DETECTION AND CHARACTERIZATION OF WATER-INDUCED REVERSION OF EPOXY AND URETHANE POTTING COMPOUNDS

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AUGUST 1976

FINAL REPORT FOR THE PERIOD
JULY 1, 1975 - JUNE 30, 1976

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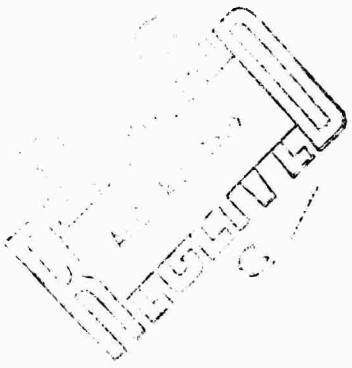

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Chemiluminescence, infrared, and nuclear magnetic resonance measurements have all been successfully used to detect changes in epoxy and urethane systems which soften when subjected to moisture and/or temperature. The data from these measurements correlate with changes in the polymer systems as determined by weight gain (or loss) and hardness tests. →

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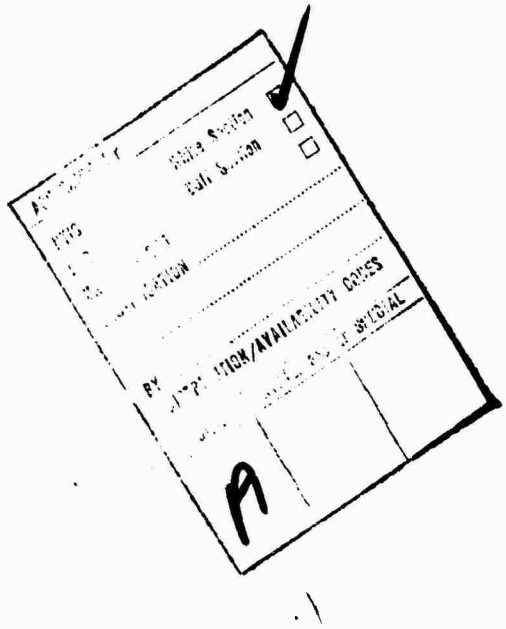
From the spectroscopic data, chemical changes induced by moisture can be differentiated from chemical changes induced by temperature. Either of these changes can, in turn, be differentiated from the chemical changes induced by a combination of moisture and temperature. This ability to relate the cause and type of chemical change, coupled with the hardness measurements, indicates that certain chemical changes may be directly related to the softening or reversion process.

From the infrared data, a reaction sequence involving water pickup or gain, conversion of ester to acid, and formation of a new carbonyl species can be postulated for the epoxy systems. For the urethanes, IR, and NMR indicate moisture attack, alcohol formation, and either additional alcohol formation or ether formation.

Even though several techniques can be used to follow chemical changes in samples which soften, further work is needed to:

(1) Definitely ascertain all (or more) of the chemical changes that are directly related to the reversion process.

(2) Ascertain which of the measurement techniques best follows this softening process.



SUMMARY

Chemiluminescence, infrared, and nuclear magnetic resonance measurements have all been successfully used to detect changes in epoxy and urethane systems which soften when subjected to moisture and/or temperature. The data from these measurements correlate with changes in the polymer systems as determined by weight gain (or loss) and hardness tests.

From the spectroscopic data, chemical changes induced by moisture can be differentiated from chemical changes induced by temperature. Either of these changes can, in turn, be differentiated from the chemical changes induced by a combination of moisture and temperature. This ability to relate the cause and type of chemical change, coupled with the hardness measurements, indicates that certain chemical changes may be directly related to the softening or reversion process.

From the infrared data, a reaction sequence involving water pickup or gain, conversion of ester to acid, and formation of a new carbonyl species can be postulated for the epoxy systems. For the urethanes, IR and NMR indicate moisture attack, alcohol formation, and either additional alcohol formation or ether formation.

Even though several techniques can be used to follow chemical changes in samples which soften, further work is needed to:

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DETECTION AND CHARACTERIZATION OF WATER-INDUCED REVERSION OF EPOXY AND URETHANE POTTING COMPOUNDS

by

R. J. Jakobsen, P. A. Clarke, R. A. Markle,
and G. D. Mendenhall

INTRODUCTION

Urethane and epoxy potting compounds for use in electrical functions have been a problem in aircraft for more than a decade. When exposed to high humidity environments these compounds can revert to liquids. The problem becomes critical when the electrical functions short out resulting in loss of control of the aircraft. Improvements have been made in the composition of these materials and test procedures[1] are known that can aid in selection of materials with higher hydrolytic stability. However, many materials still have been found to revert in an unpredictable manner.

Although epoxy and polyurethane resin plasticization by water is known to occur, it is generally believed to be a reversible reaction and as such does not account for permanent property degradation. Further, the detection of chemical changes, for the most part, have not been considered in earlier studies of the reversion process. Due to the persistence of this problem, it is important to develop a better understanding of the chemical mechanisms and processes involved in reversion. Such an understanding can provide several benefits, including the ability to develop more stable systems and also to predict the useful service life of the systems with some degree of confidence.

This report describes such research which utilizes sophisticated analytical instrumentation to elucidate the chemical and physical changes that occur when epoxy and urethane compounds are exposed to high humidity conditions. Hopefully, this information can eventually be used to develop a mechanistic model for predicting service life of the polymer systems and to evaluate which instrumentation best follows the reversion process. The instrumentation used includes chemiluminescence, nuclear magnetic resonance spectroscopy (NMR), Fourier Transform infrared spectroscopy (FT-IR), and characterization of the dynamic mechanical properties with the Weissenberg Rheogoniometer.

EXPERIMENTAL

Analytical Instrumentation

Chemiluminescence

Chemiluminescence from the samples was measured with a Battelle-constructed apparatus consisting of a light-tight aluminum box with inner dimensions 8" height x 11" width x 9" depth. The sample was placed on a glass or aluminum dish on top of a hot plate inside the apparatus. The temperature of the hot plate was regulated with a Foxboro proportional controller. Chemiluminescence emission was detected with a RCA Model 4501/V4 12-stage photomultiplier on the top of the apparatus whose output was averaged over 10-second periods. The value of counts/sec was displayed digitally, and when appropriate the signal was converted to analog form and recorded with a conventional strip-chart recorder.

Nuclear Magnetic Resonance (NMR)

The NMR spectra were run on a Varian CFT-20 Fourier transform NMR equipped with an 8-mm variable temperature carbon-13 probe. Samples were run using a 60 degree pulse angle, a 2-second delay, and were observed for up to 5000 transients.

The polymer films were sliced into thin strips and slipped into the NMR tube in such a manner that they formed a rough circle about 1-1/2 inches high. A micro-capillary tube filled with D_2O was suspended in the tube inside this circle to provide a lock signal for the NMR. The 60 degree flip angle was chosen to provide the maximum range of possible T_1 relaxation values. In the case of solid polymers the relaxation time is dependent on the internal motion of the polymer; the more motion in the polymer backbone, the sharper the carbon-13 resonance lines. A 2-second delay time between pulses was chosen to allow the polymer carbon-13 nuclei time to reorient themselves with respect to the ground state before the next pulse; a step intended to maximize peak heights. A variable number of transients (up to 5000) were run on each sample in an attempt to obtain a good signal-to-noise ratio.

Fourier Transform Infrared Spectroscopy (IR)

The infrared spectra were run on a Digilab FTS-14 Fourier Transform infrared system using a Harrick attenuated total reflection (ATR) accessory specially designed to match the optics of the FTS-14. The polymer films were cut into 50-mm by 3-mm strips and mounted on the faces of the ATR crystal. ATR infrared techniques were used because the

polymer films could be used as is, i.e., without having to alter the film by grinding or dissolving the film. Each ATR infrared run of a polymer film was ratioed against a run of a blank ATR crystal (which had been stored in the computer).

Spectra were obtained on each polymer used, both before and after exposure (to humidity and temperature), and each spectrum was stored in the computer memory. Such spectral storage permitted computer subtraction of various pairs of spectra (such as spectra of a polymer film before and after exposure). Thus, small spectral differences, indicative of small chemical changes due to exposure, could be detected when such changes were not visible in the individual spectra. This will be further discussed and illustrated in the results section.

Polymer Studies

Sample Selection and Preparation

A group of seven epoxy and urethane materials, in which reversion is known to occur, was selected for the original screening. Infrared spectra of these seven materials were obtained. On the basis of the spectral data, coupled with the physical and composition data obtained from the manufacturer, a representative epoxy (Scotchcast 280) and a representative urethane (Hexcel Uralite 3113) were selected for further experiments.

A more defined system to serve as a model was also selected for some experiments. This system consisted of the same epoxy resin (EPON 828) as claimed to be used for Scotchcast 280. The curing agent used was dodecenylsuccinic anhydride (DDSA), which was selected in order

to yield a polymer system similar to Scotchcast 280 (in which the manufacturers indicate the use of a proprietary anhydride). Such a more defined system (labeled as EPOX) is needed to maximize knowledge of the chemical structure of the major components and to minimize the presence of additives. The actual formulation used was an approximate stoichiometric ratio of reactants.

Material	Parts
EPON 828	100
DDSA	134
BDMA*	1

* Benzyldimethylamine

The EPON 828 and DDSA were thoroughly mixed, the BDMA added to the liquid mixture vaccum deaerated, and the mixture cured 2 hours at 90 C+ 3 hours at 150 C.

Cured samples of two-part casting elastomers, such as Scotchcast 280 epoxy and Hexcel Uralite 3113, were prepared by premixing the two liquid portions (resin and hardener) according to manufacturer's specifications. Castings of 12 x 12 x 1/8 inch dimensions were made by pouring the vacuum-deareated mixes into a picture frame mold assembled by clamping 1/2- x 1/8-inch brass strips onto a flat steel plate. A 10-mil Mylar film was inserted as a barrier film between the steel plate and the epoxy resins while a 5-mil polyethylene film was used with urethanes. In addition, the urethane compositions were protected with an overlayer of the 10-mil Mylar to exclude moisture. Scotchcast 280 epoxy was cured in a thermostatically-controlled oven at 65 C for 24

hours. Uralite 3113 was cured for 3 days at 23 C. Cylindrical samples 0.4-inch high x 1-inch diameter were cured at the same time for Weissenberg Rheogoniometer tests. Cured samples were then stored in a dessicator over Drierite at 23 C until used.

The polymer films were exposed by placing them in a dessicator held at 95 percent relative humidity and heated to 85 C. Samples were exposed for time periods ranging from a few hours to several weeks, but most data were obtained on samples stored for 2-week periods.

Later in the program samples were exposed at several conditions which included exposure to (1) elevated temperature (85 C) only, (2) humidity (95 percent RH) only, and (3) both elevated temperature (85 C) and humidity (95 percent RH).

Hardness Measurements

ASTM Test D2240-68 procedures were followed. All samples were measured using a Shore A-2 durometer after conditioning for 1 day or more at 23 C in the dry atmosphere. Samples were measured immediately before and after any test or exposure condition. In recent work a Shore D durometer has been used to measure hardness of all samples measuring 90 or greater on the Shore A scale.

Weight Gain Measurements

All samples are routinely weighed on an analytical balance ($\pm$ 0.1 mg) before and after any test or exposure condition and the percentage weight gain or loss is then calculated.

Rheology Measurements (Dynamic Mechanical Properties)

In a rheology test using the dynamic mechanical mode a specimen is deformed in a sinusoidal manner and the resulting force is measured. Because the mechanical response of polymers is viscoelastic, the force and deformation do not coincide. The shift of the force curve relative to the deformation is measured in terms of angle. One full cycle shift is 360 degrees. In a purely elastic material, the two curves will coincide and therefore the angle will be zero. For a purely viscous response the force will be maximum when the velocity of the deformation is greatest and will occur when the deformation is zero. The phase angle, for a purely viscous response, will be 90 degrees or the force curve will lead the deformation curve by one quarter of a cycle.

Two kinds of information are obtained from a forced oscillation measurement; the stress, σ (force/Area), and the phase shift (θ) between the force and strain, γ. From these two measurements the following properties can be determined:

$$G^* = \sigma_m/\gamma_m \qquad (1)$$

where G* is called the complex modulus (the subscript m refers to maximum values) and is composed of two vector quantities; the storage or elastic modulus, G', and the loss or viscous modulus, G", expressed as:

$$G^* = G' + iG'' \qquad (2)$$

or

$$G' = |G^*| \cos \theta$$

$$G'' = |G^*| \sin \theta$$

and consequently

$$G''/G' = \tan \theta \qquad (3)$$

The tangent of the phase or shift angle is called the loss tangent and, as shown in Equation 3, is the ratio of viscous to elastic response. This term is directly proportional to the damping or energy absorption in an oscillation deformation.

In the present work rheological measurements were made on Uralite 3113 after dry conditioning at 23 C and then after 2 weeks exposure at 85 C and 95 percent relative humidity. Dynamic mechanical tests were carried out on cylindrical samples over the frequency range of 0.0019-60 cycles per second, or a 4-decade frequency range experiment. Parameters calculated included complex modulus and loss tangent.

RESULTS

Two series of experiments were initiated to gain maximum information about the relationship between chemical changes and the reversion process. These experiments were designed to (1) study the changes in softening with length of exposure time and (2) to differentiate between the changes due to reversion and those due to other causes.

Effects of Length of Exposure

In order to ascertain what changes could be observed by the measuring techniques, experiments were initiated which emphasized variation of the length of exposure time.

