WEIGHT LOSS WHICH OCCURS DURING THE CURING PROCESS OF POWDER COATINGS

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TITLE: **Weight Loss Which Occurs During the Curing Process of Powder Coatings**

ABSTRACT:

As powder coatings continue to grow in the U. S. market, at over 12% per year, more interest has been shown in how much and what actually evolves during the cure of powder coatings.

Supposedly non-emissive chemistries such as TGIC cured systems, hybrids and epoxies actually lose approximately 1 percent weight during cure. Much of this weight loss can be attributed to absorbed moisture. Other materials given off during cure include oligomers, cyclic materials, etc.

Concern about E-caprolactam blocking agent evolved during the cure of PU powder coatings caused us to ask the question. How much E-caprolactam evolves during the cure of typical thin film PU powder coatings?

Some thin film PU powder coatings lose as little as 2 percent E-caprolactam during cure.

It is the purpose of this paper to quantify weight loss occurring during the curing process of powder coatings and to identify some of the principal components evolved during the curing process.

Introduction:

Powder coatings are known to provide many advantages:

economic
performance
efficiency
environmental

Powder coatings are truly unique among the coating options available to industry today. Powder coatings are essentially 100% solids. The other technologies used, are liquids. High solids, water borne, electrodeposition or UV all contain liquid which contribute to weight loss during cure. Weight loss during the cross-linking or curing process of thermosetting powder coatings is considerably less than the liquid compliant products used today.

So what we're dealing with in this paper is the relatively low weight loss that occurs during cure of a 100% solids material.

Weight loss during cure for various thermosetting powder coatings usually falls in the range of 1.0-10.0 percent by weight of the powder coating, with the majority of thermosetting powder coatings falling in the range of 1.0-5.0% weight loss during cure.

Concerns about the weight loss during the curing process of powder coatings center around:

Environmental
Health and Safety

Health and safety concerns about powder coatings must be considered in real world terms.

Questions should be answered about the possibility and route of exposure to potentially harmful materials.

Exposure to powder coating, materials evolved during cure, or combustion products can be prevented by:

Good work place practices
Dust control
Oven air locks
Oven exhaust

It is not the purpose of this paper to cover work place practices or dust control standards. Although some summarized information is necessary.

The current OSHA standard for **respirable** dusts, which all powder applicators are required to achieve, is set at 5mg/m^3. Spray booth units used in powder coating applications are covered by a National Fire Protection Association standard, NFPA 33. The standard specifically states in Chapter 13, section 5(E) "Ventilation for fluidized bed and electrostatic fluidized beds shall be designed to effectively prevent escape of any undeposited powder from the enclosure."

Powder coating units that are properly maintained according to manufactuer's instructions are intended to prevent the escape of powders into the surrounding space and should provide additional protection below 3mg/m^3.

For example, the current TLV (Threshold Limit Values) or OEL (Occupational Exposure Limit), recommended by European powder coating manufacturers and Ciba-Geigy Limited (under the auspices of CEPE) is 3mg/m^3 air for TGIC containing powder coatings.[2]

Health and Safety[6]

Ventilation should be sufficient to keep the workplace air free of hazardous materials. Nuisance dust levels must be kept below the industry maximum (10 mg/m^3).

Proper airflow must be maintained in powder coating spray booths to contain the powder. This prevents powder from contaminating the workplace air and creating additional exposure. It also prevents powders from being drawn into oven combustion areas where powder can be transformed to toxic combustion products.

Air from the workplace should always be flowing into the oven openings. Ovens should not be fuming into the workplace. Oven gas burners should be properly exhausted. This air should not be returned to the workplace. Oven cure zones should be exhausted. This air should not be returned to the workplace. One possible indication that an oven is not properly vented, is the presence of a haze in the workplace.

If there is any question about workplace air quality, an industrial hygienist should be consulted and specific measurements should be made.

The National Fire Protection Association in publication NFPA 86 specifies oven ventilation requirements for fire protection. NFPA 86 should be reviewed in its entirety. Some of the NFPA 86 recommendations (air intake basis at 70%F) and other considerations are as follows:

- One ft^3/min for every 5700 btu/hr oven capacity rating for removal of by-products of combustion of natural gas, plus

- 2.2 ft^3/min for every lb/hr of powder through the oven for removal of potential volatile compounds which may be generated in the powder curing operation.

