ROLE OF MOISTURE IN PROCESSING, APPLICATION, AND CURE OF 2K POLYURETHANE COATINGS

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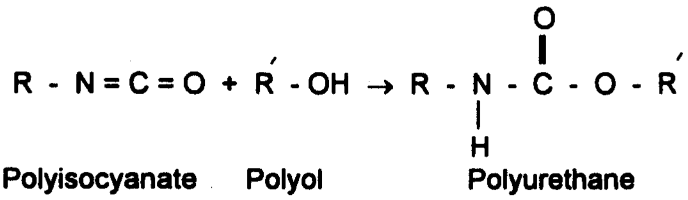
INTRODUCTION

This discussion is based upon experience with and primarily applicable to high gloss, high solids exterior automotive type, two component polyurethane coatings for plastics which are typically force cured at low bake temperatures, 150 to 190°F (66 to 88°C), for relatively short times, 15 to 60 minutes, depending on specific formulation or process requirements. Such products are usually applied with two component mixing equipment, wherein the polyol component and polyisocyanate hardener component are fed separately into a static mixing tube just prior to spraying. This is in contrast to one component polyurethanes of which there are generally three types. One type is designed to cure at ambient or low temperatures in the presence of moisture, thus the term "moisture cured urethanes". Another type must be cured at fairly high temperatures, 275°F (132°C) or above, based on blocked polyisocyanate chemistries. The third are low solids lacquers which are already crosslinked and simply deposited and dried.

Being exterior type coatings, aliphatic rather than aromatic type polyisocyante prepolymer components are used for this technology. That is, polyisocyanate prepolymer based on hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI) rather than the toluene diisocyanate (TDI) based prepolmers often used for interior and some general industrial applications where exposure to ultraviolet light is minimal. The TDI based products discolor and degrade when exposed to exterior sunlight, while HDI and IPDI products do not, relatively speaking.

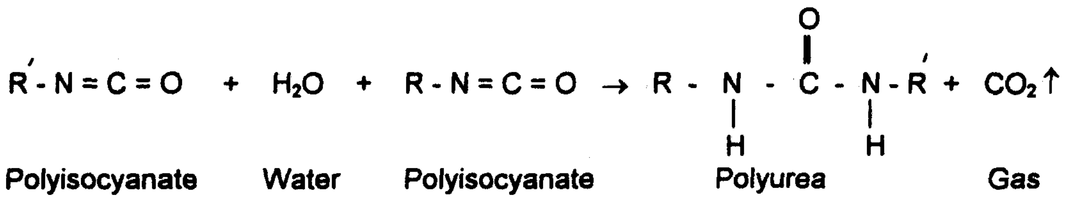
The primary simplified chemical reactions of concern for 2k polyurethanes are those for the urethane formation and the polyurea formation reactions as follows:

(1)



$$R-N=C=O+R'-OH \rightarrow R-\underset{\overset{|}{H}}{N}-\overset{\overset{O}{|}}{C}-O-R'$$

(2)



$$R'-N=C=O + H_2O + R-N=C=O \rightarrow R-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-\underset{H}{\underset{|}{N}}-R' + CO_2\uparrow$$

The chemical and physical ramifications of these reaction will be touched upon as we discuss separately the role of moisture in three areas of processing, application, and cure.

MANUFACTURING PROCESS

Obviously when discussing the manufacturing of 2k polyurethanes, we must discuss two components, the polyol and the polyisocyante sides as follows:

Polyol Component

This component may be clear or pigmented, but must contain a hydroxy functional resin or polymer, as the vehicle or binder, in order that it may be crosslinked by the polyisocyanate as in reaction (1) described above. Good manufacturing practice suggests that mills, vessels, and raw materials be dry prior to use. Urethane grade solvents, water and alcohol free, are generally recommended and available.