Shore A hardness measurements and weights were obtained on films of Scotchcast 280 and Hexcel Uralite 3113. Samples of each film were placed in the dessicator held at 85 C and 95 percent relative humidity. Periodically, samples were removed from the dessicator. Each of these samples was subjected to weight, hardness, IR, and chemiluminescence measurements. The data obtained from these experiments are shown in Tables 1 and 2.

At the end of a 2-week period, the remaining samples were removed from the dessicator and weight, hardness, IR, and chemiluminescence measurements were made on these samples. Some of these data (labeled as Samples 280 - March or 3113 - March) are shown in Tables 3 and 4. These tables also list corresponding data for control samples (samples not subjected to temperature and moisture) and for samples subjected to 85 C and 95 percent humidity for 2 weeks in December, but which had been stored at room temperature until March (labeled as Samples 280 - December or 3113 - December).

From the data in Tables 1, 2, and 3, several observations can be made.

(1) The hardness measurements on duplicate samples indicate that the urethane films are homogeneous, but there is a lack of homogeneity in the epoxy

film. This has been confirmed by the chemiluminescence and infrared measurements.

(2) There is a consistent weight gain (with time) for the epoxy and a weight loss for the urethane after an initial rapid weight gain.

(3) Changes in chemiluminescence values with time have been detected and these changes correspond to changes in hardness measurements.

Thus, as the samples are subjected to temperature and moisture, there are weight changes and softening and these changes can be followed by chemiluminescence measurements.

TABLE 1. DATA ON SCOTCHCAST 280 SUBJECTED TO 85 C AND 95 PERCENT RELATIVE HUMIDITY FOR INDICATED PERIODS OF TIME

Time	Hardness (Shore A)	Weight Gain, percent	Chemiluminescence (Count)
19.5 hours	100	1.2	—
	99	1.5	644
67.5 hours	92	2.3	822
	86	2.2	—
187.5 hours	100	2.2	—
	58	3.9	137
259.5 hours	60	3.9	—
	60	4.2	—

TABLE 2. DATA ON HEXCEL URALITE 3113 SUBJECTED TO 85 C AND 95 PERCENT RELATIVE HUMIDITY FOR INDICATED PERIODS OF TIME

Time	Hardness (Shore A)	Weight Gain, percent	Chemiluminescence (Count)
19.5 hours	61	2.3	—
	53	1.9	361
67.5 hours	51	2.4	260
	45	2.0	—
187.5 hours	45	1.7	—
	41	1.2	1033
259.5 hours	45	1.7	
	48	1.7	

TABLE 3. DATA ON VARIOUS SCOTCHCAST 280 SAMPLES

Sample[(a)]	Date of Experiment	Hardness (Shore A)	Weight Gain, percent	Chemiluminescence
280-Control	—	100	—	6560
280-December	December	48	—	—
280-December	March	Stuck to beaker	—	681
280-March A	March	70	2.8	464
280-March B	March	Too soft	4.1	315

(a) 280-December + 280-March, samples exposed 2 weeks at 95 percent relative humidity and at 85 C. March A and March B refer to duplicate samples.

TABLE 4. DATA ON VARIOUS HEXCEL URALITE 3113 SAMPLES

Sample[a]	Date of Experiment	Hardness (Shore A)	Weight Gain, percent	Chemiluminescence
3113-Control	—	59	—	612
3113-December	December	38	—	—
3113-December	March	47	—	281
3113-March A	March	45	0.8	—
3113-March B	March	38	0.2	137

(a) 3113-December + 3113-March, samples exposed 2 weeks at 95 percent relative humidity and at 85 C. March A and March B refer to duplicate samples.

The changes in samples subjected to moisture and temperature can also be followed by spectroscopic techniques and these measurements can also be used to identify some of the chemical changes. Infrared measurements of the samples periodically removed from the dessicator mainly show water pickup (when compared to the control samples, 280 - Control or 3113 - Control). This is even true when the 2-week (in the dessicator) samples (280 or 3113 - March) are compared to the controls. However, when various pairs of spectra are subtracted, differences not observed in the individual spectra become apparent in the subtracted spectra. This is illustrated in Figure 1 which shows the absorbance infrared spectra of Samples 280 - March A (bottom) and 280 - March B (top). The subtracted spectrum is shown in the middle (280 - March B, 280 - March A).

Three carbonyl absorption bands can be observed in the subtracted spectrum (middle) of Figure 1 at 1745, 1720, and 1710 cm^{-1}. From these spectra and others an initial reaction scheme can be proposed. For Scotchcast 280, several reactions occur:

(1) The first reaction is water pickup, which could be either physical adsorption or chemical interaction.

(2) The second reaction is conversion of ester (1745 cm^{-1} band) to acid (1720 cm^{-1} band).

(3) A third reaction is formation of a new carbonyl species (likely to be an unsaturated acid) shown by an absorption band at 1710 cm^{-1}.

For Hexcel Uralite 3113, the initial spectroscopic results are more difficult to interpret in terms of a mechanism, but the following observations can be made:

(1) There is initial water pickup or gain.

(2) This is followed by formation of a new type of C-O bond near 1100 cm^{-1} (likely to be an ether group) and another type of bond (1630 cm^{-1}) which could be attributed to a variety of chemical groups.

(3) Towards the end of the 2-week period alcohol formation can be observed.

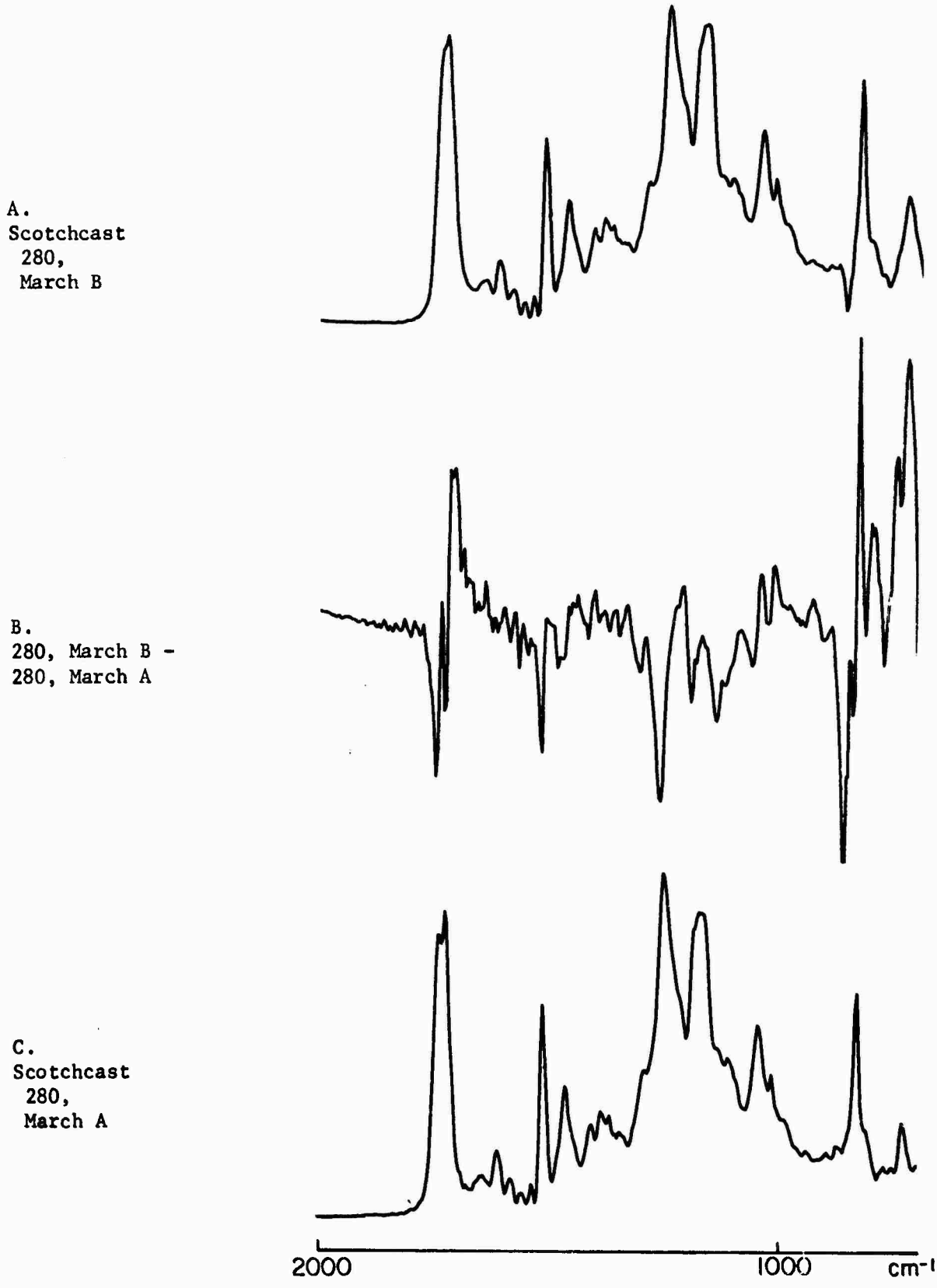

FIGURE 1. INFRARED SPECTRA OF SCOTCHCAST 280 - MARCH FILMS

(2 weeks at 85 C and 95 percent relative humidity.)

The dynamic mechanical properties of the Uralite 3113 were determined before and after aging. The effect of aging on the complex modulus, G*, and loss tangent, tan θ, are shown in Figures 2 and 3. The complex modulus decreases by almost two orders of magnitude over the entire frequency range of the measurements, reflecting an overall decline in stiffness of the urethane material. At low frequencies the loss factor also decreases, suggesting that aging has in general induced a loss of elasticity (or increase in viscous behavior). At higher frequencies (∿ 1.5 cps), the curves for the aged and unaged materials cross over. This effect has not been confirmed by repeat measurements but is believed to be real. It could reflect the presence of a transition temperature. These data suggest that in future experiments the effect of temperature and moisture content in the dynamic mechanical properties should be examined, and that DTA or DSC should be used to identify major transitions and the influence of aging in these transitions.

These initial measurements show that the dynamic mechanical properties of the Uralite material are very sensitive to the aging process. This suggests that mechanical property measurements such as creep or stress relaxation should also reflect the aging process and perhaps would be correlatable with the mechanistic data being generated by FT-IR and chemiluminescence.

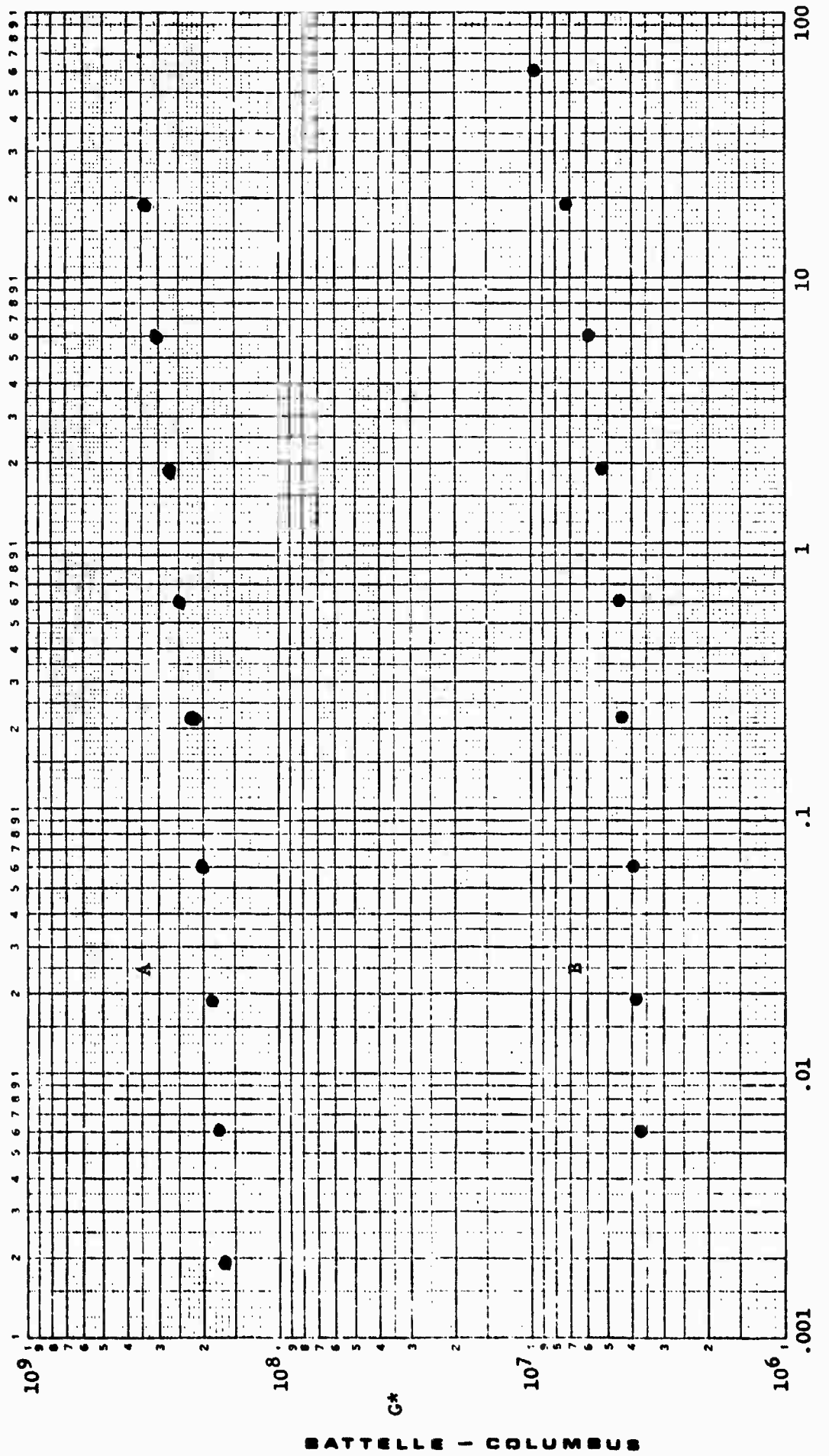

FIGURE 2. EFFECT OF EXPOSURE (85 C, 95 PERCENT RH, 2 WEEKS) ON THE COMPLEX MODULUS OF HXUR 3113: A - BEFORE EXPOSURE; B - AFTER EXPOSURE