- The workplace environment should be monitored to ensure that the combination of bake oven venting and room air turnover is sufficient to meet Permissible Exposure Limits (PEL) and other exposure limits for regulated substances as outlined on the powder MSDS (Material Safety Data Sheet) and in this publication.

To summarize the above data, one could say that:

- Good workplace ventilation is necessary.
- Powder should always be contained within the spray booth.
- Ovens should not be smoking or fuming into the workplace. (Exhaust rates should be adjusted to achieve this.)

Exposure to hazardous decomposition products can be avoided by providing proper cure oven exhaust and by not allowing powder to come in contact with flame in a direct fired gas oven or having powder come in contact with electric heating elements.

A good analogy of the toxic nature of oven combustion gases is burning firewood in a home fireplace. If the fireplace flue is not open, toxic combustion products, smoke, enters the home. People do not remain inside a smoke filled house, they either open the flue to properly ventilate the fireplace or leave the area.

The risks associated with burning a powder coating which is an organic material, or burning wood which is an organic material, are similar. Both produce toxic combustion products which can be harmful.

Environmental

Powder coatings have demonstrated in many applications that they offer improved performance and environmental compliance at lower cost.

Environmental impact. Probably the most widely discussed advantage of powder coatings is the potential for environmental compliance. The 1990 Clean Air Act Amendments have set the environmental standards for the rest of the century.

Tough new standards for VOC (volatile organic emissions) have been set by Title I of the 1990 Clean Air Act.

189 HAPs (hazardous air pollutants) are specified in Title III. Some of the HAPs described are routinely used in paints.4

E-caprolactam is listed as one of the 189 HAPs materials. (E-cap has since been de-listed.)

Since E-caprolactam is a solid at room temperature, it is difficult to believe that it would stay air borne for very long.

EPA officials that I have talked to, have said that E-caprolactam could be regulated as a particulate emission rather than a VOC.

Controls or limits could be set for regions or areas that have exceeded EPA standards for particulates.

To summarize the environmental impact of powder coatings:

Powder coatings are manufactured, applied and cured without solvents.

Powder coatings generate practically no VOC emissions.

Reclaim systems for powder overspray greatly reduce potential waste.

Powder coatings can be described as a complete environmental answer to the tough new standards.

A brief description of the various thermosetting powder coating chemistries is called for:

There are two distinct mechanisms at work during the curing process of thermosetting powder coatings:

- Crosslinking or curing via the **addition mechanism**. This process involves no reaction by-products and is described by some people as non-emissive.

- Crosslinking or curing via the **condensation mechanism.** This process results in the liberation of a reaction by-product.

  Reaction by-products can be water or methanol, for example.

- Crosslinking via chemically blocked curing agents utilizes the addition crosslinking mechanism, but liberates the blocking agent during the baking or curing process.

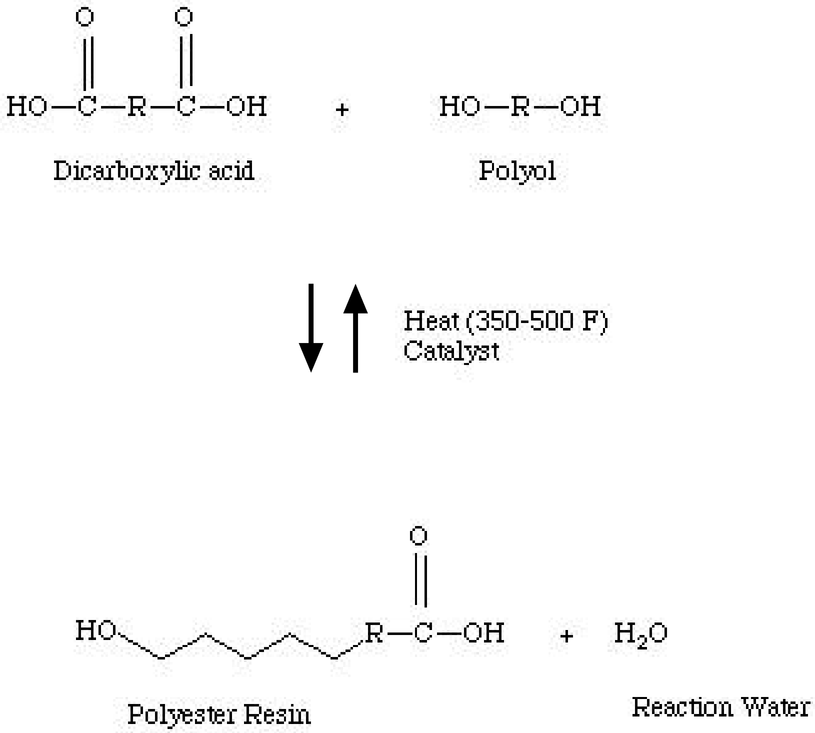
  As with most processes, there are advantages and disadvantages associated with blocked polymeric diisocyanates.

