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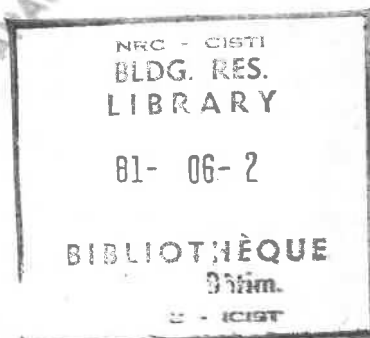
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**ATMOSPHERIC GASES AND THE
HARDENING OF AN AMINE-CURED EPOXY
COATING**

by S.G. Croll

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SOMMAIRE

En atmosphère de dioxyde de carbone humide, le durcissement d'une résine époxyde liquide traitée avec de la diéthylène-triamine est fortement inhibé. Les autres principaux constituants de l'air, que ce dernier soit sec ou humide, n'exercent aucun effet. Étant donné que les feuil minces sont facilement imprégnés par le dioxyde de carbone et la vapeur d'eau contenus dans l'atmosphère, ils durcissent plus lentement que les feuil épais, comme on le constate dans la pratique. L'eau et le dioxyde de carbone agissent ensemble pour produire un "pseudo-réseau cristallin" de l'amine, bloquant ainsi son hydrogène actif qui, autrement, provoquerait la réticulation de la résine. La réaction semble réversible et, dans l'air normal, elle ne fait que ralentir le processus de réticulation des feuil minces d'époxy.

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Atmospheric Gases and the Hardening Of an Amine-Cured Epoxy Coating

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National Research Council of Canada*

An atmosphere of humid carbon dioxide greatly inhibits the hardening of a liquid epoxy resin cured with diethylenetriamine. Other major components of air, whether dry or moist, do not produce an effect. Because thin films are readily permeated by carbon dioxide and water from the atmosphere, they harden more slowly than do thick films, as is found in practice. Water and carbon dioxide act together producing a network salt of the amine thus blocking its active hydrogen which would otherwise crosslink the resin. The reaction appears to be reversible and in normal air merely slows the crosslinking of thin epoxy films.

INTRODUCTION

It is commonly recognized that many "cold" curing epoxy coatings and adhesives cure faster under normal ambient conditions if applied in thicker films. One might expect that this would be explained by the exothermic nature of the crosslinking reaction: presumably thicker coatings would heat up due to slower heat loss, thus accelerating the crosslinking process. A previous study¹ on the residual stress developed in Epon® 828 cured with diethylenetriamine (DETA) showed that the temperature increase in this case was negligible and could not account for the differences found between thick and thin coatings. It was suggested that diffusion of water, etc., from the ambient atmosphere was more likely to cause the difference in behavior.

Following a suggestion by Ashton,² that carbon dioxide may react with the basic amine or that water vapor might be absorbed by it and thus affect the curing of this system, a more detailed investigation into the effect of various atmospheric gases upon the curing of Epon 828 by DETA was made and is reported here. In fact, the use

of carbon dioxide to extend the pot life of epoxy/amine formulations has been proposed.³

In this investigation, the cure of the coating was followed by monitoring hardness as a function of time and coating thickness.

EXPERIMENTAL

In all cases, the Epon 828 was mixed for one minute at a particular rate with 11 parts per hundred of DETA. After standing for 15 min, coatings of various thicknesses were drawn down on flat glass substrates 3 mm thick. All the experiments were performed at a temperature of $22 (\pm 1)^\circ\text{C}$.

The hardness of the curing coating was measured to be the depth of penetration of a cone attached to a micrometer dial gauge during 20 seconds. The apparatus was that used in ASTM D1005 for film thickness except that the flat pressor plate was replaced by a cone with a 1.19 mm radius ball end. By gently lowering the gauge foot, using the lever, it was quite easy to see on the dial at what point it first touched the coating. The pressure on the foot was such that the penetration into the coating could be conveniently measured at 20 seconds. All the hardness results are presented as depth of penetration (μm).