The moisture content of urethane grade solvents is considered to be 500 ppm maximum. Alcohols, including glycol ethers, are to be avoided, as they are monofunctional and monomeric, and as such, then, are essentially chain stoppers in the urethane reaction. That is, they do not crosslink nor add significantly to polymer backbone molecular structure. In large amounts, alcohols will essentially block the cure. Indeed, one recommends the addition of isopropanol to purged 2k urethanes from the spray application lines when it is desired to keep the mixed waste in a liquid state prior to reclamation or disposal.

Some moisture, that absorbed from the air, and that naturally absorbed on the surface of most pigments, cannot be avoided. It is not unusual for the moisture content of completed polyol side products to reach 0.1% for clears and 0.5% for highly pigmented products. And that is OK. The objective is to keep these products as dry as possible, in order that they can better tolerate water contamination which may occur later. This will be discussed in more detail in the Application Process section.

Polyisocyanate Hardener Component

This component is generally supplied as a fairly high solids solution of polyisocyanate, 60% non-volatile, having been let down in certified urethane grade solvents, processed and stored under a dry nitrogen "blanket".

Both incoming raw material and finished letdown should be gel free, since hardener gels are sometimes found as particulate defects or at the center of fisheyes or craters in applied 2k polyurethane coatings. This is best accomplished by processing the product in a closed loop dry nitrogen charged system which includes 1 to 5 micron cartridge filtration capability. Hardener gels are believed to form at static liquid-air interfaces where moist air has time to react with the polyisocyanate by reaction (2) to form an insoluble polyurea species. This would tend to occur in the head space of vessels or in pipes, hoses, and connectors wetted with polyisocyanate and exposed over time to moist air. The insoluble gels once formed, are believed to become entrained in the hardener solution primarily by physical or mechanical means.

Moisture in the bulk of the hardener solution, the homogeneous solution phase, would be expected rather to react to simply raise the overall viscosity of the solution and produce carbon dioxide gas. In a closed system, pressure would build up due to the CO_2 gas evolution. This would readily be noticed by bulging, and/or popping of lids on typical quart or gallon double-tite containers, creating a potential flammability, if not explosion hazard in storage areas. Under these conditions, hardener gels, per se, would not be expected to form until near the solidification point, at or around the 1% moisture content level.

In regard to higher concentration of moisture, droplets of water entering the hardener solution without agitation, will first form polyurea balloons around the droplet, eventually becoming large solid polyurea spheres. If not filtered out, these would likely appear as dirt or particulate defects on painted parts. If on the other hand, as mentioned above, the droplets are quickly dispersed and dissolved in the hardener solution, up to saturation, viscosity increase will be the observation, followed by solidification if total moisture content has reached approximately one percent or more.

Back to avoiding insoluble polyurea particles becoming entrained in the hardener solution, one has two alternatives: (A) either clean each time and/or use completely new vessels and transfer hoses during each manufacturing sequence or, (B) maintain closed loop system into which moist air is never allowed to enter. This means that with hardener product supplied in returnable totes, that the totes must be kept under dry nitrogen pressure during discharge, and returned in a sealed, dry nitrogen pressurized condition. Outer connectors and valves exposed to moist air during return and storage of "empty" totes must be removed, cleaned, or replaced.

It must also be pointed out that our common use of the term nitrogen blanket is somewhat of a misnomer, as nitrogen doesn't really form a blanket as it is indeed slightly lighter than air. Special effort is needed to be sure that "all" air in hardener solution vessels is completely displaced by the dry nitrogen through an infinite dilution procedure wherein valves or baffles prevent reentry of air during the process. Once air has entered a vessel, simply creating a positive pressure by addition of nitrogen does not itself assure that air is no longer present in the vessel.