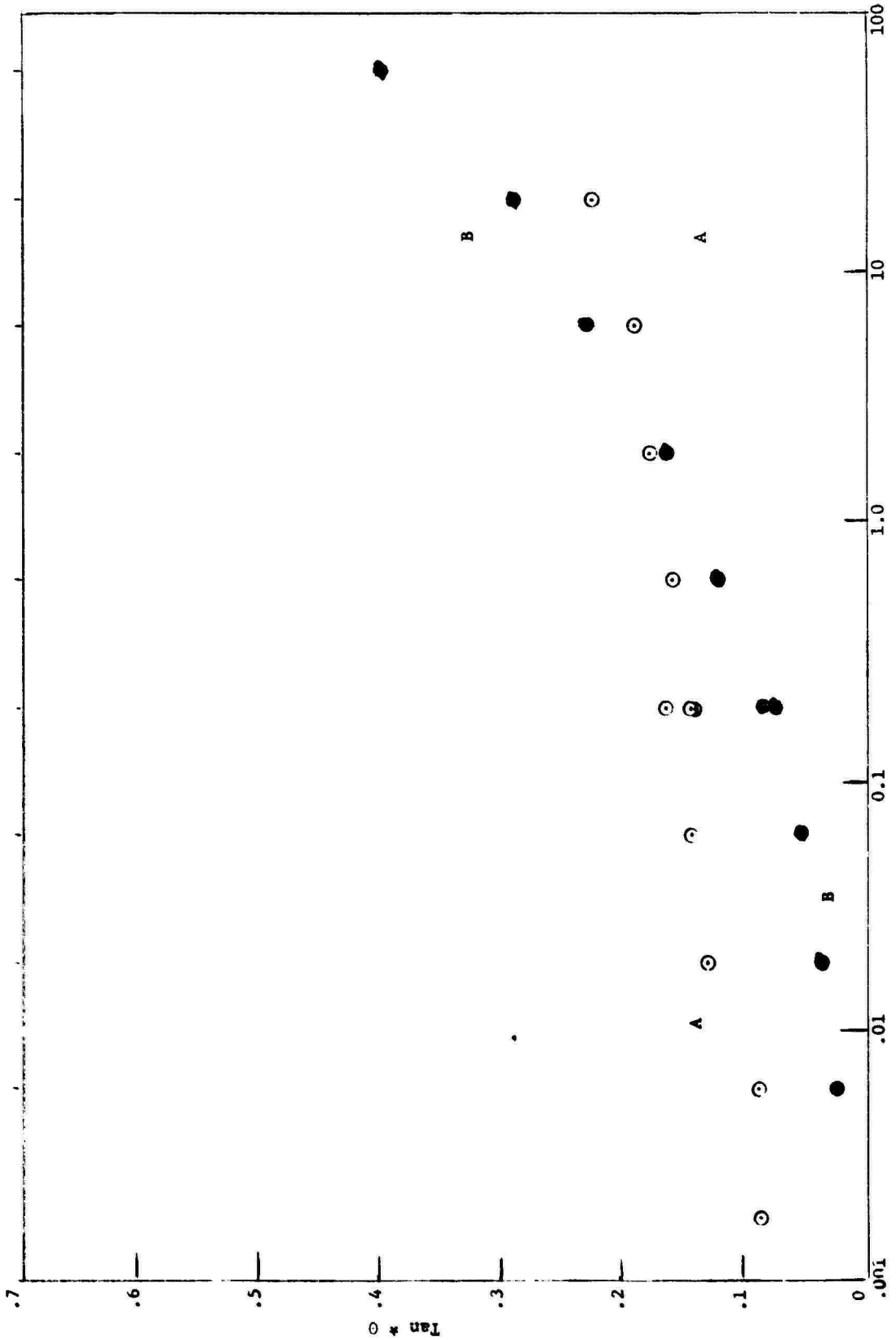

FIGURE 3. EFFECT OF EXPOSURE (85 C, 95 PERCENT RH, 2 WEEKS) ON THE LOSS TANGENT OF HXUR 3113: A - BEFORE EXPOSURE, θ; B - AFTER EXPOSURE, ●

Variation of Exposure Conditions

In order to learn more about the relationship between the observed changes and the reversion process, new experiments were initiated which emphasized variation of the exposure conditions. The samples used in these experiments consisted of Scotchcast 280 (SCTH 280), Hexcel Uralite 3113 (HXUR 3113), and the model (or rather more defined) epoxy (EPOX) described in the Experimental Section. In addition, since the manufacturer of Scotchcast 280 suggested three sets of curing conditions, separate SCTH 280 films were prepared at each of these three conditions. These curing conditions are: (1) 65 C for 24 hours (labeled as low cure), (2) 95 C for 5 hours (labeled as medium cure), and (3) 120 C for 3 hours (labeled as high cure).

Shore A or Shore D hardness measurements and weights were obtained on films of the five samples (three samples of SCTH 280, HXUR 3113, and EPOX). Samples of each were stored in dessicators at the following four conditions:

(1) 23 C and 0 percent relative humidity (labeled control samples)

(2) 23 C and 95 percent RH (labeled humidity or moisture samples)

(3) 85 C and 0 percent RH (labeled temperature or heat samples)

(4) 85 C and 95 percent RH (labeled temperature/humidity samples).

At the end of a 2-week period, the samples were removed from the dessicator and weight, hardness, NMR, IR, and chemiluminescence measurements were made on these samples. The hardness and weight gain data for these samples are given in Tables 5 and 6, respectively. These hardness measurements are illustrated graphically in Figure 4. Table 5 lists the change in hardness value of each sample after the 2-week period. This table (and the succeeding tables) can be studied from two interesting and informative approaches. The first is to study the effect of varying conditions on a particular sample and the second is to observe the data differences between the five samples at one condition. It can be seen in Table 5 that the low cure SCTH 280 increases in hardness after a 2-week period at 23 C and 0 percent RH. The other SCTH 280 samples and EPOX show little change in hardness at these exposure conditions, while the urethane (HXUR 3113) shows a slight decrease in hardness. These differences can be graphically observed in Figure 4 and indicate that the low cure epoxy further cures on standing at 23 C and 0 percent RH. The other two SCTH 280 samples and EPOX were initially reasonably well cured and thus show little change on standing under these conditions. The urethane shows slight signs of softening even upon standing.

The effects of moisture on these five samples can be observed in Figure 4B or by examining the data in Table 5 at 23 C and 95 percent RH. These data indicate that moisture by itself (no heat) has little effect on the hardness of the epoxy polymers - even the low cure SCTH 280. Since urethanes are known to be subject to hydrolysis, it is not surprising the urethane exposed to moisture shows a marked softening effect. No hardness value was given for the high cure SCTH 280 since only a very

thin film of this sample was used and the hardness measurements were not considered experimentally valid.

TABLE 5. CHANGES IN HARDNESS VALUES (SHORE A) OF EPOXY AND URETHANE POLYMERS SUBJECTED TO VARIOUS CONDITIONS FOR 2 WEEKS

Conditions	SCTH 280 Low Cure	SCTH 280 Medium Cure	SCTH 280 High Cure	EPOX	HXUR 3113
23 C, 0 percent RH	+ 9	- 1	0	+1	- 5
23 C, 95 percent RH	- 2	+ 1	--	+1	-13
85 C, 0 percent RH	+11	- 1	+2	-3	- 2
85 C, 95 percent RH	-66	-11	-5	-3	-29

TABLE 6. PERCENTAGE WEIGHT GAIN OR LOSS FOR EPOXY AND URETHANE POLYMERS SUBJECTED TO VARIOUS CONDITIONS FOR 2 WEEKS

Conditions	SCTH 280 Low Cure	SCTH 280 Medium Cure	SCTH 280 High Cure	EPOX	HXUR 3113
23 C, 0 percent RH	+0.02	+0.04	+0.03	0	-0.16
23 C, 95 percent RH	+0.7	+0.56	+0.5	+0.32	+3.11
85 C, 0 percent RH	-1.0	-0.29	0	+0.05	-0.36
85 C, 95 percent RH	+3.78	+1.04	+0.07	+0.48	+0.93

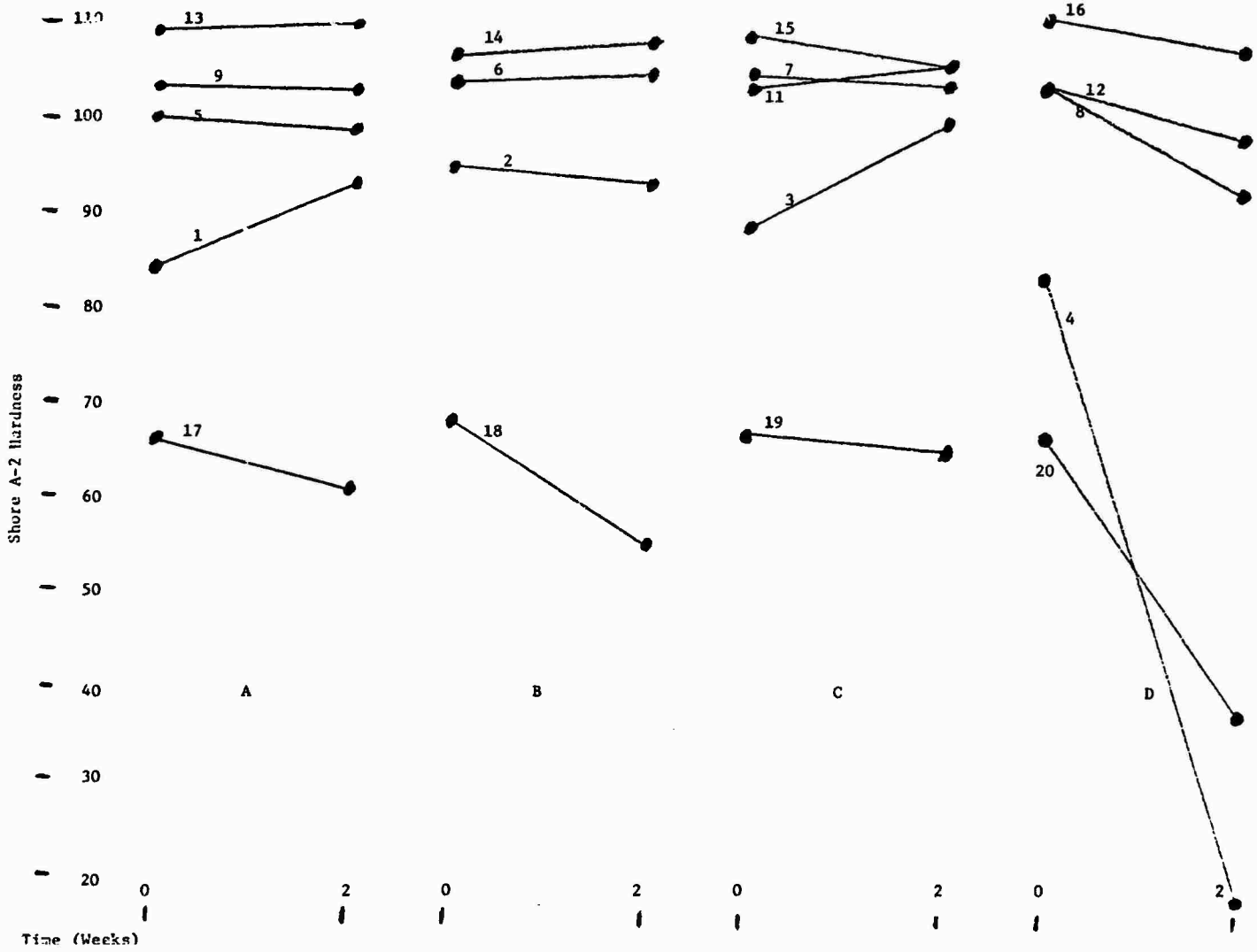

FIGURE 4. CHANGE IN SHORE A HARDNESS VALUES FOR SCTH 280, EPOX, AND HXUR 3113 FILMS* AFTER 2 WEEKS AT (A) 23 C, 0 PERCENT RH; (B) 23 C, 95 PERCENT RH; (C) 85 C, 0 PERCENT RH; AND (D) 85 C, 95 PERCENT RH

*1, 2, 3, 4 = low cure SCTH 280
5, 6, 7, 8 = medium cure SCTH 280
9, 10, 11, 12 = high cure SCTH 280
13, 14, 15, 16 = EPOX
17, 18, 19, 20 = HXUR 3113.

Elevated temperature (85 C) by itself (at 0 percent RH) has little effect (Figure 4C) on any of the samples except for the low cure SCTH 280 which again shows a marked hardening (or curing) effect. This hardness increase for low cure SCTH 280 demonstrates that this epoxy polymer was initially undercured. Likewise, the data on the heated samples demonstrate that the other epoxy samples initially were fairly well cured.