The relative humidity for the tests carried out in the laboratory under normal air conditions was $50\% (\pm 2\%)$. For experiments in particular atmospheres, the apparatus and coating mixture, etc., were transferred to a glove box, wherein the coatings were mixed and measured. When a dry atmosphere was required, the nominally dry gas from a cylinder was passed over a bed of magnesium perchlorate to ensure dryness. By this means the humidity in the glove box was maintained at much less than 1% RH. For all tests the glove box was kept under a slight positive pressure to prevent changes in the atmosphere due to leaks from the outside. To maintain a humid atmosphere inside, the gas was passed over a stirred, saturated solution of sodium bromide. In a sealed environment this would produce 57% RH, but the actual humidity varied from 50 to 57% depending on the rate at

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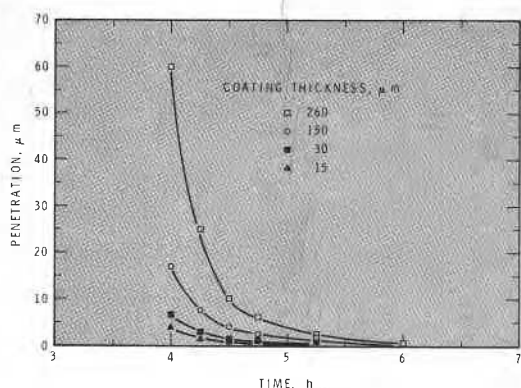


Figure 1—Hardening of epoxy-DETA coatings in an atmosphere of dry nitrogen

which the gas was bled into the glove box. Experimental results did not seem to be affected by this range in humidity (50 to 57%).

RESULTS AND DISCUSSION

In all the graphs presented here, the data omitted at short times corresponds to the gauge foot completely penetrating the coating and coming to rest on the glass substrate within 20 seconds, or to the foot penetrating too quickly for an accurate reading to be made.

Hardening in Dry Nitrogen

In *Figure 1*, the hardening of films of various thicknesses is presented as a function of time, under an atmosphere of dry nitrogen. There is no great difference in the time taken for the coating to harden to a small penetration value. Thicker coatings give higher values of penetration because there is more compressible material under the gauge foot. Also the coating material has more opportunity to flow away from the gauge foot, and, thus, allow penetration, because it is more remote from the constraint imposed by adhesion to the rigid substrate.

It seems that, in this case, the thin coatings harden over the initial 4- to 5-hr period just as fast as the thick coatings, which is consistent with other findings.⁴

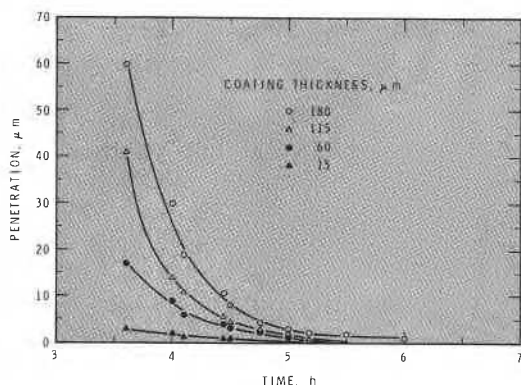


Figure 2—Hardening of epoxy-DETA coatings in an atmosphere of dry carbon dioxide

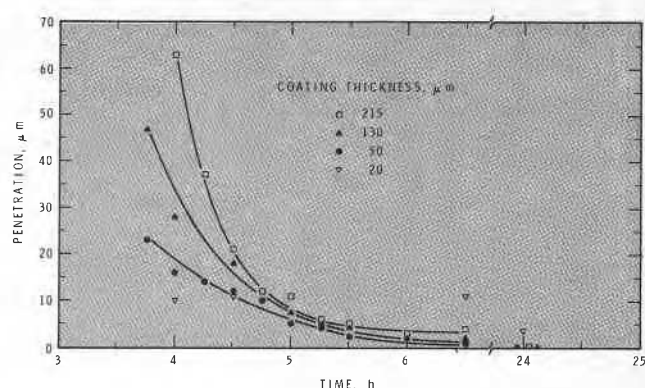


Figure 3—Hardening of epoxy-DETA coatings in an atmosphere of dry air (1% RH)

Hardening in Dry Carbon Dioxide

These data are presented in *Figure 2*. The behavior is essentially identical to that under dry nitrogen.