Powder coatings in the market place today can be defined by the two crosslinking (curing) mechanisms, addition and condensation.

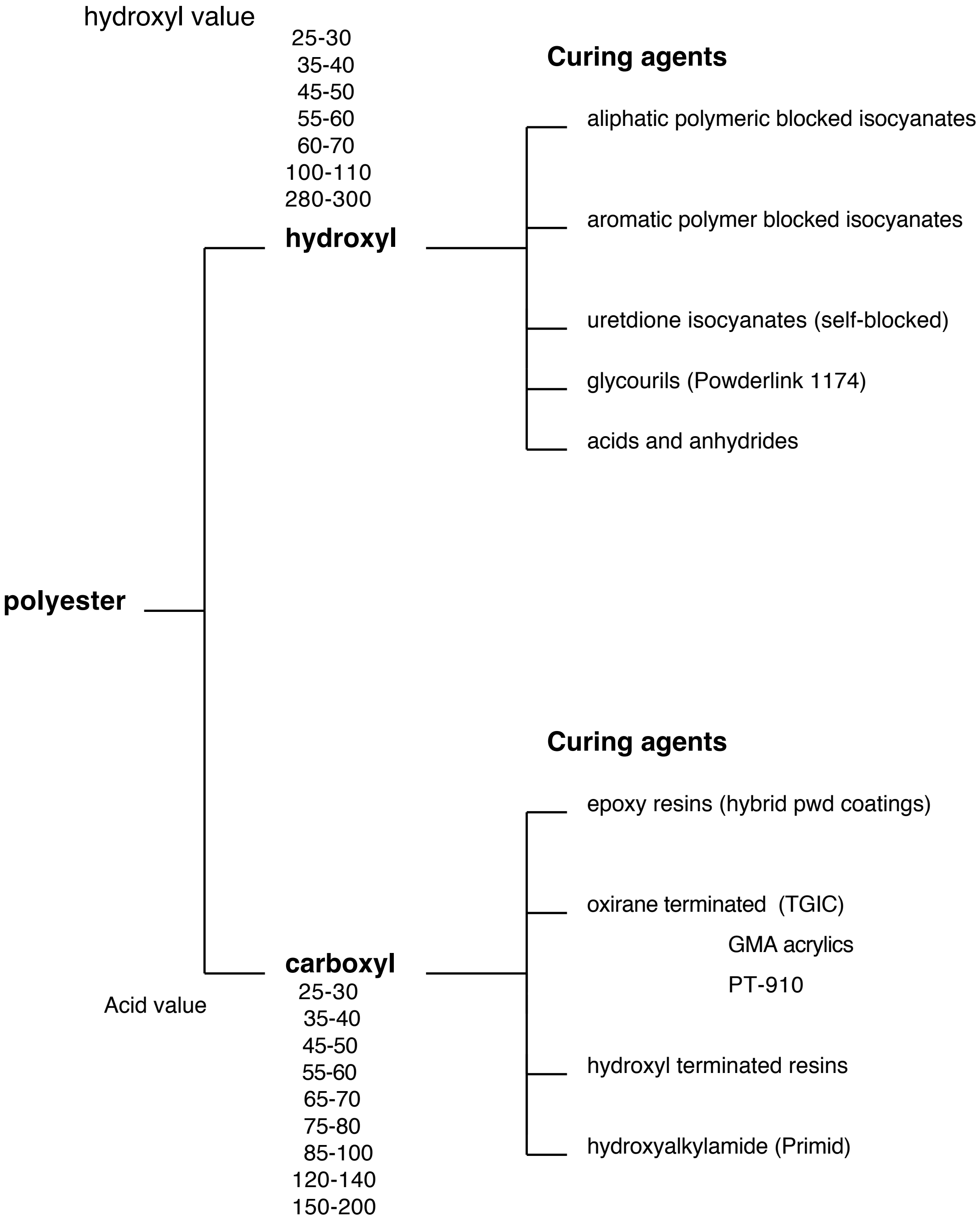
Powder Coating Type	Typical Curing (Cross-linking) Mechanism	Typical Reaction by-products
Epoxy powder coatings	Addition	traces of absorbed water
Hybrid (polyester/epoxies)	Addition	traces of absorbed water
Polyester/TGIC	Addition	traces of absorbed water
Polyester/urethane	Addition	traces of absorbed water blocking agent typically 2-6%
Polyester/HAA	Condensation	water 0.5-1.0% typically
Polyester/glycoluril	Condensation	Methanol typically 1-3%
GMA Acrylic/diacid	Addition	traces of absorbed water
OH Acrylic/urethane	Addition	traces of absorbed water blocking agent typically 2-6%