APPLICATION PROCESS

Once paint products are manufactured and delivered in a "dry" condition, what then is the role of moisture in the finishers paint kitchen, liquid supply systems, at the spray gun, and in his spraybooth? Most important here is avoiding discreet particles of water getting to the painted part. Once on the part or in the applied film, water drops are seen as craters or pops, due either to separation of the coating from the water droplet or due to reaction of the polyisocyanate with the water to create a discreet bubble of carbon dioxide gas. A homogeneous solution of small amounts of water on the other hand would not be likely to separate, cause craters, or create more than only microscopic discreet carbon dioxide bubbles, reacting more on a molecular level.

How then do we avoid generating discreet particles of water in our painting system. First, the water contamination level must be kept low, below the saturation point for the paint. Typical high solids clearcoats are compatible with no more than one to two percent water. Solid colors with inorganic pigmentation can perhaps tolerate a little more. In this regard, it might be surprising to some that the tolerance of 2k polyurethanes for water is so low, given that somewhat polar solvents must be used to dissolve the somewhat polar resin and polymer components. However, perhaps it should not be surprising, given as discussed in the Manufacturing Process section, that the really polar solvents with which water would be most compatible, cannot be used. We are talking about the alcohols and the ether alcohols which are so common to other coating technologies. Table 1 lists the amounts of water which can be held by various individual solvents and perhaps illustrates this point. The higher solids levels of today's 2k polyurethane coatings also contributes to this intolerance for water, the polymer itself having little tolerance for water and being itself at high concentrations.

TABLE 1 SOLUBILITY OF WATER IN ORGANIC SOLVENTS

Acetone	Infinite
Methyl Ethyl Ketone	12.5%
Cyclohexanone	8.0%
Propylene Glycol Methyl Ether Acetate	5.9%
Dibasic Esters	3.1%
n-Butyl Acetate	1.6%
Ethylene Glycol Butyl Ether Acetate	1.6%
Methyl Amyl Ketone	1.3%
2-Ethylhexyl Acetate	0.9%
Alkyl Acetates*	0.6%
Aromatics	Insoluble

*EXXATE® family of esters from Exxon Chemicals

We will now discuss specific concerns or issues with moisture at the various stages in the application process as follows:

Paint Kitchen

To avoid moisture contamination above the saturation point, paint should be reduced only with urethane grade thinner in clean, dry vats. Vats should be sealed and protected from water condensates which might leak into vats from overhead pumps, pipes, or air motors.

The polyisocyanate hardener system should be specifically designed and compatible with the product delivery system in a closed loop configuration continuously charged with a slight pressure of dry nitrogen as discussed in the Manufacturing Process section. It may be designed in what we commonly call a dead head system where the nitrogen is used to push the hardener to the static mix heads prior to the spray guns, or it may be designed as a circulating system so long as a dry nitrogen charge is maintained to exclude entry of moist ambient air.

All the warnings given in the Manufacturing Process section as to excluding moist air and replacing or cleaning outer connectors and valves "wetted" with hardener solution and exposed to moist air, apply here as well. Where hardener is supplied in drums and drawn off for use over an extended period of time, transfer vessels should be freshly cleaned prior to each use and the drum should be facilitized so that the gas displacing the draw off be dry nitrogen or dry air. One suggestion for accomplishing this would be installation of a desiccant drier device in the upper bung of the drum to dry the air prior to it being pulled into the drum by the product drawoff.

Spraybooth

Spraybooths for automated automotive finish lines are generally temperature and humidity controlled for uniformity of application and film formation. Such booths are typically controlled around 75°F (24°C) at relative humidities of 50 to 65%. Humidities above 50% RH are believed to reduce build up of static charges on parts and thus reduce attraction of dirt to the parts. Variations in humidity tend to vary evaporation of organic solvents to some extent, though not to the direct degree as it does for water as a solvent in waterborne coatings.

Those are the normal conditions. Under those conditions then, what are the other situations or concerns with water during spraying of 2k polyurethane coatings?

As is true of most coatings, the compressed air used for spray atomization must be water and oil free. Discreet droplets of water going onto the sprayed parts, as mentioned earlier will inevitably cause either craters or pops, and therefore is obviously to be avoided.