Hardening in Dry Air

Unfortunately, it was impossible to obtain air as dry as the other gases and the humidity remained about 1% RH. The data, however, (*Figure 3*), largely follow that of the other dry gases (except for the very thinnest coating). Because a glove box full of oxygen would be rather hazardous, the effect of oxygen can only be deduced indirectly from this dry air data. It is probable that dry oxygen has no effect on the hardening of the epoxy coatings.

Hardening in Air of 50% RH

This represents the normal state of affairs. As is common experience, the thin coatings take much longer to harden than do the thick coatings (see *Figure 4*). In fact, the order in which the coatings harden is reversed from that found under the dry gases. The thin coatings, $<25\mu\text{m}$, require days to harden even to penetration values as high as $5\mu\text{m}$ and after many days harden to a penetration of $1\mu\text{m}$. The thickest coating, however, hardened almost as rapidly as it did under dry gases.

It is obvious that the hardening of the coatings is affected by absorption of moisture from the atmosphere, by itself or in combination with another component gas. The thin coatings are affected the most because the moisture can diffuse more completely throughout their thickness.

In order to investigate the effect of moisture, hardening under moist component gases ($\sim 50\%$ RH) was measured, as presented in the following sections.

Hardening in a Humid Nitrogen Atmosphere

The results are presented in *Figure 5*. All the curves for penetration attain a value of $<1\mu\text{m}$ in 24 hr.

Here, the hardening of the thick coatings ($\geq 65\mu\text{m}$) follows the same pattern as under dry nitrogen, i.e., the thicker coatings allow more penetration at a specified time. Films of low thickness ($\leq 25\mu\text{m}$) follow the pattern

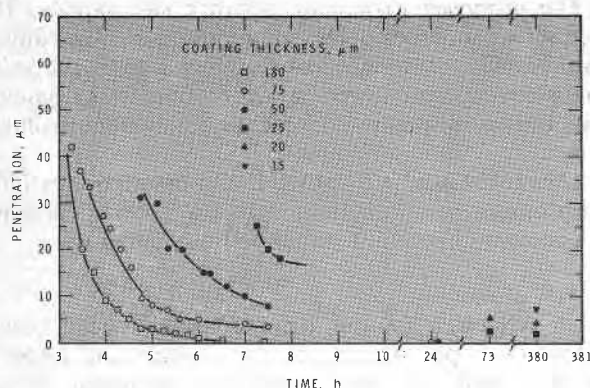


Figure 4—Hardening of epoxy-DETA coatings in air (50% RH)

of the humid air data with the thicker ones allowing more penetration at a particular time. The effect, however, is small and the delay in hardening is slight.

As nitrogen is chemically unreactive, it would not be expected to combine with the absorbed water or to react with either the epoxy or hardener. Thus the differences in curing must be due to water alone. It is unlikely that reaction occurs between water and epoxy under normal conditions, although both resin and hardener absorb water. The difference produced by the humidity in moist nitrogen is small and so water alone cannot account for the great differences found between thin and thick coatings in humid air. The small effect in humid nitrogen may be because the water merely plasticizes the films, rendering them softer and more easily penetrated. Thin coatings would be affected more since the water could diffuse into a greater proportion of the film.

Hardening in a Humid Carbon Dioxide Atmosphere

As can be seen in Figure 6, when the coating is under a humid carbon dioxide atmosphere it will not harden beyond a penetration of about 22 μm . The combination of water and CO_2 is obviously one that produces large differences between thick and thin films under normal humid atmospheric conditions. The atmosphere of humid CO_2 affects even very thick coatings. Anomalous results for very thin coatings in "dry" air are probably due to carbon dioxide and residual humidity. Carbon dioxide is present in air at a level of 300 ppm (by volume in dry air) which is a very small concentration but which is probably enough to affect the hardening when one considers that the films do not harden at all under 100% moist carbon dioxide.

