PANELIST'S REMARKS

URETHANE FOUNDRY BINDERS - AN INDUSTRIAL HYGIENE APPRAISAL

R. H. Toeniskoetter, Ph.D
Manager, Environmental & Occupational Safety
Ashland Chemical Company
Dublin, Ohio

INTRODUCTION

Three types of urethane binders are used by foundries: alkyd-isocyanate no-bake; phenolic-urethane no-bake; and phenolic-urethane cold box. The alkyd-isocyanate no-bake was introduced in 1965; the phenolic-urethane cold box in 1968, and the phenolic-urethane no-bake in 1970. Usage of these binders has grown steadily since their respective introductions to the foundry industry. In 1979, approximately one hundred million pounds of urethane binders will be consumed by the United States Foundry Industry, and an additional one hundred million pounds throughout the rest of the world. Since their introduction in 1965, over five hundred million pounds of urethane binders have been consumed by the United States Foundry Industry with an equal amount being used elsewhere in the world.

This rapid increase in the use of these types of binders can be attributed to their many desirable characteristics for production foundry operations. Urethane foundry binders provide ease of handling, excellent coremaking and molding properties, high productivity, excellent casting quality, good energy conservation and favorable environmental and ecological characteristics. The foundry industry has enjoyed a good safety and health record in the use of these binders. Because of their chemical makeup, however, urethane binders can present potential occupational hazards if misused. By providing adequate safety and health information and guidance on their use, Ashland Chemical Company has been able to assist foundries in adapting these binder processes to their operations without excessive difficulties or safety/health problems.

COMPOSITION AND USE

Urethane binders are three-part systems consisting of polyol, polymeric isocyanate and catalyst components. In the presence of the catalyst, the polyol combines chemically with the polymeric isocyanate to produce a highly cross-linked urethane bond. Specific components of the three types of urethane binders are shown in Table 1. Part A of the alkyd-isocyanate system consists of an alkyd resin dissolved in an aliphatic hydrocarbon solvent. These are usually modified with a petroleum hydrocarbon resin. Part A's of alkyd-isocyanate binders are similar to core oils. Part C of the alkyd-

Table 1. Components of urethane binders.

	Alkyd isocyanate No bake	Phenolic urethane No bake	Phenolic urethane cold box
Polyol	Alkyd resin	Phenolic resin	Phenolic resin
Polyisocyanate	Polymeric MDI	Polymeric MDI	Polymeric MDI
Catalyst	Metal drier and amine	Pyridine derivative	t-Aliphatic amine
Solvent	Aliphatic hydrocarbon	Aromatic hydrocarbon	Aromatic hydrocarbon
		Aliphatic ester	Aromatic ester

isocyanate system is a polymeric isocyanate of the methylene bis phenyl-isocyanate (MDI) type. It is a dark colored liquid of moderate viscosity and extremely low vapor pressure. Part B of the alkyd-isocyanate system is the catalyst. It contains a metal drier to facilitate the final oxidative-polymerization of the binder and also an amine catalyst for the urethane reaction which provides the initial set or curing.

The phenolic-urethane no-bake system uses a phenol-formaldehyde resin (phenolic resin) dissolved in solvent as the polyol component. The isocyanate component is a polymeric MDI dissolved in solvent. The catalyst is a low volatility pyridine derivative which may be supplied neat or dissolved in solvent depending on the use characteristics desired. Solvents used in these phenolic urethane components are high boiling aromatic petroleum hydrocarbons and aliphatic esters.

The phenolic urethane cold box binder system is similar to the corresponding no-bake. Part I is a phenol formaldehyde resin dissolved in a solvent blend which consists of highboiling aromatic petroleum hydrocarbons and esters. Part II is the polymeric MDI in aromatic petroleum hydrocarbon solvent. The catalyst for the phenolic urethane cold box system can be either triethylamine (TEA) or dimethylethylamine (DMEA). These catalysts are provided in liquid form but are vaporized into a stream of air, nitrogen or carbon dioxide and introduced into the sand/binder mixture as a gas.

The alkyd-isocyanate and the phenolic urethane binders are no-bake systems. After polyol, polymeric isocyanate and catalyst components are mixed together on sand, a spontaneous chemical reaction occurs and results in hardening, or cure, of the sand mass. No external heat is required. Settling or curing times with the alkyd-isocyanate no-bake range from ten minutes to one hour or more and as a result of these working characteristics this type of binder is generally used for larger core or mold work, or where high production rates are not desired. The phenolic urethane no-bake is a very fast setting system providing strip times in the range of 3 to 8 minutes. This fast setting characteristic allows the phenolic urethane no-bake to be used on high production lines for cores or molds.