The combination of heat and moisture bring about dramatic changes in hardness for the low cure SCTH 280 and for HXUR 3113 (Figure 4D). The medium cure SCTH 280 shows some softening, but the high cure SCTH 280 and EPOX only show slight signs of softening. Thus, the model or more defined system (EPOX) shows little reversion. On the one hand this is unfortunate and indicates that either different recipe conditions, or a new model system are needed to study the changes due to reversion. However, on the other hand this has proven to be of great value because many of the non-reversion heat and moisture effects can be determined. This will be further discussed and emphasized in the sections which describe the spectroscopic results. In addition, some epoxy samples are still being stored at 85 C and 95 percent RH. When the new program begins these samples will be available for study and by then might be much softer (show reversion).

Thus, the low cure SCTH 280 hardness data indicate that ambient conditions (23 C, 0 percent RH) or heat further cure the sample and no softening or reversion occurs. Interestingly, moisture by itself shows little effect on the hardness of this sample. However, at 85 C and 95 percent RH the major change in hardness gives the first indication that heat greatly accelerates the moisture attack or reversion process.

The medium cure SCTH 280 shows little change in hardness values for the various samples except that softening is beginning to be observed after 2 weeks at 85 C and 95 percent RH. For both the high cure SCTH 280 and for EPOX there is little evidence for softening or reversion.

The data for the urethane (HXUR 3113) provide marked evidence for softening when exposed to moisture and this is accelerated by the combined effect of temperature and moisture. As for the other samples, the urethane shows little change in hardness when exposed to heat alone.

It is of great interest to compare the hardness data for the three SCTH 280 samples and observe that the low cure epoxy shows by far, the greatest amount of softening. Since one of the differences between the samples is likely to be the amount of cross linking, this may be an indication that the reversion process is initiated at the functional groups constituting potential cross linking sites. Attempts will be made to clarify this point in next year's program.

The weight change data in Table 6 for the control samples and for the samples exposed to only heat support the hardness data since only the low cure SCTH 280 shows a significant weight change. However, the data for samples exposed to moisture show a weight gain (which infrared indicates is water). The samples exposed only to moisture show small weight gains except for the urethane which shows a large weight gain. Also, only the urethane softens appreciably. For the epoxy samples exposure to moisture results in slightly lower weight gains as the degree of cure increases.

When the samples are exposed to both heat and moisture, the weight changes follow the same pattern as the hardness data (except for the urethane). The low cure SCTH 280 shows a large weight increase and a large decrease in hardness. The similarity in the weight gain and hardness change patterns for epoxies may be another indication of moisture attack at the cross linking sites.

It is more difficult to postulate why the urethane exposed only to moisture has a larger weight gain than the HXUR 3113 exposed to both temperature and moisture, since these results do not correlate with the hardness measurements. A variation in the amount of residual free isocyanate (from sample to sample) could explain the weight gain data, but the infrared measurements have not, as yet, detected isocyanates. These data indicate either that much of the adsorbed moisture does not react with the urethane and is driven off by heat, or that a reaction with loss of volatiles occurs. Urethanes are known to be susceptible to hydrolytic attack and perhaps the weight gain and hardness data only indicate that it takes much less moisture to initiate the reversion reaction in a urethane than in an epoxy.

The chemiluminescence measurements for these five samples are given in Table 7 and these data are quite informative when compared to the hardness values as shown in Figure 4. Two values (134 and 139 counts for medium cure SCTH 280) are quite of out line with the rest of the data and cannot be explained with certainty. These values are far too high, but this may only reflect small impurities or differences in sample handling not detectable by other techniques.

TABLE 7. CHEMILUMINESCENCE VALUES (COUNTS/SQ CM) FOR EPOXY AND URETHANE POLYMERS SUBJECTED TO VARIOUS CONDITIONS FOR 2 WEEKS

Conditions	SCTH 280 Low Cure	SCTH 280 Medium Cure	SCTH 280 High Cure	EPCX	HXUR 3113
23 C, 0 percent RH	53	134	57	53	29
23 C, 95 percent RH	41	138	50	50	28
85 C, 0 percent RH	28	31	30	34	29
85 C, 95 percent RH	14	24	26	35	22

From the hardness curves in Figure 4 it can be seen that all of the control samples except for the urethane give roughly equivalent hardness values. This trend is also reflected in the chemiluminescence values. Similar trends are apparent for both the hardness and chemiluminescence values of samples exposed to only moisture and of samples exposed only to heat. At 85 C and 0 percent RH, the chemiluminescence value for the urethane sample is slightly high, but this may only reflect the experimental difficulties in measuring small changes in a number small to begin with. For samples exposed to both temperature and moisture, the trend in chemiluminescence values again follows the changes in hardness values.

However, when comparing the chemiluminescence changes (for any one sample) due to different exposure conditions, it can be seen that these changes do not follow the trends in hardness values. The chemiluminescence values show a consistent change (decrease) on going from the

control sample to the moisture sample to the heated sample to the sample exposed to both heat and moisture (except for HXUR 3113). However, moisture or heat alone have little effect on the hardness values. The spectroscopic measurements indicate that complex chemical changes are occurring at all exposure conditions. These changes (likely to be a slight degradation, perhaps oxidative, of the polymer) are not necessarily related to the reversion process. The chemiluminescence data indicate that the chemiluminescence measurements are following many of these changes, in addition to the reversion process.

Nuclear magnetic resonance (C-13) spectra were obtained on the four polyurethane samples (HXUR 3113) which had been exposed to various conditions. The polyurethane bulk samples proved to have more segmental motion (chain mobility) than the low-cure epoxy samples. That is, solution spectra of the polymers were not necessary in order to obtain good spectra.

Figures 5 and 6 are representative of the data obtainable for the polyurethane samples. Figure 5 shows a spectrum of the control sample, while Figure 6 shows a spectrum for the temperature plus humidity sample. For all four samples a singlet appeared in the region of 30 ppm downfield from an external standard. Carbon-13 resonances appearing in this region can be attributed to methyl carbons adjacent to carbons, methylene carbons adjacent to a vinyl group, or methine carbons adjacent to a methylene carbon. The resonances appearing at approximately 88 ppm have for convenience been labelled as a doublet. In actuality they are two resonances with very similar chemical shifts. Peaks in this region of a carbon-13 spectrum can be attributed to carbons of an ether group (not carbonyl carbons). Both regions of all four spectra show shoulders or broadness near the main resonances.

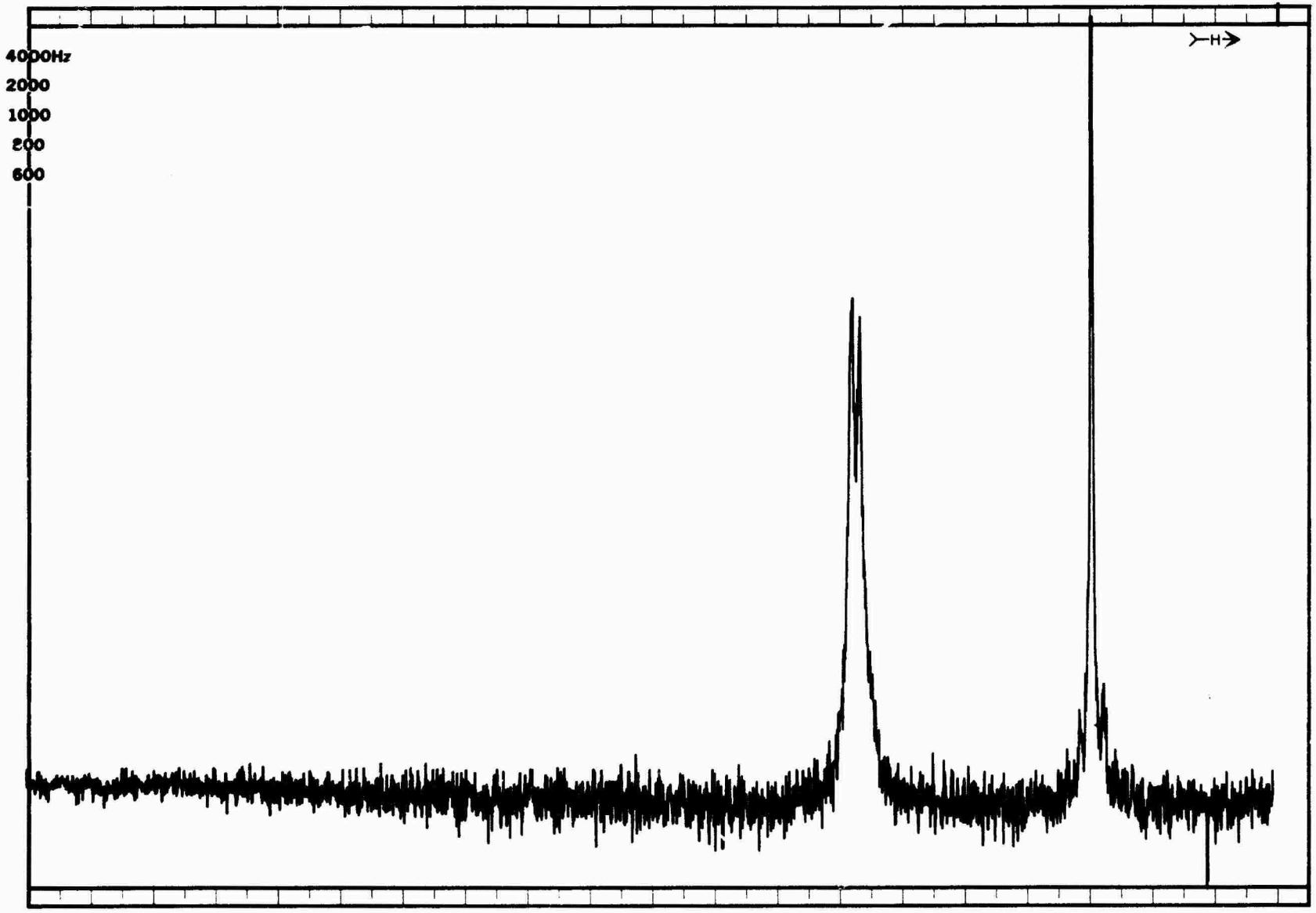

FIGURE 5. ^{13}C SPECTRUM OF SOLID HXUR 3113 (23 C, 0 PERCENT RH)

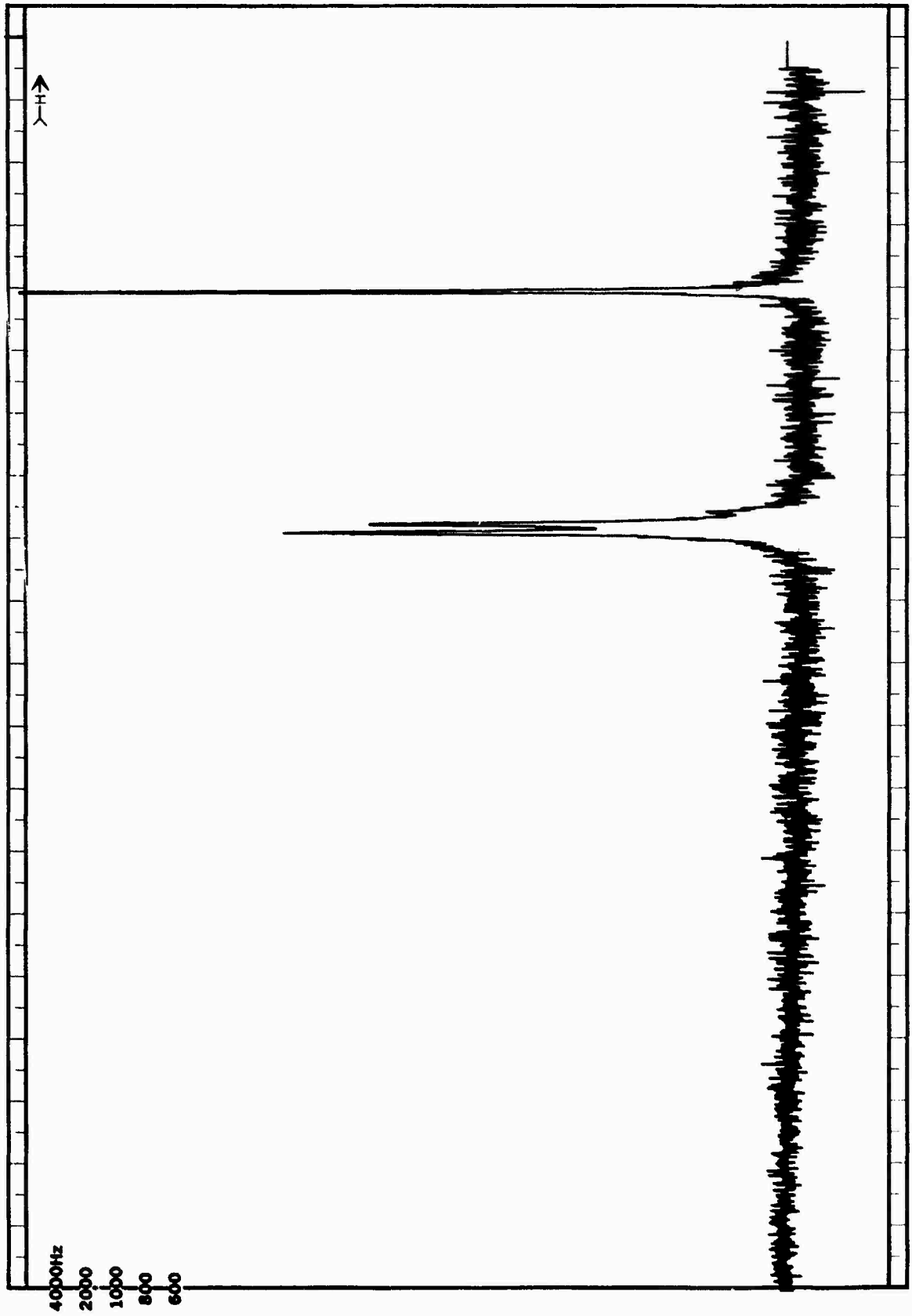

FIGURE 6. ^{13}C SPECTRUM OF SOLID HXUR 3113 (85 C, 95 PERCENT RH)

Table 8 shows a comparison of the resonances for the four polyurethane samples. In all four samples, the high field side of the singlet shows a broadness. For the control and temperature plus humidity samples this broadness appears as a distinct peak while the other two samples exhibit only a broadness. These peaks can be seen in the smoothed spectra shown in Figure 7. Similar differences among the four samples can be seen from observation of the low field side of the singlet and both sides of the doublet resonances.