The coatings formed in this atmosphere were semi-opaque and soft. They were, however, crosslinked because they proved to be quite insoluble in acetone and methyl ethyl ketone although it is possible that they are not as highly crosslinked as they would be under ideal circumstances or that the crosslinks themselves have been rendered more flexible.

It appears that coatings and adhesives containing an epoxy-amine mixture would be best cured in a very dry atmosphere, since dry carbon dioxide does not seem to have a deleterious effect.

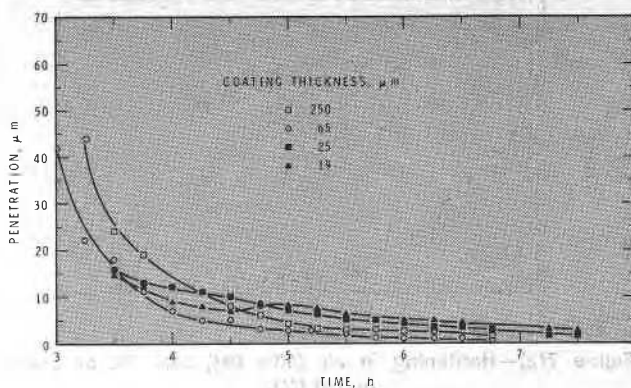


Figure 5—Hardening of epoxy-DETA coatings in nitrogen (50% RH)

Subsequent Exposure to a Normal Atmosphere

The soft coatings formed under a humid carbon dioxide atmosphere were exposed to normal air at 50% RH and did harden after some time.

Hardening data on coatings taken from the moist carbon dioxide after 22 hr are presented in Figure 7(a), and after 30 hr in Figure 7(b). In the former, it can be seen that all the coatings harden at about the same rate and are essentially cured after 120 hr. In the second case, after 30 hr under humid carbon dioxide the thinner coatings take very much longer to harden although the thickest coatings behave as after 22 hr exposure.

The extra eight hours exposure to humid carbon dioxide seems to reduce the subsequent hardening capability of the thin coatings considerably and it takes much longer to recover. Thick coatings are not affected so much because presumably there is relatively little additional diffusion of the carbon dioxide and water and thus they behave much as they might after 22 hr of exposure.

Reaction of Carbon Dioxide with DETA

Carbon dioxide, with or without water, does not appear to react with the Epon 828 resin under normal conditions. It does, however, react readily with DETA. When carbon dioxide gas was bubbled gently through DETA, the liquid became more viscous, then a white precipitate slowly formed. A considerable amount of heat was given off. The precipitate proved to be insoluble

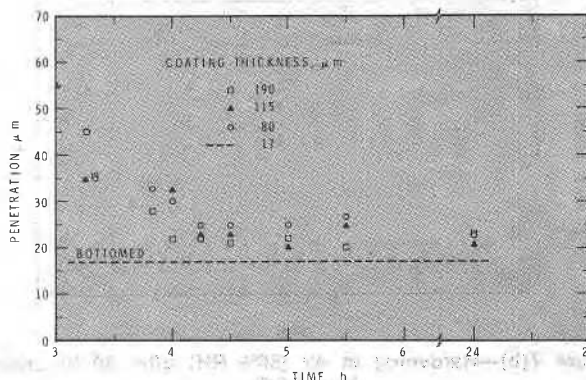


Figure 6—Hardening of epoxy-DETA coatings in humid CO_2

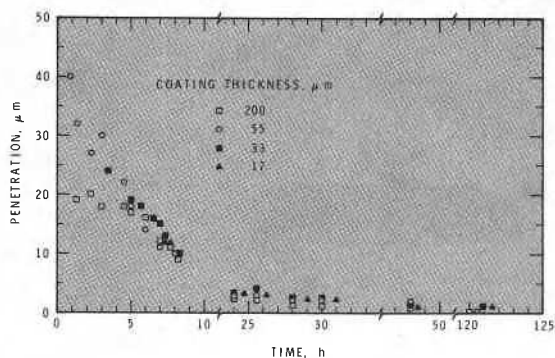
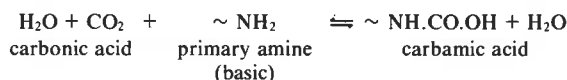


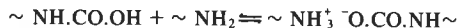
Figure 7(a)—Hardening in air (50% RH) after 22 hr under humid CO_2

in common organic solvents including acetone, chloroform, dimethyl sulfoxide, and dimethyl formamide. It was, however, readily soluble in water. If left in air for sufficient time it would convert into a liquid again, presumably reverting to DETA, which is hygroscopic.