The phenolic urethane cold box binder system is designed primarily for high production coremaking or molding where curing can be controlled by an external triggering agent. The triggering agent in this case is the gaseous catalyst, triethylamine or dimethylethylamine, which is introduced into the sand binder mix as a vapor. As this gaseous amine is absorbed into the resin system, the curing reaction is initiated and occurs almost instantaneously. Cured cores or molds can then be ejected from the core box or pattern within a matter of seconds. The phenolic urethane cold box system is readily adapted to fast machine production of cores and molds.

POTENTIAL EMISSIONS

Table 2 shows the potential emissions that need to be considered when using urethane binders. Permissible Exposure Limits (PEL's) are shown where applicable. Whether a potential exposure problem could exist in the use of a urethane binder is dependent on the nature of the operation and the

Table 2. Potential emissions from urethane binders.

Emission	PEL (OSHA)*	Source
Phenol	5 ppm-skin	Volatilization Decomposition
Formaldehyde	3 ppm	Volatilization Decomposition
Solvent	Various	Volatilization Decomposition
MDI	0.02 ppm C	Volatilization Decomposition
Triethylamine	25 ppm	Volatilization
Dimethylethylamine		Volatilization
Carbon monoxide	50 ppm	Decomposition
Carbon dioxide	5,000 ppm	Decomposition
Hydrocarbons	Various	Decomposition
Hydrogen cyanide	10 ppm	Decomposition
Ammonia	50 ppm	Decomposition
Smoke		Decomposition

*Permissible exposure limit.

particular stage of the foundry process involved. When sand is being mixed with binder materials, the volatile components can evaporate into the work environment. Similarly, volatiles can be produced while the sand-binder mix is being worked in preparation of the core or mold. Once the binder has set or cured, the components are chemically or physically entrapped and emissions by volatilization are extremely low.

During mixing, molding, coremaking and other operations prior to cure of the binder, the principal volatile component from the alkyd-isocyanate system is the aliphatic petroleum hydrocarbon solvent. Because this material has a low vapor pressure and a PEL of 500 ppm, exposure has not been a problem. When phenolic urethane binders are mixed with sand, potential emissions of phenol, formaldehyde and the solvent components are possible. These emissions are greatest for operations employing a high speed continuous mixer which sprays sand from the mixing chamber at a high rate. High sand temperature can increase the potential emissions. At such an operation, the operator stands close to the mixer discharge and works the sand onto the pattern or into the core box. Exposures under such working conditions can be significant and one usually needs to conduct a monitoring survey to establish the levels of airborne contaminants in the work environment. General exhaust in the work area may be adequate to control exposures below permissible exposure limits, however, when exposures are excessive further local ventilation is necessary. Exhaust ventilation at the discharge port of the mixer can be quite effective.

Organic isocyanates are toxic chemicals. They are respiratory irritants and potential sensitizers. The OSHA PEL for organic isocyanates is only 0.02 ppm (ceiling) and NIOSH has recommended lower exposure limits. Recognizing potential problems as a result of organic isocyanate exposure, urethane foundry binders are only formulated with the polymeric forms of MDI. The vapor pressure of these polymeric forms of MDI is in the neighborhood of 0.000024 mmHg at $75^{O}C$. With such a low vapor pressure, it is extremely unlikely that vapor concentration in a work area where no heat is involved could reach the PEL level of 0.02 ppm. Extensive monitoring of foundry mixing, coremaking and molding stations by Ashland Chemical Company and others has confirmed the very low likelihood of isocyanate exposure being a problem at these operations. In fact, essentially all monitoring results have been near or below the detectable limit of 0.002 ppm at such work stations.

Cold box coremaking presents a potential exposure hazard from the triethylamine or dimethylethylamine catalyst. These compounds are irritants of the mucous membranes and have very strong, unpleasant odors. They are also known to cause edema of the corneal membranes which results in blurred vision or the "blue haze" effect. Triethylamine has an OSHA established PEL of 25 ppm. Dimethylethylamine has no established PEL but based on limited data its toxicological properties appear similar to that of triethylamine which it resembles structurally and chemically. We recommend that exposures at the work station should be controlled to well below 10 ppm for either triethylamine or dimethylethylamine. Control of exposures to below 10 ppm is needed at any rate to provide a relatively pleasant work station free of strongly obnoxious odor. The odor thresholds for triethylamine and dimethylethylamine appear to be in the range of 1 ppm or less.