Several conclusions can be drawn from these data. The shoulder on the low field side of the singlet decreases in intensity when the sample is exposed to humidity conditions, whether humidity alone or temperature plus humidity. The appearance of a shoulder on the high field side of the doublet under the same conditions is also noted. The fact that these changes appear only under humidity conditions, suggests a reversion process due to moisture. One way to determine if the moisture is adsorbed on or bonded to the polymer would be to run proton FT-NMR spectra. Also, samples exposed to these conditions for longer than 2 weeks should be run to determine the rate of change of these resonances.

The data also show that the relative intensities of the peaks in the doublet change with exposure conditions. On comparison of the individual components (see Table 9), the upfield peak shows a slight decrease in intensity under humidity conditions, while the downfield peak increases slightly under temperature plus humidity conditions. The temperature plus humidity sample exhibits the sharpest signals of the four samples. The relative intensities of the doublet to the singlet do not appear to change under any of the conditions studied. The appearance

TABLE 8. COMPARISON OF CARBON-13 FT-NMR DATA FOR HXUR 3113

Resonance	23 C, 0 percent RH	23 C, 95 percent RH	85 C, 0 percent RH	85 C, 95 percent RH
High field side of singlet	shoulder[a]	broadened[a]	broadened[a]	shoulder[a]
Low field side of singlet	shoulder	small shoulder	shoulder	small shoulder
High field side of singlet	no shoulder	shoulder	no shoulder	shoulder
Low field side	broadened	more broadened	more broadened	broadened

(a) These samples all exhibit a broadness. "Shoulder" is an indication of a definite peak, while "broadened" indicates that no definite peak appeared for the broadness.

TABLE 9. COMPARISON OF HXUR 3113 DOUBLET RESONANCE INTENSITIES

Doublet Resonance	Intensity (mm, Chart Height) 23 C 0 percent RH	23 C 95 percent RH	85 C 0 percent RH	85 C 95 percent RH
Upfield peak	13	11.7	12.0	11.5
Downfield peak	13.5	13.5	13.7	13.8

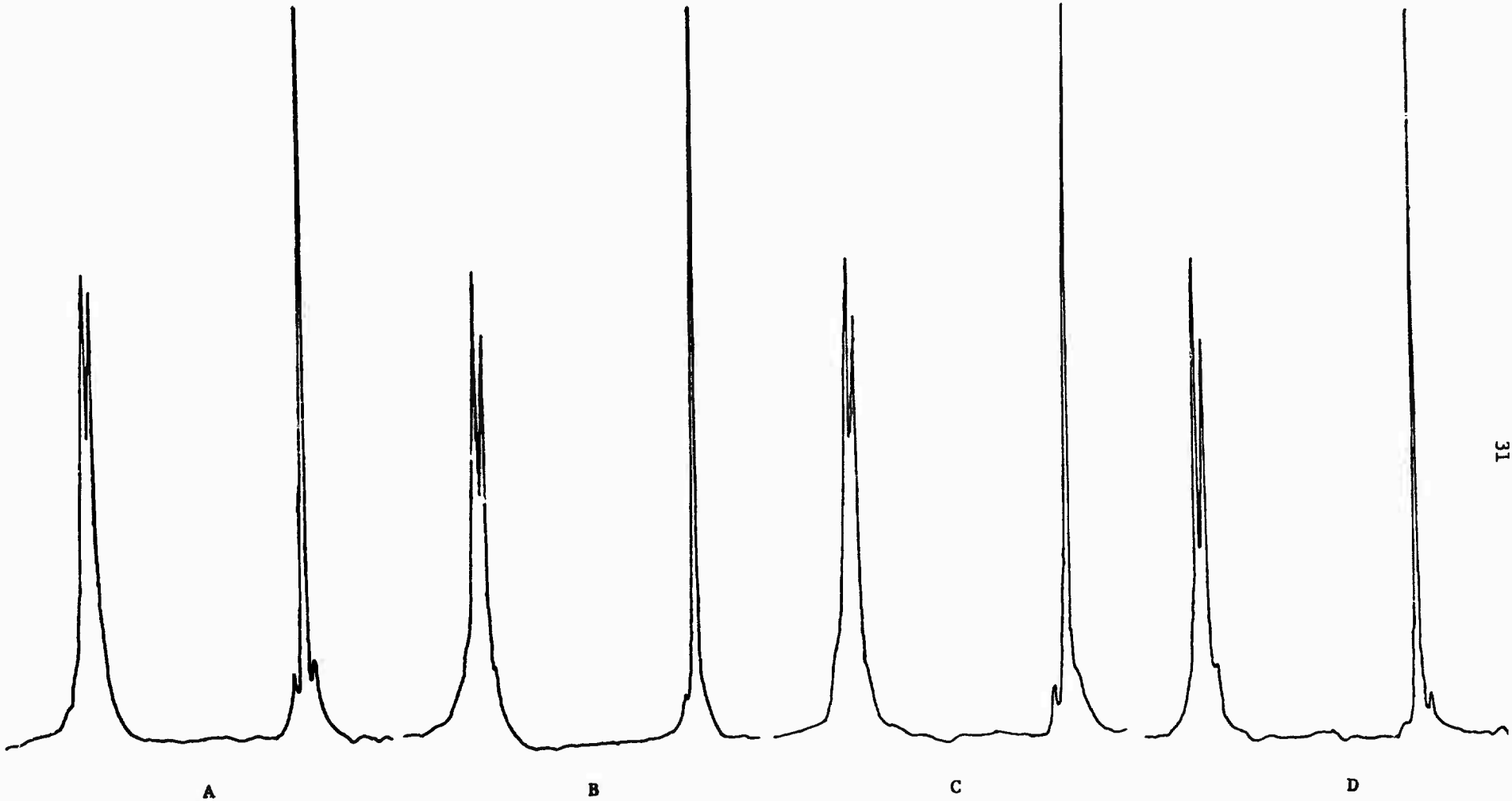

FIGURE 7. SMOOTHED ^{13}C SPECTRA OF SOLID HX-R 3113 AFTER 2 WEEKS AT (A) 23 C, 0 PERCENT RH; (B) 23 C, 95 PERCENT RH; (C) 85 C, 0 PERCENT RH; AND (D) 85 C, 95 PERCENT RH

of these ratio changes can be consistent with attack at the crosslinking sites rather than degradation of the main polymer chains. However, samples exposed to the various conditions for longer periods of time must be studied in order to verify the origin of these intensity ratio changes.

In contrast to the polyurethane samples, epoxy polymers are rigid, glass-like systems with little chain mobility (segmental motion). These characteristics make bulk epoxies difficult to study using FT-NMR. However, as can be seen in Figure 8, resonances can be observed for both bulk samples and $CDCl_3$ solutions of the temperature plus humidity low cure epoxy (SCTH 280) sample. Two of these resonances occur in both bulk and solution samples. The positive negative aspect of these peaks may be due to relaxation times or noise from the NMR experiment. Even though these peaks cannot as yet be assigned to carbon nuclei in either the polymer or additives, their intensity ratios change on going from bulk to solution. During the next year, work will be undertaken to verify the origin of these resonances. Approaches to this problem may include multiple pulse sequences, high-temperature studies and double resonance experiments.

Fourier Transform infrared (FT-IR) spectra have been run on each of the 20 samples (five polymer systems at four exposure conditions). These spectra were stored in the dedicated computer of the FT-IR system and various pairs of spectra were subtracted in order to bring out spectral differences not apparent by a comparison of the individual absorbance spectra. The value of the spectral subtraction capability has already

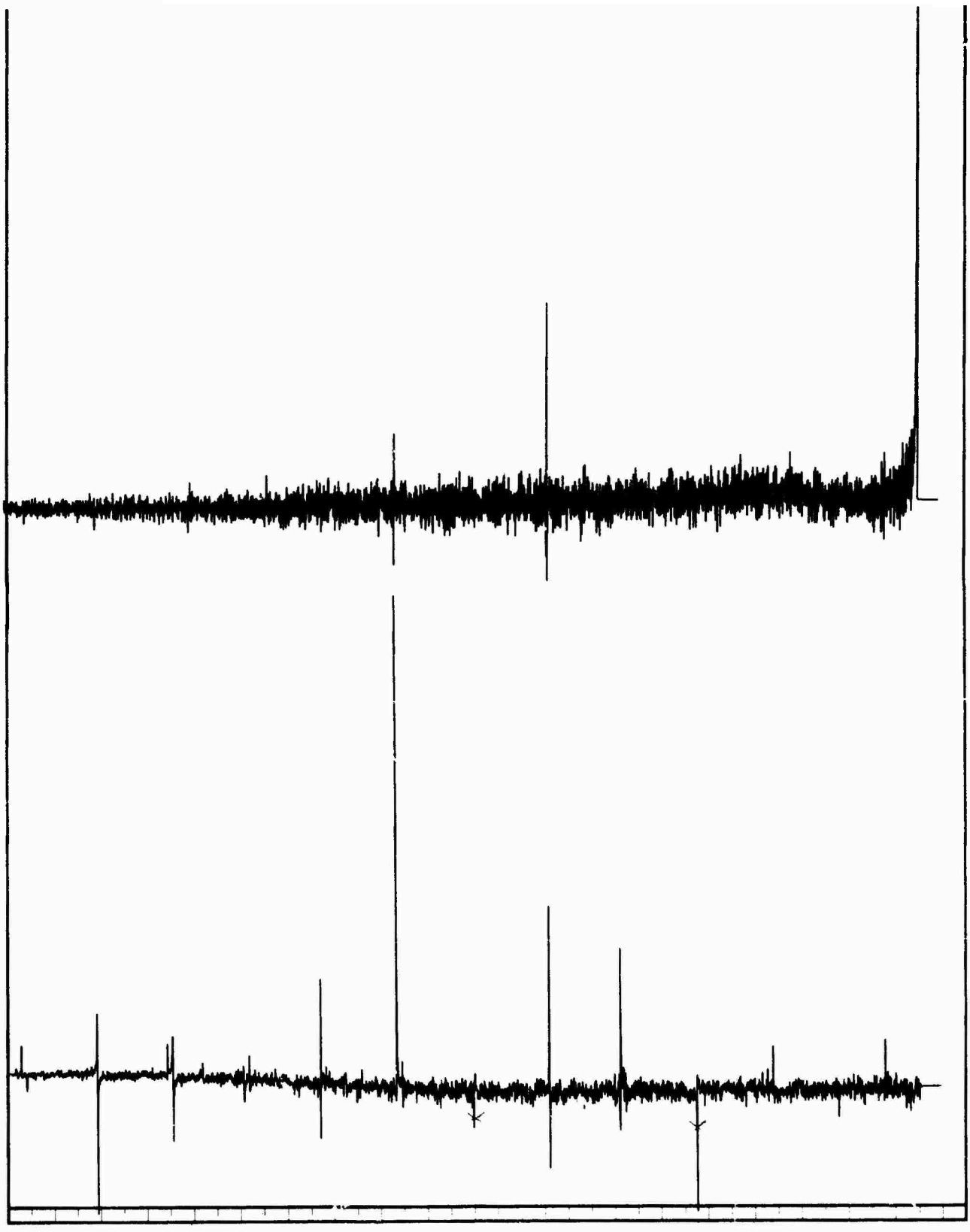

FIGURE 8. ^{13}C SPECTRA OF LOW CURE SCTH 280 (85 C, 95 PERCENT RH)

A – Spectrum of solid low cure SCTH 280.

B – Spectrum of $CDCl_3$ solution of low cure SCTH 280.

been demonstrated in the previous discussion centering about Figure 1 and will be reiterated when Figure 11 is discussed.