The chemistry of amines is very similar to that of ammonia and, like ammonia, aliphatic amines react with carbon dioxide to produce amine carbamates. It is probably necessary for the carbon dioxide to associate with water in order to react with the basic amine and produce carbamic acid.



Carbamic acid would not exist in isolation but would produce carbamates^{3,5,6} after reacting further with an amine



Secondary amine groups can undergo similar reactions. Because there is more than one amine group on a DETA molecule, one can see that a network of amine molecules crosslinked with carbamate linkages would be formed.

In a polyamine, such as DETA, there is also a possibility that an internal salt might be produced using another amine group on the same molecule. This would produce a strained ring compound so that linkage between separate molecules is much more likely.

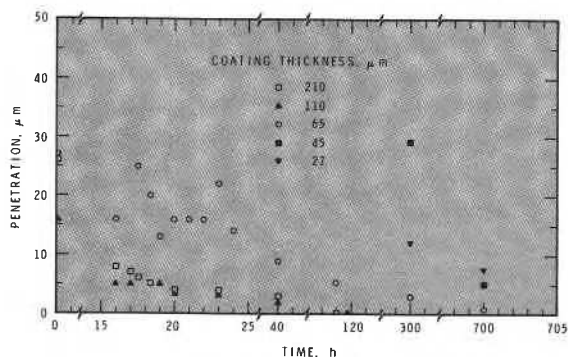


Figure 7(b)—Hardening in air (50% RH) after 30 hr under humid CO_2

The proposed carbamate network salt explains the solubility properties of the white precipitate. The amine has become more or less crosslinked and, therefore, is insoluble in organic solvents; however, since the carbamate linkage is at least partially ionic, the salt is readily soluble in water.

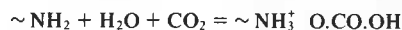
The reactions just proposed are reversible and require the presence of carbon dioxide to drive them to the right.

The over-all reaction could be represented by



as in reference (3), but the presence of water seems necessary to polarize the carbon dioxide and allow it to react with the basic amine, as indicated in the present experiments.

Aliphatic amines in general are more basic than ammonia,⁷ but they undergo analogous reactions. Thus the formation of a bicarbonate rather than a carbonate would be expected



This may well be fairly stable but does require a greater concentration of carbon dioxide, and particularly water, with respect to the amine. Under the conditions where carbon dioxide and water diffuse into a coating from the atmosphere, the carbamate is much more likely to be formed.

The formation of a network salt crosslinked with carbon dioxide does explain the hardness results. Once a pair of amine groups are connected with a carbamate linkage, the N-H bonds therein are no longer available to crosslink the epoxy. Thus an epoxy coating formed under an atmosphere of humid carbon dioxide will have a much lower crosslink density and will be very soft. Hardening will take place once the carbon dioxide is removed because the carbamate reactions are reversible. The persistent slight softness of very thin coatings reflects the availability of carbon dioxide and water by diffusion from normal air. Increased resistance to the subsequent hardening shown by the coatings, which had been under humid carbon dioxide for 30 hr, is probably due to the formation of a more extensive amine network salt or possibly the formation of amine bicarbonates.

Infrared Spectra of DETA, etc.

Infrared spectra of crosslinked coatings prepared under dry nitrogen and under humid carbon dioxide are very similar and provide little information on reasons for the differences in hardening. There are, however, large differences between the spectra of DETA and the white precipitate produced after reaction with carbon dioxide, as shown in Figure 8.

To obtain these spectra the DETA was contained in a potassium bromide cell; the white precipitate was first washed with chloroform and then incorporated into a potassium bromide pellet.

As in all infrared analysis, particularly of unknown compounds, the assignment of absorption peaks is not always certain. There are, however, features consistent with the formation of an ionic amine carbamate network.

