order No. 8-76 (41 FR 25059); 29 CFR Part 1911; secs. 6, 8, 84 Stat. 1593, 1600 (29 U.S.C. 655, 657); Secretary of Labor's Order No. 9-83 (48 FR 35736); 29 CFR Part 1911)

(39 FR 23502, June 27, 1974, as amended at 43 FR 49748, Oct. 24, 1978; 49 FR 5322, Feb. 10, 1984; 49 FR 18295, Apr. 30, 1984.)