As with the chemiluminescence and NMR results, these IR data show certain trends which correlate with the hardness values and, in addition, yield information on the chemical functional group changes brought about by various exposure conditions. Some of the IR results in the low cure SCTH 280 are shown in Figure 9 and Table 10. Figure 9 shows subtracted spectra of low cure SCTH 280 as follows: Figure 9A, spectrum of low cure SCTH 280 after 2 weeks at 23 C and 95 percent RH minus the control spectrum (low cure SCTH 280 after 2 weeks at 23 C and 0 percent RH); Figure 9B, low cure SCTH 280 at 85 C and 0 percent RH minus the control spectrum of low cure SCTH 280; and Figure 9C, low cure SCTH 280 at 85 C and 95 percent RH minus control spectrum of low cure SCTH 280. Thus Figure 9A shows the effect of moisture on the spectrum of low cure SCTH 280, Figure 9B shows the effect of heat, and Figure 9C shows the effect of the combination of heat and moisture. Table 10 lists the IR frequencies due to these exposure conditions and allows an easier comparison of the effects of each exposure condition. From the subtracted spectra of Figure 9, it can be seen that there are marked differences in the carbonyl absorption region of the spectra. The effect of moisture (Figure 9A) is to convert some of the ester carbonyl at 1740 cm^{-1} to an acid carbonyl near 1725 cm^{-1}. However, heat alone (Figure 9B) produces a different change which is to produce a carbonyl absorption near 1730 cm^{-1}. Moisture and heat produce still a different effect which is to decrease the ester carbonyl and produce a carbonyl species (unsaturated acid?) near 1710 cm^{-1}. Other changes can be observed

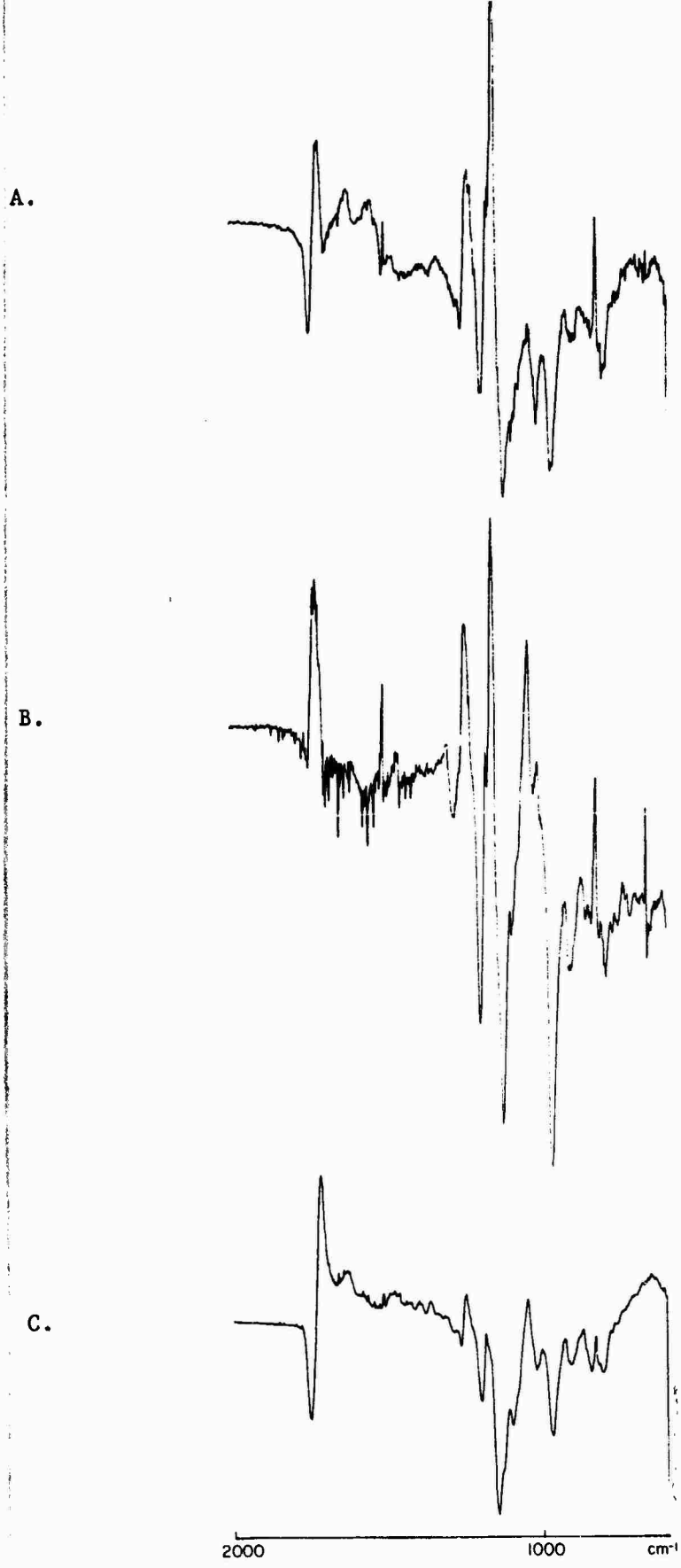

FIGURE 9. SUBTRACTED INFRARED SPECTRA OF LOW CURE SCTH 280

A – Low cure SCTH 280 (23 C, 95 percent RH) minus low cure SCTH 280 (23 C, 0 percent RH).

B – Low cure SCTH 280 (85 C, 0 percent RH) minus low cure SCTH 280 (23 C, 0 percent RH).

C – Low cure SCTH 280 (85 C, 95 percent RH) minus low cure SCTH 280 (23 C, 0 percent RH).

TABLE 10. INFRARED FREQUENCIES OF A LOW CURE EPOXY, AFTER SUBTRACTION

Conditions[a]	Infrared Frequencies (cm^{-1}, From Subtracted Spectra														
	1740	1725–1730	1710	1625	1555	1285	1240	1190	1160	1130	1090	1045	970	930	870
23 C, 0 percent RH	✓					✓		✓		✓			✓		
23 C, 95 percent RH	✓	✓		✓	✓	✓	✓	✓	✓	✓	✓		✓		
85 C, 0 percent RH	✓	✓					✓		✓		✓	✓			
85 C, 95 percent RH			✓	✓			✓					✓		✓	✓

(a) A check mark indicates a band at that frequency is present in the spectrum of the epoxy of the condition listed after subtraction of the spectra of an epoxy at other conditions.

in the subtracted spectra of Figure 9 and from the frequencies listed in Table 10. From the table it can be seen that certain bands appear under some exposure conditions and not others. A band at 970 cm^{-1} appears only in the spectra of control samples or those exposed only to moisture. This band is not seen in the spectra of samples subjected to heat. This infrared band is commonly used to measure degree of cure in anhydride-cured epoxy systems and likely arises from a vibration of the anhydride curing agent. This behavior demonstrates that curing takes place (for a heated epoxy) and correlates with the hardness data for this sample (Table 5 and Figure 4). Three other infrared absorption bands exhibit the same behavior as the 970 cm^{-1} absorption and therefore can be related to the curing process. These are frequencies at 1285, 1190, and 1130 cm^{-1} and like the 970 cm^{-1} vibration are not observed in low cure SCTH 280 polymers subjected to heat. On the other hand, a frequency at 1045 cm^{-1} appears only in the samples exposed to heat. Thus, the curing process can be monitored by the disappearance of absorption at 1285, 1190, 1130, and 970 cm^{-1} and the formation of a new structure as evidenced by the apperance of a 1045 cm^{-1} (alcoholic OH?) band.

From Table 10, it can also be seen that certain bands only appear in the low cure SCTH 280 polymer exposed to both heat and moisture. These are frequencies at 1710, 930, and 870 cm^{-1}. The hardness data (Table 5 and Figure 4) show that this is the only low cure SCTH 280 sample exposure conditions that produces a major amount of softening or reversion. It also is the only SCTH 280 where the 1710 cm^{-1} band is observed. This certainly supports the hypothesis (posed in the previous section on "Effects of Length of Exposure") that the formation of the

structures giving rise to the 1710 cm^{-1} (and the 930 and 870 cm) band is directly related to the reversion reaction.

Thus, the effect of moisture alone on the spectrum of low cure SCTH 280 is to produce changes which are neither a curing process (hardness values do not increase) or a reversion process (hardness values do not appreciably decrease). That this change is not a curing process is shown by the fact that the 1285, 1190, 1130, and 970 cm^{-1} absorption bands do not appreciably decrease in intensity or disappear. In addition, no 1045 cm^{-1} absorption is observed. This process (effect of moisture alone) is not reversion since no 1710, 930, and 870 cm^{-1} absorptions are observed. This effect of moisture alone appears to be a separate and distinct process* which may be related to adsorption of moisture and conversion of ester carbonyl to acid carbonyl (1740 cm^{-1} absorption goes to 1725 cm^{-1}). This adsorption of moisture is also indicated by the appearance of 1625 cm^{-1} absorption (H_2O) in the samples exposed to moisture.

The effect of heat alone on the spectrum of low cure SCTH 280 is to bring about a curing reaction. This is evidenced by the disappearance of 1285, 1190, 1130, and 970 cm^{-1} frequencies and the appearance of absorption at 1045 cm^{-1} (there is also a marked increase in hardness values). No reversion (no 1710, 930, or 870 cm^{-1} absorption) is observed and no changes similar to those produced by moisture alone can be detected (a 1730 cm^{-1} carbonyl is seen in place of a 1720-1725 cm^{-1} band).

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* It must be noted that these interpretations are based on subtracted, i.e., difference spectra. Thus, it cannot be stated that no reversion or curing reactions are taking place. It means that the moisture effect is the predominate reaction and that the reversion or curing reactions are not the predominate ones.

The effect of both heat and moisture on the spectrum of low cure SCTH 280 is to bring about changes which are directly related to the reversion process (the hardness values indicate a marked softening of the polymer). These changes are associated with the appearance of 1710, 930, and 870 cm^{-1} infrared bands.

Thus, each type of exposure condition seems to produce a different type of predominant reaction (as evidenced by infrared observed structural differences). It is only by the combination of heat and moisture that much reversion appears to be initiated.

Both the medium and the high cure SCTH 280 (as well as EPOX) are reasonably well cured epoxy systems. As such, the infrared spectra are quite similar and can be illustrated by any one of the three polymer systems. We choose to use the data on EPOX for these data demonstrate not only the changes in a well-cured epoxy, but show the effects of a slightly different epoxy polymer (EPOX, described in the section on Sample Selection and Preparation).

An absorbance spectrum of EPOX is shown in Figure 10B where it is compared to an absorbance spectrum of low cure SCTH 280 (Figure 10A). While slight differences can be observed between the two spectra, it can be seen that the main structure of each system appears to be quite similar, if not identical.

Figure 11C repeats the spectrum of EPOX control (2 weeks at 23 C and 0 percent RH), while Figure 11A shows the spectrum of EPOX after 2 weeks at 85 C and 95 percent RH. These individual absorbance spectra of EPOX are quite similar (almost identical). Yet when these spectra are subtracted, large scale differences become apparent. This again

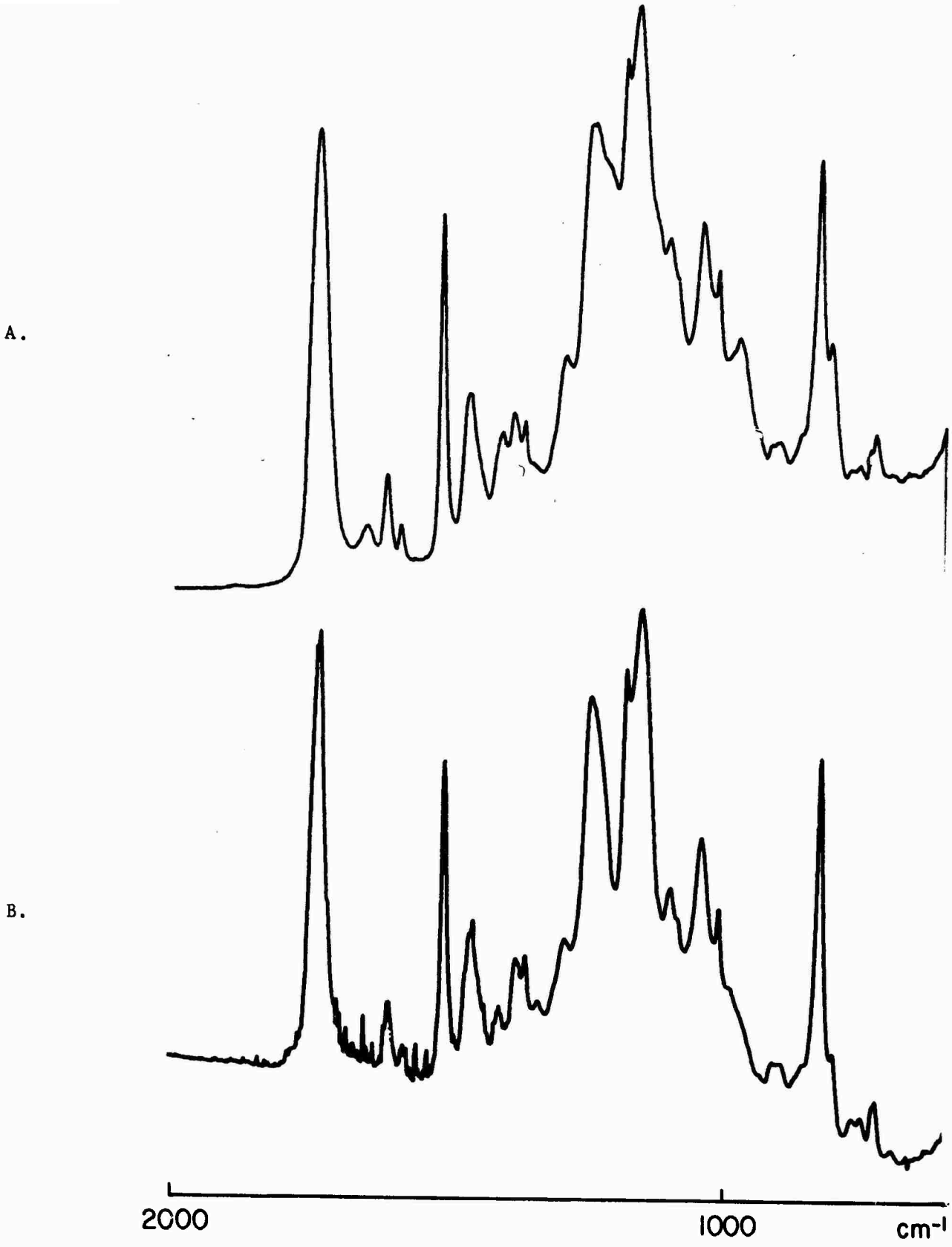

FIGURE 10. ABSORBANCE INFRARED SPECTRA OF EPOXY POLYMERS

A - Low cure SCTH 280 (23 C, 0 percent RH).