Other sources of water droplets during spraying can be residual powerwash rinse water, splashes from baffles or irregular build-ups behind the water curtain or in water wash stream in spray booth (sometimes aggravated by electrostatic charge attraction on parts), leaks in the roof coupled with leaky seams in the spray booth itself, condensation drops from cold spots on booth ceiling, and even condensation in spray cone due to evaporative cooling below dew point of booth air.

Before leaving the spraybooth and beginning a discussion of the 2k polyurethane cure process itself, it should be stated that spraybooth humidity can play a role in the cure mechanism. This will be discussed in more detail as the relationship of moisture in the cure reaction is more fully developed.

CURE PROCESS

Two component polyurethane coatings will cure under a wide range of time and temperature conditions, from air dry to high bake. In the past it was generally believed to end up at basically the same point after a two day to two week ambient post cure period. From the standpoint of meeting normal use or specification requirements, that still appears to be the case. However, recent experience with variations in recoatability has led to the discovery that final film characteristics do vary with the cure process.

The major factor in these variations has indeed been shown to be the degree to which moisture has been allowed to participate in the cure. Or another way of putting it: To what degree the polyurea reaction (2) has been able to compete with the urethane reaction (1) Or: To what degree the water has been able to compete with the polyol for the isocyanate.

There are three periods in the cure process which have been considered as follows:

Spraying

As mentioned earlier, laboratory experience has demonstrated a variation in final film properties and recoatability of a particular coating and color with product sprayed under relatively low humidity booth conditions versus the same coating and color sprayed under normal 60 to 65% RH conditions, everything else being equal. This was concluded to be due to the likely greater amount of water contained by the wet film sprayed under the higher humidity conditions, giving the polyurea reaction (2) a head start so to speak, once the cure begins. This would be primarily because more moisture is already present in the bulk portions of the uncured film, and does not need to diffuse into the film during bake. That will be discussed next.

Bake Oven

Based upon field experience, later duplicated in laboratory experiments replicating the field condition, parts painted with some specific colors overbaked under extreme Winter conditions consistently exhibited recoatability problems, while the same colors overbaked under Summer conditions did not. Here again, the difference in conditions are clearly only differences in the moisture content of the Winter and Summer air available to the oven. Table 2 summarizes typical ambient air humidities for Summers and Winters in two US locations.

Table 2 Typical* Ambient Air Humidities

Season and Location	Average Temperature	Average Relative Humidity	Average RH Adjusted to 75°F	Average Dew Point	Average Water Content
Summer (July)					
Evansville, IN	79°F (26°C)	75%	86%	70°F (21°C)	1.6%
Detroit, MI	73°F (23°C)	71%	68%	64°F (18°C)	1.3%
Winter (January)					
Evansville, IN	35°F (2°C)	74%	17%	26°F (-3°C)	0.3%
Detroit, MI	25°F(-4°C)	77%	13%	20°F (-7°C)	0.2%

*Five Year Ave, National Weather Service Summaries,
Estimated by Traci Pearce & Jim McGinness

To overcome this variation in recoatability, a humidification system was installed in the bake oven by the finisher to maintain Summer humidity conditions in their oven year round. The recoatability problem sometimes experienced in Winter when parts painted with certain coating formulations were overbaked was thereby eliminated. The humidified oven also generally widened the recoat window for parts with the standard 30 minutes bake with that particular system.