During pouring, cooling and shakeout operations involving urethane cores or molds, a wide range of degradation and volatile products are produced. These have been generally described in the published literature (1). As with any organic foundry binder, the range of thermal degradation products is quite broad and attempts to measure the full range of potential exposures in an operating foundry would be a task of great magnitude. We suggest that the initial focus should be on insuring that smoke and carbon monoxide levels are maintained within reasonable and acceptable limits. The composition of smoke from decomposing foundry binders is largely unknown at this time. Where urethane binders are used it is also important to ensure that levels of organic isocyanates are within exposure limits. MDI is formed at very low levels as a result of the thermal degradation processes occuring in urethane binders. Concentrations of MDI in excess of the 0.02 ppm PEL are possible when the work place has inadequate ventilation. Experience has shown that, with a reasonable amount of local and general exhaust ventilation, the exposure levels to MDI can be kept well below the established or recommended exposure limits.

MONITORING PROGRAM

Captive foundries and many independent jobbing foundries have capable industrial hygiene and safety staffs. As a supplier of foundry products, Ashland Chemical Company provides safety and health information to its customers in the form of material safety data sheets, labels, technical brochures and through seminars and personal communications. Foundries with in-house capabilities generally conduct their own monitoring surveys and establish engineering controls to ensure healthful work environments which at least meet minimum standards for occupational exposures. Foundries without in-house capabilities, especially in the industrial hygiene area, need support to recognize and evaluate potential exposure hazards and for recommendations regarding engineering controls and work practices. Ashland provides such a service by sending a qualified Industrial Hygienist to customer foundry plants to conduct preliminary monitoring surveys. The scope of such surveys is always tailored to the particular operation involved and the nature of the binder products that are employed. Results of such monitoring surveys are reported to appropriate foundry management along with interpretations as to the significance of the data and recommendations regarding engineering controls that should be considered. Frequently, followup surveys are conducted to ensure that engineering controls that were implemented are doing the job intended. Thereafter, we expect the foundry organization to follow up with any further required actions and to establish an ongoing program for monitoring their in-plant environment. Ashland's function here is that of technical service and is intended to assist the customer in recognizing and evaluating potential problems. It is not a substitute for a foundry's own in-house program in the areas of industrial hygiene or safety. We strongly recommend that foundries unable to provide this in-house capability should retain suitable outside help in the form of a consultant or independent laboratory.

MONITORING RESULTS

An initial summary of results of monitoring surveys in our customer plants was reported in 1974 (2). There was evidence at that time of potentially significant exposures to MDI in the foundry work environment. Exposures above the permissible exposure limit for MDI, however, were found only at pouring, cooling or shakeout stations.

Since that time, our ongoing program for inplant monitoring has established significant new data as is summarized in Tables 3, 4, 5, and 6. It is most noteworthy that in 29 iron and steel foundries using urethane binders, of a total of 203 samples taken for MDI measurement, only four samples showed airborne contaminant levels in excess of 0.02 ppm. Our measurements for MDI always include a simultaneous measurement for aromatic amine, calculated as methylene bisaniline (MBA) because organic amines are known interferences in the isocyanate determination. Of 185 samples collected in 28 foundries, 183 showed levels of MBA less than 0.1 ppm. The remaining two samples indicated levels of MBA in the range 0.1 to 0.2 ppm.

In the last few years, there has been expanded use of the phenolic urethane cold box system for production of cores to be used in gravity-fed, permanent mold aluminum casting applications. In these automated operations, cores are placed in the permanent molds which are at temperatures in the range of 316-427^{o}C (600 - 800^{o}F). After the mold closes, it is automatically poured and opened for ejection of the casting after a rather short solidification time of 1-2 minutes. Under these conditions, considerable thermal degradation of the core binder occurs. Because temperatures are relatively low, most of the degradation products escape unburned to the work environment. Smoke and decomposition products can be quite heavy as the casting is removed from the permanent mold and inspected prior to being placed on the cooling conveyor. Monitoring surveys have shown that the MDI concentration in these smokes can exceed 0.02 ppm. In eight foundries, of a total of 42 samples taken, 23 showed concentrations in excess of the PEL for MDI. Similarly, the concentrations of MBA were found to be correspondingly high, with seven of 40 samples showing levels in the range of 0.1 to 0.2 ppm and two samples being in excess of 0.2 ppm.

This data from the monitoring surveys in these new aluminum casting operations exposed a new potential hazard. Since these were all new operations, initial recognition of a potential problem was the observation of heavy smoke during the casting pickup and inspection operation. The results of our monitoring surveys alerted foundry management to the potential problem. In all cases actions have been, or presently are being, taken to bring these situations under control. Installation of suitable local exhaust ventilation has been effective in reducing these exposures to well below permissible exposure limits. While engineering controls were being implemented, foundry management prudently curtailed operations, required use of appropriate respirators for workers, or took other temporary control measures at these work stations. We believe that by prompt action on the part of foundry management, and Ashland as a supplier, this potential hazard was quickly recognized, evaluated and suitable engineering controls implemented.