B - EPOX (23 C, 0 percent RH).

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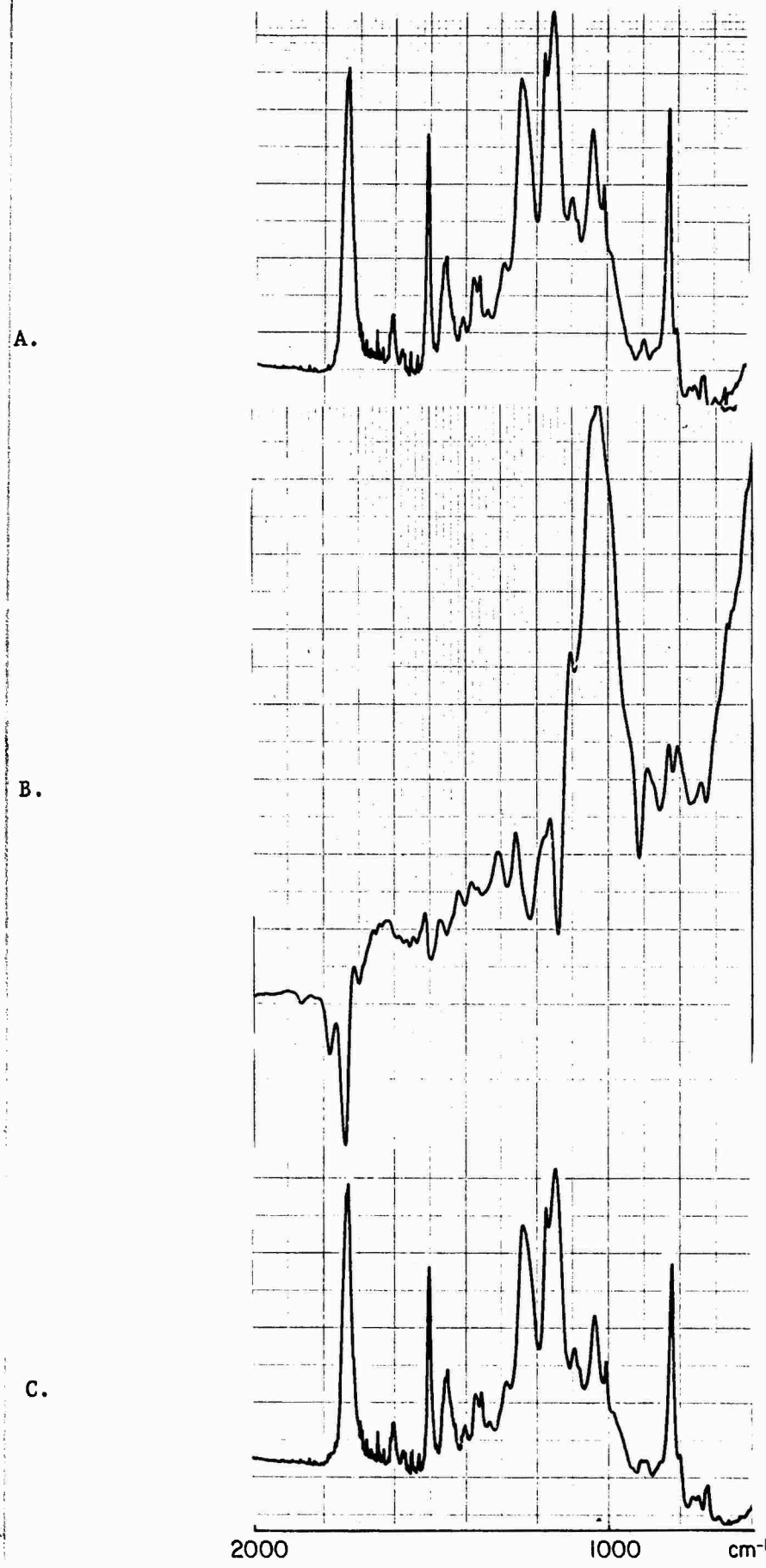

FIGURE 11. INFRARED SPECTRA OF EPOX

A – Absorbance spectrum of EPOX (85 C, 95 percent RH).

B – Subtracted spectrum, EPOX (85 C, 95 percent RH) minus EPOX (23 C, 0 percent RH).

C – Absorbance spectrum of EPOX (23 C, 0 percent RH).

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illustrates the value of computer aided spectral subtraction (i.e., the value of FT-IR). While there are many small differences between the two spectra, the major differences are in the carbonyl region (1780-1740 cm^{-1}) and in the region around 1030 cm^{-1}. From the intensity, band shape, and frequency of the 1030 cm^{-1} band, it is likely that this band indicates a small Si conteining impurity in the EPOX film at 85 C and 95 percent RH. The carbonyl doublet at 1780 and 1740 cm^{-1} probably arises from the anhydride curing agent. The fact that some anhydride is left after curing indicates that the ratio of curing agent to polymer for the EPOX system is somewhat higher than used for the SCTH system.

Figure 12 and Table 11 present the effect of various exposure conditions on EPOX in the same manner as shown for low cure SCTH 280 (Figure 9 and Table 10). That is, Figure 12A shows the effects of moisture only, Figure 12B the effects of heat only, and Figure 12C shows the effects of both heat and moisture. Table 11 lists the frequencies due to these exposure conditions. The hardness values (Table 5 and Figure 4) indicate that the EPOX exposed to different conditions neither cures further (increase in hardness) or shows much sign of reversion (decrease in hardness). Yet the infrared spectra indicate a small amount of additional cure (loss of anhydride carbonyl bands at 1780 and 1740 cm^{-1} and loss of bands near 1140 and 920 cm^{-1}) with exposure of the EPOX to heat. The 1140 and 920 cm^{-1} bands are similar in frequency to some of the curing changes seen in the SCTH samples. This <u>small</u> amount of curing is also supported by the appearance of a band (for samples exposed to heat) in the 1030-1050 cm^{-1} range. The detection of this small amount

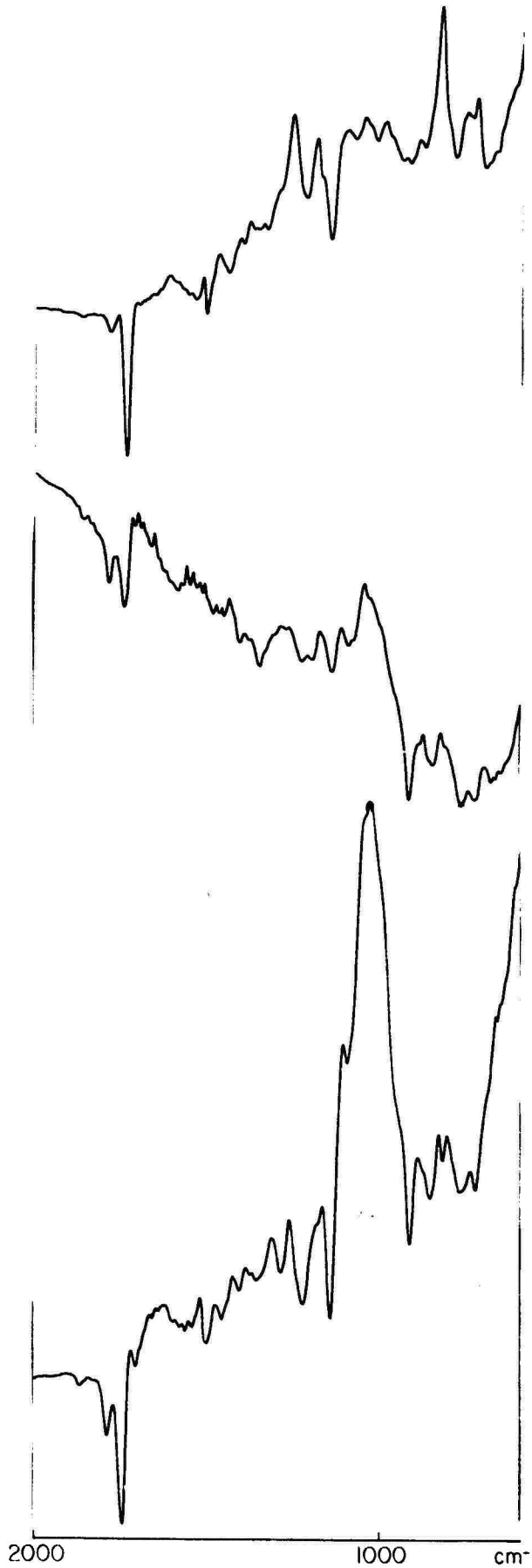

FIGURE 12. SUBTRACTED INFRARED SPECTRA OF EPOX

A – EPOX (23 C, 95 percent RH) minus EPOX (23 C, 0 percent RH).

B – EPOX (85 C, 0 percent RH) minus EPOX (23 C, 0 percent RH).

C – EPOX (85 C, 95 percent RH) minus EPOX (23 C, 0 percent RH).

TABLE 11. INFRARED FREQUENCIES OF A MODEL EPOX, AFTER SUBTRACTION

Conditions[a]	Infrared Frequencies (cm^{-1}), From Subtracted Spectra)															
	1780–1740	1730	1650	1260	1230	1190	1160	1140	1110	1050–1030	920	890	850	830	800	770	730
23 C, 0 percent RH	✓				✓			✓			✓		✓			✓	✓
23 C, 95 percent RH	✓			✓		✓		✓			✓			✓		✓	✓
85 C, 0 percent RH		✓			✓	✓	✓			✓		✓			✓		
85 C, 95 percent RH		✓	✓	✓		✓	✓		✓	✓		✓		✓	✓		

(a) A check mark indicates a band at that frequency is present in the spectrum of the epoxy of the condition listed after subtraction of the spectra of an epoxy at other conditions.

of curing reaction may be a reflection of the sensitivity of the FT-IR technique as opposed to hardness measurements.

The spectral measurements support the hardness data in so far as reversion is concerned. There are no bands which appear only in the spectrum of the sample subjected to both moisture and heat, and no 1710 cm^{-1} absorption is observed in any of the EPOX samples. This further supports the postulate that the appearance of the 1710 cm^{-1} absorption is related to the reversion process.

However, chemical changes can be observed in the spectra of EPOX for each of the exposure conditions. These changes are similar (but not identical) to those observed for medium cure SCTH 280 and high cure SCTH 280. These changes are not due to reversion* since there is little decrease in hardness for these samples. Thus, these spectra of well-cured epoxy polymers give us a means of defining non-reversion changes and therefore, distinguishing between changes related to the reversion process and changes brought about by other means. The spectra emphasize the complex nature of the chemical changes in epoxy systems exposed to moisture and/or heat and indicate that many of these changes may not be related to the reversion process.

The spectrum of the control polyurethane film (HXUR 3113, 23 C and 0 percent RH) is shown in Figure 13A along with the spectrum of HXUR 3113 exposed to both moisture and heat (Figure 13B). Again the individual absorbance spectra are quite similar and differences cannot

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* These well-cured epoxy samples may eventually show signs of softening or reversion if exposed for periods longer than 2 weeks. These experiments are in progress (see Discussion Section) and should yield much information relating to curing and the reversion process.