Polyester/urethane powder coatings are made from the following ingredients:

Polyester Resins: are most typically made by condensation reactions between multifunctional organic acids, anhydrides, polyols and esters.



Range of Polyesters With Crosslinker Options



Carboxyl Polyesters[3]

Carboxyl (acid) functional polyesters are available for various powder coating application. Powder coatings formulated with carboxyl functional polyesters fall into two categories:

Exterior Durable (Acid Values 20-35)	Polyesters/TGIC Cured Polyester/Hydroxyalkyl Amide Cured Hydroxyl Polyester Cured
Non-Exterior Durable (Acid Values 40 & greater)	"Hybrids", Epoxy cured

There is an overlap in the function of the TGIC (triglycidyl isocyanurate) cured carboxyl polyesters and the blocked polyisocyanate cured hydroxyl polyesters; both are used extensively for exterior durable applications. Durability is good to excellent for both the TGIC cured polyesters and the hydroxyl based systems.

Carboxyl functional polyesters cured with TGIC are typically used in applications where thick films are required. Recent advances in carboxyl polyester formulating have made thin film polyester/TGIC powder coatings a reality.

Hybrids are defined as carboxyl functional polyesters cured with epoxy resins. Mix ratios of polyesters to epoxies range from 80:20 to 40:60. Hybrids typically have better overbake resistance than epoxies.

A hybrid powder resin "clear" system cost is less than the epoxy "clear" system cost.

Hydroxyl Polyesters[3]

Hydroxyl polyesters can be cross-linked by blocked aliphatic polyisocyanates, blocked aromatic polyisocyanates, glycolurils, acids or anhydrides, and carboxyl polyesters.

Currently, in the United States, acids, anhydrides and carboxyl polyesters are not widely used as curing agents for polyester powder systems.

Many combinations are possible if blends of the polyesters and blocked polymeric isocyanate curing agents are considered. Where a high degree of exterior durability is required, aliphatic isocyanate based curing agents are used. In applications where less durability is required, aromatic isocyanate based curing agents are used. These systems have the added advantage of costing less than their aliphatic counterparts.

Polyester/urethanes provide advantages to the powder coatings formulator. Polyester/urethanes can be described as achieving the **ideal attributes** of a thermosetting coating; namely to be a highly reactive system during cure conditions and to be virtually unreactive during manufacture, storage and application. These ideals are achieved by the blocked polymeric isocyanate curing agents used with hydroxyl terminated polyesters. Today's world also seeks products which have a low order of toxicity. Polyester/urethane powder coatings meet this challenge. Blocking agents have been selected to present minimum risks to health and safety.

E-caprolactam or other blocking agents are chemically bound to the curing agent polymer until heated in the baking oven. Exposure to E-caprolactam or other blocking agents is possible if the curing/baking oven is not properly vented.6

Trace ppm levels of diisocyanate monomer can be present in oven exhaust gas. If a caprolactam blocked polyester urethane powder coating is decomposed from exposure to heat greater than 600%F, or burned, toxic combustion products will be formed. These toxic decomposition products are: carbon dioxide, carbon monoxide, nitrous oxides, hydrogen cyanide, isocyanate and various hydrocarbons.6

The Powder Coatings Institute, PCI, has published a "white paper" covering Polyester/urethane health and safety information. The conclusion is reached that polyester/urethane powder coatings are inherently safe when used properly.6

Some countries in Europe associated powder polyester urethanes with some not so safe liquid two component polyurethanes which can have substantial levels of monomeric isocyanate present.