Table 3. Summary of monitoring data for MDI/MBA*; iron and steel foundries.

	MDI	MBA
Total foundries	29	28
Total samples	203	185
No. in range N.D. to 0.005 ppm	185	
No. in range >0.005 to 0.02 ppm	14	
No. in range >0.02 ppm	4	
No. in range N.D. to 0.1 ppm		183
No. in range >0.1 to 0.2 ppm		2
No. in range >0.2 ppm		0

*MDI = Methylene bisphenyl-isocyanate.
*MBA = Methylene bisaniline.

Table 4. Summary of monitoring data for MDI/MBA*; aluminum foundries.

	MDI	MBA
Total foundries	8	7
Total samples	42	40
No. in range N.D. to 0.005 ppm	8	
No. in range >0.005 to 0.02 ppm	12	
No. in range >0.02 ppm	23	
No. in range N.D. to 0.1 ppm		31
No. in range >0.1 to 0.2 ppm		7
No. in range >0.2 ppm		2

*MDI = Methylene bisphenyl-isocyanate.
*MBA = Methylene bisaniline.

Table 5. Summary of monitoring data for phenol; iron, steel and aluminum foundries.

Total foundries	25
Total samples	102
No. in range N.D. to 1 ppm	95
No. in range >1 to 5 ppm	6
No. in range >5 ppm	1

Table 6. Summary of monitoring data for TEA/DMEA; iron, steel and aluminum foundries.

Total foundries	27
Total samples	210
No. in range N.D. to 5 ppm	100
No. in range >5 to 10 ppm	34
No. in range >10 to 25 ppm	51
No. in range >25 ppm	25

At mixing stations utilizing the phenolic urethane no-bake, exposures to phenol, formaldehyde and solvent vapors are the principal concerns. Our monitoring surveys have established that exposure levels to solvent vapors are generally well below the respective permissible exposure limits. Phenol exposure also appears not to be a problem. In 18 foundries, 90 samples were collected for phenol and in 85 of those the phenol concentration was less than 1 ppm. Five other samples showed concentrations in the range of 1-5 ppm and none were in excess of 5 ppm. Airborne formaldehyde at sand mixing stations employing phenolic urethane binders is difficult to monitor because of interference from phenol. Because of this interference, we have not been able to obtain monitoring data using long-term sampling techniques. Results from Dräger Tube measurements have indicated that the concentrations of formaldehyde at a phenolic urethane sand mixing station seldom exceed the permissible exposure limit of 3 ppm. In those few instances where formaldehyde levels did exceed 3 ppm, we were usually able to trace a potential problem to the use of hot sand which would increase the rate of evolution of formaldehyde. In those cases, suitable recommendations were made to foundry management to control the temperature of the sand going to the mixers more carefully.

A final potential exposure to be considered is that of triethylamine or dimethylethylamine at phenolic urethane cold box coremaking operations. One monitoring program has taken us to 27 foundries where 210 samples have been collected. A summary of the ranges of data obtained is shown in Table 6. Approximately 12% of the samples showed concentration levels in excess of 25 ppm with an additional 25% of the samples being in the range of 10 to 25 ppm. High amine levels at a phenolic urethane cold box work station are usually the result of leaking fittings, inadequate core box seals or excessive use of the amine catalyst. When this monitoring data was reported to foundry management, steps were taken to improve the engineering controls on the work operation. As a result, in almost all cases these excessive exposures were quickly brought under control. We continue to work with any of the foundries that have remaining problems.

SUMMARY

Urethane foundry binders are well established in production foundry operations. During 14 years of use and consumption of over 500 million pounds throughout the world, the record with regard to safety and health problems has been excellent.

Because of the composition of urethane binders, some potential hazards due to chemical exposures exist. Ashland Chemical Company has strived to provide its customers with adequate safety and health information regarding these products and to assist them in establishing safe operations. We have also provided extensive technical service by conducting monitoring surveys and working with foundry management to correct problem areas. Foundry management has done its part in recognizing that potential hazards could exist in the use of these products and has been diligent and prudent in taking management actions and effecting engineering controls to ensure safe and healthful work environments for its employees.

Monitoring data obtained during our surveys has established a history regarding contaminant levels in the foundry work environment and techniques for their control. It is expected that this program will continue and be of further value to the foundry industry in its continuing efforts to maintain safe working environments for its employees.

REFERENCES

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Division of Physical Sciences and Engineering
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NIOSH Project Officer: Dennis O'Brien
Project Manager: Robert C. Scholz

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