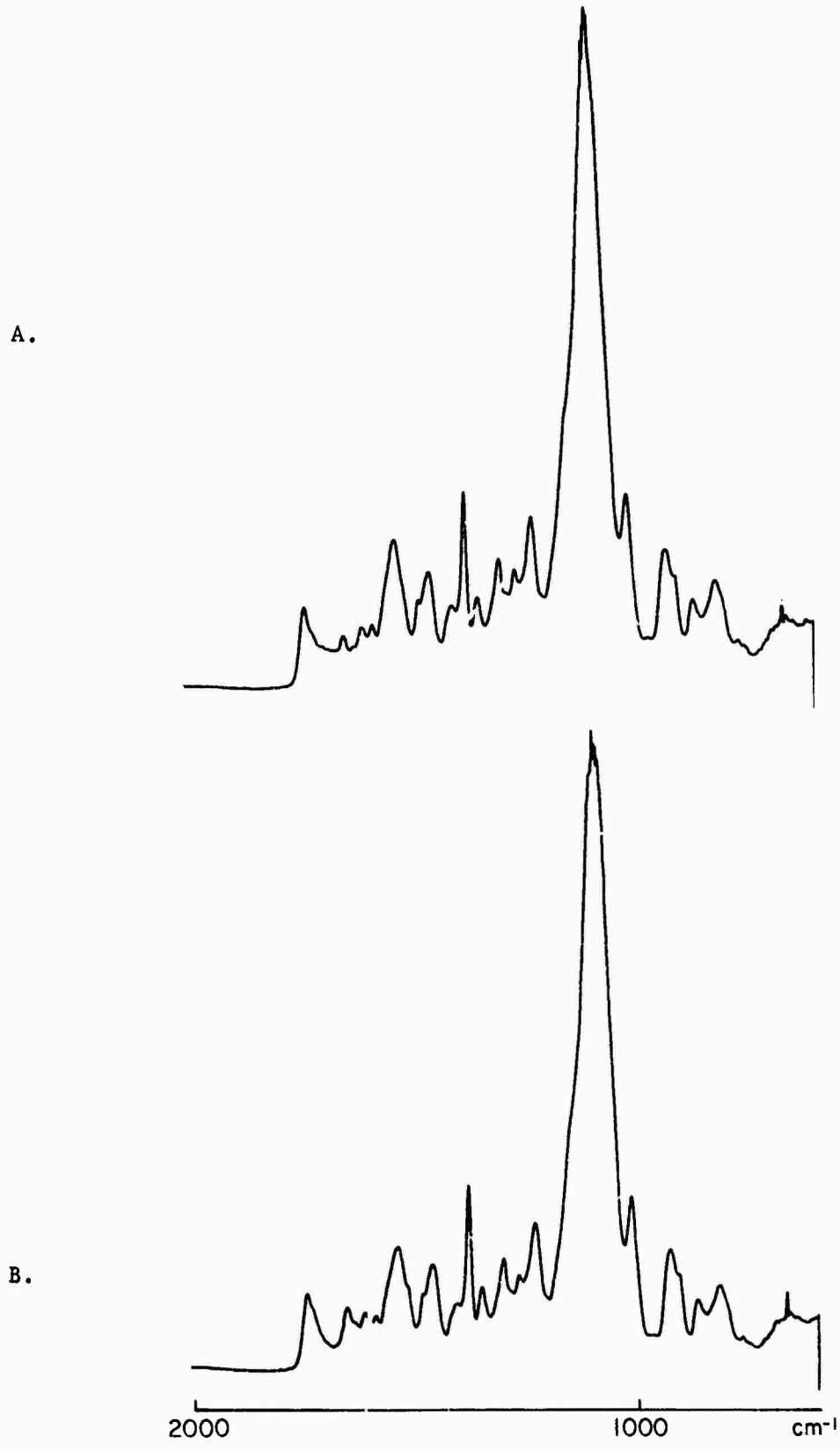

FIGURE 13. INFRARED ABSORBANCE SPECTRA OF (A) HXUR 3113 (23 C, 0 PERCENT RH); AND (B) HXUR 3113 (85 C, 95 PERCENT RH).

be readily detected until subtraction techniques are applied. The results of subtraction can be seen in Figure 14 which shows the effects of various exposure conditions on the spectra of HXUR 3113. The effect of exposure to moisture can be observed in Figure 14A. Here the major changes are a loss of ether absorption at 1100 cm^{-1} and gain of alcohol absorptions at 1050 and 1010 cm^{-1}. However, for the sample subjected to heat only, the 1050 cm^{-1} alcohol frequency can possibly be seen, but there is no loss of ether absorption or gain of 1010 cm^{-1} alcohol absorption. The sample subjected to both heat and moisture shows still a third type of change. Here a 1630 cm^{-1} band forms along with a major absorption band at 1090 cm^{-1}. The hardness values (Table 5 and Figure 4) for HXUR 3113 show a softening for the sample exposed to water and Table 6 indicates a substantial weight gain (moisture?) for this sample. If so, there is moisture attack leading to softening and this moisture attack is spectrally observed by the formation of alcohols (1010 and 1050 cm^{-1}). The loss of ether absorption at 1100 cm^{-1} might indicate that the moisture attack takes place at the ether C-O bond, which breaks and forms an alcohol. While such a proposed mechanism requires much more proof, there certainly are enough spectral changes to clearly support softening due to moisture attack.

The sample exposed to only heat shows little change in hardness and only a small weight change. This is reflected in the lack of major spectral changes in this sample (Figure 14B). Even the formation of alcohol (1050 cm^{-1}) is not certain because the cancellation of ether absorption in the subtracted spectrum leaves the spectrum very noisy in this region and it is difficult to be certain of the 1050 cm^{-1} alcohol band.

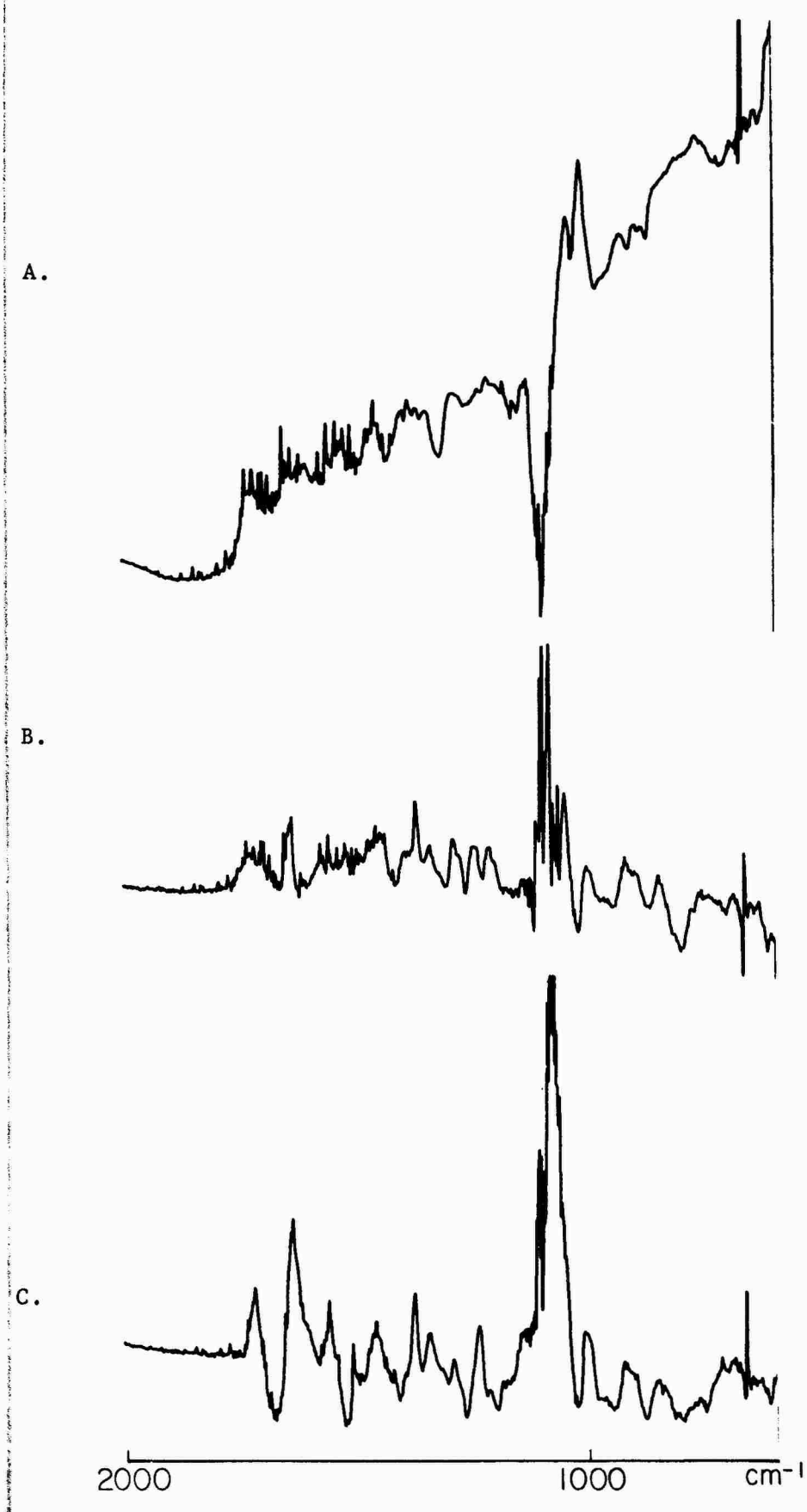

FIGURE 14. SUBTRACTED INFRARED SPECTRA OF HXUR 3113

A – HXUR 3113 (23 C, 95 percent RH) minus HXUR 3113 (23 C, 0 percent RH).

B – HXUR 3113 (85 C, 0 percent RH) minus HXUR 3113 (23 C, 0 percent RH).

C – HXUR 3113 (85 C, 95 percent RH) minus HXUR 3113 (23 C, 0 percent RH).

The sample exposed to both heat and moisture softens more than the HXUR 3113 samples exposed to other conditions, but does not show as much of a weight gain as the sample exposed only to moisture. Again this behavior is reflected in the spectrum (Figure 14C) which shows the effect of both heat and moisture. A large softening occurs and a major band forms near 1090 cm^{-1}. However, this sample gains much less weight than the sample exposed only to moisture and indeed the spectral changes are different for the two samples. From these spectra it is difficult to tell if the 1090 cm^{-1} band (sample exposed to both heat and moisture, Figure 14C) arises from an alcoholic C-O vibration or is a new type of ether C-O band (as postulated in the section on Effects of Length of Exposure). The lack of a major weight gain might indicate that an ether is formed, but more evidence is needed before this can be established. The fact that the HXUR 3113 exposed to only moisture forms alcohols (and softens) might indicate that the 1090 cm^{-1} band (in the sample exposed to both heat and moisture) is an alcohol (since this sample shows even more softening). However, even if this is true, the 1090 cm^{-1} band has to be due to a different type of alcohol than those represented by the 1010 and 1050 cm^{-1} bands of Figure 14B.

DISCUSSION

The data from the two major sets of experiments (effects of length of exposure and effects of variation of exposure conditions) clearly indicate that all the measurement techniques (IR, NMR, chemiluminescence, and dynamic mechanical measurements) can detect changes in epoxy and urethane systems. These data combined with the data from weight change

and hardness tests demonstrate the complex nature of the changes in the polymer systems (indicate that the reversion process is only a part of the chemical changes taking place). In spite of this complexity, some progress has been made on directly relating some of the chemical changes to the reversion process. This has enabled us to begin thinking about a mechanism for the reversion reaction.

For epoxy polymers several phenomena occur, among which are:

(1) Water pickup or gain

(2) Conversion of ester to acid

(3) Formation of a new carbonyl species (unsaturated acid?).

While all three reactions may be necessary to the production of reversion, only the last reaction appears to be directly related to the reversion process. It is only when this new carbonyl species is observed that there is marked softening of the epoxy polymer. Water pickup and conversion of acid to ester can be observed without marked softening of the polymer.

In addition, the experiments on epoxy polymers exposed to a variety of conditions showed that for the 2-week time of exposure only under-cured epoxy polymers showed much indication of reversion as evidenced by either softening or appearance of the new carbonyl species. This suggests the possibility that the reversion reaction is initiated at the same sites that would crosslink if the epoxy was further cured. The hardness data, the weight gain data, and the spectroscopic data all show the same trend or correlation of less change (on exposure

to heat and moisture) with increasing degree of cure. Thus, the reversion mechanism could be initiated by moisture attack at the cross linking site, followed by addition of H_2O or OH, bond dissociation, and formation of a carbonyl species.

For the urethane polymer, it appears to be possible to induce reversion just by exposure of the polymer to only moisture, but the reversion process is accelerated by exposure to both heat and moisture. However, different chemical species are formed by each exposure condition. Alcohols (1010 and 1050 cm^{-1}) are formed by exposure of a urethane to moisture only, but the combination of heat and moisture either forms a different alcohol structure (1090 cm^{-1}) than formed by moisture alone or a different ether than present in the original polymer. It would seem that the reaction sequence (as outlined on page 13) might be somewhat changed. There is initial water pickup or gain (as shown by the weight gain data) and this leads to alcohol formation. However, with continued exposure of the urethane to moisture and heat, there is weight loss (loss of OH or H_2O) which leads to formation of a new type of alcohol or ether. This weight loss can probably be best explained by ether formation, but more proof is needed before either structure can be definitely established. The NMR data are also consistent with attack at ether carbons.

Until now, we have not discussed whether the exposure experiments shed any light on reversibility of the reversion reaction. Part of the reason for this is that the experiments that will be most informative on this point are still in progress and will be completed during the next project year. These experiments consist of following the

hardness changes, weight changes, and especially the spectroscopic changes of the samples already exposed to various conditions for 2 weeks. These samples are now being stored at 23 C (and either at 0 or 95 percent RH). If the reversion is reversible, the samples will return to the original hardness values and the spectroscopic changes (1710 cm^{-1} carbonyl for epoxys and alcohol formation for urethanes) attributed to reversion will also disappear. While these experiments still need to be completed, it is certain that there are irreversible chemical changes occurring in both systems. Solubility data (obtained in the process of the NMR experiments) indicate that exposed samples are more soluble than control samples (indicating degradation of the polymer). In addition, it is highly unlikely that all of the changes observed by spectroscopy are reversible. What is not known with certainty is whether the changes attributed to reversion will reverse or not.

The reversibility of the reversion process can be determined by continued experiments (hardness tests; weight changes; IR, NMR, and chemiluminescence measurements) on the samples already exposed for 2 weeks and now in storage. In addition, the role of curing (cross linking sites) in the reversion process can be determined by testing a group of samples still being exposed (to temperature, to moisture, and to temperature and moisture) beyond the 2-week period of the samples discussed in the last section. If the well-cured epoxies eventually show reversion, it can be determined whether the changes are the same as for the low-cured epoxy.

Thus, the initial experiments of the new program year are not only well defined, but already in progress. Besides these experiments

there is need to study a polyester urethane (HXUR 3113 is a polyether urethane). From these experiments more evidence on the mechanism of reversion will be obtained and thus, we will be able to better ascertain which of the measurement techniques best follows the softening process. Work in the new program will utilize not only IR, NMR, and chemiluminescence, but also new tools such as gel permeation chromatography and differential thermal analysis.

REFERENCE

(1) Naval Ordnance Laboratory Technical Report NOLTR-74-82, D. S. Liquin and R. D. Willer, May, 1974.

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