This is not the case with the blocked polymeric isocyanate curing agents used in polyurethane powder coatings. Risks of exposure to monomeric isocyanates is minimal when using polyurethane powder coatings. The only possibility for exposure to isocyanate monomer occurs when polyurethane powder coatings are burned or otherwise thermally decomposed. Good oven exhaust will prevent exposure in this case.

Polymeric blocked isocyanate curing agents are well known in the powder coating industry. These compounds have been used for many years to produce polyester/urethane powder coating compositions. The most widely used polymeric blocked isocyanate curing agent is based on isophorone diisocyate and its higher functionality adducts. Some other polymeric blocked diisocyanate curing agents are based on e-caprolactam blocked methylene-bis-4-cyclohexyl diisocyanate, and toluene diisocyanate. Polyester/urethane powder coatings, used in the thin-film decorative market, represent approximately 25-30 percent of the volume in the North American market.

Other types of isocyanate blocking agents have been used with some success. These include ketoximes, such as methyl ethyl ketoxime. Isocyanates blocked with oximes deblock at temperatures lower than those required to deblock caprolactam-based curatives. Low temperature cures are achieved without sacrificing package stability.

TOXICOLOGICAL PROFILE OF THE BLOCKING AGENT E-CAPROLACTAM[6]

The toxicology of E-Caprolactam has been extensively investigated. The most likely route of exposure to powder coating applicators is through inhalation of vapors produced during baking of coated parts. The valid exposure limits at the moment have been established by ACGIH and OSHA: Vapor: 5ppm TWA, 10ppm STEL; Dust: 1mg/m^3 TWA, 3mg/m^3 STEL. (The current MAK value is 5 mg/m^3 for vapor and dust.)

Inhalation of caprolactam vapors may cause irritation of the mucous membranes of the nose, throat and respiratory tract. Prolonged exposure to high concentrations may cause nausea, vomiting, dizziness, headache and tremors.

For that reason, you have to make sure that during the curing process, no exhaust fumes from the oven get into the working area. This goes for all exhaust fumes no matter what kind of powder coating system will be used.

A LD$_{50}$ value for ingestion by rates has been reported to be 1155-2140 mg/kg.

The ACGIH has indicated in its 1986 Documentation that caprolactam is a dermal sensitizer. A producer of caprolactam, however, states that the studies cited do not support this contention but rather provide evidence that caprolactam causes dermatitis.

Numerous studies indicate that caprolactam is clearly non-carcinogenic, non-teratogenic, non-mutagenic and has a relatively low toxicity to humans.

To summarize what we know about E-caprolactam:

E-caprolactam or other blocking agents are chemically bound to the curing agent polymer until heated in the baking oven. Exposure to E-caprolactam or other blocking agents is possible if the curing/baking oven is not properly vented.

Since E-caprolactam is considered an irritant, avoid skin contact with E-caprolactam which may condense in oven air ducts or on roofs near oven exhausts. Avoid breathing oven exhaust or "smoke" from ovens that finds its way back into the workplace. Make sure that oven exhaust rates are sufficient to prevent "smoke" in the workplace.

To help gain a perspective about the oral toxicity of blocking agents used for polyester/urethane curing agents, review of the following data is necessary.[3]

APPROXIMATE ORAL ACUTE LD_{50}S OF A SELECTED VARIETY OF CHEMICALS

	LD50(MG/KG)
ETHYL ALCOHOL	10,000
POWDER LINK 1174 GLYCOURIL	7,100
PRIMID®XL-552	>5,000
SODIUM CHLORIDE	**4,000**
MEKO (METHYL ETHYL KETOXIME)	3,700
FERROUS SULFATE	1,500
E-CAPROLACTAM	**1,100**
PHENOBARBITAL SODIUM	150
DDT	100
PICROTOXIN	5
STRYCHNINE SULFATE	2
NICOTINE	1
D-TUBOCURARINE	0.5
HEMICHOLINIUM-3	0.2
TETRODOTOXIN	0.10
DIOXIN (TCDD)	0.001
BOTULINUS TOXIN	0.00001

BASED ON LOOMIS (1974)

One could reach the conclusion that E-caprolactam has an oral toxicity similar to sodium chloride (table salt).

Concern about E-caprolactam evolved during the curing of polyester/urethane powder coatings caused us to ask the question: How much E-caprolactam evolves from typical thin film polyester/urethanes during the baking process?[1]

Six powder coatings were prepared as follows:

	wt%
Binder	65.0
Acrynol 4F (flow control agent)	0.6
Benzoin (anti-pinholing agent)	0.6
TiO_2 (titanium dioxide pigment)	33.8
	100.0

Pigment to Binder Ratio = 33.8/66.2 = .51/1.0

These powder coating formulations were all processed in a Werner & Pfleiderer ZSK-30 twin screw extruder.