The humidified oven parameters are summarized in Table 3. A recent paper by the author provides a case history of that overbake/recoat problem resolution in detail.$^{-1}$

Table 3 Summary of Humidified Bake Oven Parameters**

Set Points	4% RH @ 180°F (82°C) or 65°F (18°C) Dew Point
Oven Air Volume	58,000 ft ^{3}
Oven Exhaust Rate	5,000 ft ^{3} per minute
Heat Output, Peak	12 million Btu's per hour
Water Input as Steam	258 lbs water per hour
Steam Supply	11 psi, 3 in line, 2 in valve
Gas Fired Ovens	Maxon Series 400 Oven Packs, 3 zones
Steam Control	Two Armstrong Series 80/90 Manifolds, Model HEM-94 Control Valve
Automatic Humidity Controller	Honeywell VOC 3000 Single input, proportional output, 4-20 milliamp
Optional Humidity Gauge	Solomat® Model MPM 500e with Model 358 RHX high temp probe

** Estimated Average Winter Operation

Post Cure

As stated earlier, 2k polyurethane coatings eventually cure to approximately the same point whether air dried, low baked, or high baked, subject to an ambient post cure period of a week or two. Table 4 provides a cure profile for a 2k polyurethane, the one described above, based upon measuring the loss of the isocyanate group at 2280 cm^{-1} in the FTIR spectrum of the curing clearcoat.

Table 4 Cure Profile/Isocyanate Consumption

Cure Interval	Dry Oven	Wet Oven
Wet as Sprayed	0%	0%
12 Min. Warm Flash	3%	0%
30 Min. Bake 180°F (82°C)	39%	42%
3 Hr. Bake 180°F (82°C)	70%	77%
One Week Post Cure	100%	100%

Table 5 provides data on another 2k polyurethane cure study based upon Sward hardness measurements. In this case three different bake temperatures were used with relative humidity of ambient air held constant and bake times of thirty minutes. These results again support the point that 2k polyrethanes generally do achieve the same ultimate cure properties after a week or two when cured under the same humidity conditions. Therein lies one of the significant advantages of 2k polyurethane over high bake 1k acid cured thermoset enamels. If the latter do not see adequate bake, they do not cure.

Table 5 Cure Profile/Sward Hardness

	Bake Temperatures for 30 Minutes		
Age After Bake	After 170°F(77°C)	After 190°F (88°C)	After 250°F (121°C)
Initial	1	2	8
3 Days	3	4	7.6
6 Days	9.6	9.3	10
10 Days	9.3	10	10.6
14 Days	9.3	11	11.6

Internal Lab Study, EA13410, by R. Pierce
Materials were 2k clearcoat, white 2k basecoat, and adhesion promoter on a TPO substrate.
Higher Sward numbers indicates greater hardness.

Given the opportunity to diffuse into the partially cured film, moisture is believed to play a significant role in the final crosslinking of the polyurethane coating over time. The extent of this is dependent somewhat upon the degree and type of cure achieved in the oven versus the ambient air moisture content during post cure. Under certain conditions with some of the products in the overbake/recoat problem described above in the Bake Oven section, recoat problems were even experienced with standard bake in non-humidified oven after a long post cure period. Those particular post cure conditions were very cold, dry weather during the standard bake and following for an extended period during post cure. Such parts had to be surface treated before they could be repainted. This was not necessary for parts painted and postcured during warmer periods.

One final note, lest their be concern that "Summer cured" product might be inferior to "Winter cured" product, it should be pointed out that the difference in recoatability is believed to be due mostly to slight differences in solvent resistance. As for weatherability, it has fortunately been shown that the polyurea product, which forms when water reacts with aliphatic polyisocyante, has weathering characteristics similar to the pure urethane component.

SUMMARY & CONCLUSIONS

Moisture plays some role in all aspects of the manufacture, processing, application, and cure of 2k polyurethanes. It is important to understand exactly where moisture must be avoided, where it is of little concern, and where it indeed might be of benefit. The purpose of this paper was to try to provide that information in an understandable manner.

The primary places that water is to be avoided is in processing the hardener and in spraying the coating. In this manner, craters are eliminated. Humidity can be an advantage in the spraybooth to reduce static charges and dirt pickup. In one case history reported, humidification of the bake oven during Winter months resolved an otherwise troublesome recoatability problem.

References

1. McGinness, J.D., "Cure and Recoat Mechanism of 2K Polyurethane Topcoats", 950803, SAE, Detroit, MI 1995.