The new absorptions at $\sim 1310\text{ cm}^{-1}$ may be due to a C-O-N stretching vibration⁸ and may also be due to an NH_3^+ symmetric deformation mode.⁹

The small peak appearing at 1180 cm^{-1} is probably due to C-O vibration.¹⁰ A new absorption at 1390 cm^{-1} may indicate the stretching of the carbonyl group in the (CO_2O^-) ion.¹⁰

Usually in organic carbonyl compounds there is an absorption at $\sim 1700\text{ cm}^{-1}$. This does not, however, appear in carboxylate (CO_2O^-) ions; instead there is a band at $1550\text{--}1610\text{ cm}^{-1}$ ^{9,11} and at $1400\text{--}1300\text{ cm}^{-1}$. This explains the lack of a carboxyl peak in a compound which has absorbed carbon dioxide, and accounts for a shoulder appearing at $\sim 1650\text{ cm}^{-1}$ or the 1570 cm^{-1} amine peak.

The NH_3^+ ion may be involved in the broad low peak at 2110 cm^{-1} ,⁹ but this is uncertain.

In general, the peaks common to DETA liquid and the white precipitate will be broadened in the solid because of the constraints placed on the vibrations by their solid environment.

Apparently, two features typical of amines have disappeared in the solid. One is the broad absorption from $700\text{--}900\text{ cm}^{-1}$, typical of amines.¹¹ The other is the two stretching N-H vibrations (asymmetric, 3360 cm^{-1} , and symmetric, 3280 cm^{-1}) which seem to have been replaced by an absorption at $\sim 3240\text{ cm}^{-1}$. Thus, the environment of the amine groups must have been changed considerably.

There are many new small absorptions from 1150 cm^{-1} to smaller wave numbers introduced in the new compound which are difficult to assign.

Overall, the picture presented by the infrared spectra supports the chemistry put forward in the previous section.

CONCLUSIONS

For this coating formulation, Epon 828 and DETA, and presumably other similar ones, the curing reaction and its velocity are not influenced by the heat generated from the exothermic curing reaction. Under normal conditions, however, carbon dioxide and water vapor can diffuse into the coating, react with the amine curing agent and restrict the development of crosslinkages. No other atmospheric gas was found to have this effect.

The effect is greatest in thin films because the carbon dioxide and water can diffuse into a greater proportion of these coatings. Indeed, very thin coatings take many days to harden completely. The same argument would apply to this formulation used as an adhesive because prior to the second part of the joint being applied to the adhesive, the epoxy-amine film would be exposed to carbon dioxide and water vapor in the atmosphere. The top part of the epoxy-amine would be affected (which forms an interface with the second part of the joint) although adhesives are usually applied in thicker films than coatings and would be less affected overall. The results indicate that epoxy-amine coatings and adhesives are best applied in very dry conditions.

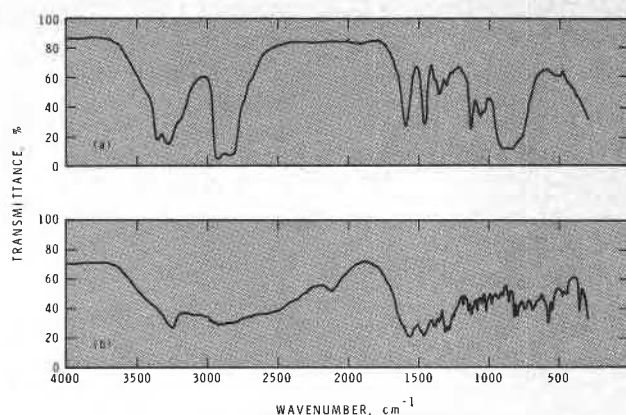


Figure 8—Infrared spectra of (a) diethylenetriamine (DETA) and (b) reaction product of DETA and carbon dioxide

When carbon dioxide reacts with DETA an ionic carbamate linkage seems to form between amine groups, thus inhibiting the crosslinking capabilities of the hydrogen atoms in those groups. Data from infrared spectroscopy support this proposed reaction.

ACKNOWLEDGMENTS

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