The resulting extrudate was cooled and ground into fine powder.

These powders were submitted to K & N Labs for thermogravimetric testing.

EXPERIMENTAL CONDITIONS[5]

Thermogravimetric Analysis

Procedure	K & N Method TGA-012
Run Conditions	40 to 190%C at 20%C/minute and hold for 37.5 minutes
Sample Matrix	Polymeric Powder Coatings

THERMOGRAVIMETRIC RESULTS[5]

Coating No.		Ratio PE to CA	Curing Agent	Theo.Wt Loss%	%Wt Loss	Adjusted %Wt Loss*
1.0	40 hydroxyl polyester	83:17	NI-2*	4.52	4.83	3.73
1.1	22 hydroxyl polyester	90:10	NI-2	2.66	3.34	2.24
1.2	40 hydroxyl polyester (TMA-free)	84:16	NI-2	4.25	4.87	3.77
1.3	36 acid value polyester	93:7	PT-810 TGIC[5]	0.0	1.12	.02
1.4	37 acid value polyester	95:5	PRIMID® XL-552[11]	0.70	1.70	.60
1.5	40 hydroxyl polyester	87:13	BF-1540 uretdione[8]	0.0	1.20	.10

***Note:** NI-2 is a aliphatic polymeric blocked isocyanate curing agent from RUCO Polymer Corp.

Typical blocked isocyanates contain approximately 40% reacted caprolactam. These curatives are used at a level of up to 60% of the total resin plus curative. In the most common systems, the curative is about 10% to 20% of the sum of resin plus curative.

***Note:** Adjusted weight loss was derived by subtracting 1.1% from % wt loss data. (This is wt loss associated with absorbed water, etc.)

Thermogravimetric Results - Conclusions:

- Actual weight loss during cure exceeded the theoretical amounts.
- Since the two non-emissive powder coatings, Coating No. 1.3 and 1.5 both lost over 1.0 percent weight during the baking process, it can be postulated that the weight loss in coatings 1.0, 1.1 and 1.2 is not all e-caprolactam.
- Some of the e-caprolactam stays in the powder coating.

Note:

A recent Gas chromatograph/Mass Spec study of volatiles released during the curing of typical powder coatings at elevated temperature detected IPDI at a level of 2% of total volatiles or .0004 parts by volume.
The conditions used to volatilize the powder coating could have inadvertantly decomposed some of the polymers.

CONCLUSIONS

- Polyester urethane (PU) powder coatings can be formulated to lose 2 percent weight during cure. (These coatings could be used anywhere the "non-emissive" systems are used.)

- E-caprolactam blocked powder coating curing agents are practically non-toxic.

- Exposure to hazardous decomposition products can be avoided by providing proper oven exhaust.

- Avoid breathing oven exhaust or "smoke".

- Good workplace ventilation is necessary.

- Powder coatings should always be contained within the spray booth.

- Ovens should not be fuming into the workplace.

REFERENCES

1. ALLIED-SIGNAL REPORT TO RUCO & CARGILL; Study of blocked isocyanate curative deblocking, Volatilization and volatiles, March 23, 1990.

2. Ciba-Geigy Corporation, 1994 Another Tempest in a Teapot, The TGIC (Araldite® PT-810) Issue

3. Danick, Chuck, Polyester/Urethane Powder Coatings, Presented at the 13th International Conference on Powder Coatings, Brussels Belgium Nov. 15-17, 1993, Sponsored by PRA.

4. Hay, Malcolm, POWDER AND AUTOMOTIVE APPLICATIONS, Products Finishing pp 66-70, April, 1992.

5. K & N Labs, Thermogravimetric Analysis, Volatiles by Thermogravimetric Analysis Lab No. R 2901 and R 1203, September 24, 1993 and August 28, 1989.

6. Powder Coatings Institute, Polyester Urethane Powder Coatings Health and Safety Information, Technical Brief No. 18.

7. Rohm and Haas, Primid® XL-552, Product Literature.

8. RUCO Polymer Corp., report to Morton Thiokol on monomeric diisocyanate detection via HPLC for IPDI and TDI, October 26, 1988.