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

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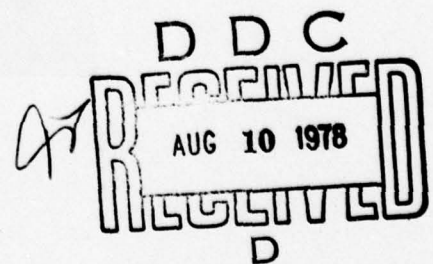
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sensitive to changes in either property. For the urethane polymers, infrared absorption (in the 1700 cm^{-1} region) appears as the sample softens. The exact frequency of this absorption (and possibly the sensitivity of this band) appears to be dependent on the particular urethane system used.

SUMMARY

Infrared and dielectric measurements have been successfully used to detect changes in epoxy and urethane systems which soften when exposed to moisture and/or temperature. The data from these measurements show correlation with softening of the polymer systems (as determined by hardness measurements) and thus, indicates that the combination of infrared and dielectric measurements may be a sensitive means of detecting reversion in potting compounds.

For the epoxy systems, the appearance of a 1710 cm^{-1} infrared absorption closely correlates with softening and loss of electrical properties and is sensitive to changes in either property. For the urethane polymers, infrared absorption (in the 1700 cm^{-1} region) appears as the sample softens. The exact frequency of this absorption (and possibly the sensitivity of this band) appears to be dependent on the particular urethane system used.

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

by

R. J. Jakobsen

INTRODUCTION

The urethane and epoxy potting compounds used 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 malfunctions in the aircraft. Improvements have been made in the composition of these materials and test procedures 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 identify the chemical changes associated with the reversion process. Such knowledge can provide several benefits, ranging from the capability to detect reversion to the capability to predict the useful service life of the epoxy and urethane systems.

This report describes the second year of research aimed at evaluating the use of sophisticated analytical instrumentation to elucidate the chemical and physical changes that occur when epoxy and urethane compounds are exposed to conditions of high humidity and high temperature. Hopefully, these changes can be related to the reversion process, i.e., related to the softening and loss of electrical properties of the polymer systems. This information can then be used to determine which instrumentation best follows the reversion process and to develop a model for predicting service life of the polymer systems.

In the first year of research chemiluminescence, infrared (IR), and nuclear magnetic resonance (NMR) measurements were all used to detect changes in epoxy and urethane systems subjected to moisture and/or temperature. These measurements were correlated with changes in the polymer systems as determined by hardness tests.

Even though several measurement techniques could be used to follow chemical changes in samples which soften, it was not possible to ascertain which of the chemical changes were directly related to the reversion process. The one exception to this was in the infrared measurements of epoxys. In these measurements, a new carbonyl species was detected when there was marked softening of the epoxy.

Thus the initial goals of the second year of research were: (1) to determine which of the observed chemical changes are related to the reversion process, (2) to ascertain if the formation of the new carbonyl species in epoxys can be used to detect reversion in all epoxys, and (3) to find a method of detecting reversion in urethanes. This information will, in turn, lead to determining which instrumentation but follows the reversion process and to predicting the service life of the polymer systems.

EXPERIMENTAL

Analytical Instrumentation

Fourier Transform Infrared Spectroscopy (FT-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 (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.

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 D₂O 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.

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.

Polymer Studies

Sample Selection

A total of eight epoxy and urethane polymers were studied during the course of this year's program. Initially, however, four polymers were selected for study. These were: two epoxy polymers (SCTH 3 and SCTH 235), a polyester urethane (SCTH 226), and a polyether urethane (HXUR 3113).

The data gathered using the two epoxy polymers coupled with the data gathered (during the first year of the program) on another epoxy polymer (SCTH 280) indicated that a combination of dielectric measurements, infrared measurements, and hardness data could be used to detect reversion in epoxy polymer systems. These results will be discussed in more detail in the following sections of this report. Here, it suffices to mention that the encouraging results on epoxy systems indicated that the research should shift to urethane systems -- especially since urethane polymers are more widely used for aircraft electrical system potting compounds.

Therefore, a polyester urethane (SCTH 226) and a polyether urethane (HXUR 3113) were first used for studies of reversion in urethanes. While polyether urethanes are not commonly used as potting compounds, HXUR 3113 was selected in order to provide a wide range of urethane behavior and for comparison to the behavior of polyester urethanes.

The data gathered on SCTH 226 were also encouraging (in terms of detection of reversion), but it was not as definitive as the epoxy data and was data on only one urethane system. Therefore studies were started on several new polyester urethane systems (6001-XA; 6001-1,4BD; 6020-XA; and 6020-1,4BD). These urethane systems were selected in order to:

- (1) utilize different prepolymers with the same curing agent (chain extenders) and to
- (2) utilize the same prepolymer with different curing agents.

It is hoped that using different prepolymers will yield information on the effect of the prepolymer on the reversion process. Using different curing agents will give different levels of initial hardness and give information on the effect of the curing agent on the reversion process.

Very little is known about the structure of the prepolymers, 6001 and 6020, except for the fact that they are polyester urethanes. However, according to the manufacturer's specifications, the curing

agents or chain extenders are 1,4-butanediol (1,4BD) or hydroquinone bis(betahydroxyethyl) ether (XA).

Sample Preparation

Cured samples of the two part casting elastomers were prepared by premixing the two portions according to the manufacturer's specifications. Castings of 12 x 12 x 1/8 inch dimensions were made for the SCTH and the HXUR polymers, while 4 x 4 x 1/8 inch castings were made for the 6001 and 6020 polymers (due to limited quantities of material).

SCTH 3 was cured in a thermostatically-controlled oven at 77 C for 16 hours, while SCTH 235 was cured at 75 C for 22 hours. The two urethanes, SCTH 226 and HXUR 3113, were cured for 72 hours at room temperature (23 C). For the 6001 and 6020 urethanes there was an initial cure for one hour at 110 C followed by post cures of 24 hours at 110 C for the 6020 urethanes; 4 hours at 110 C for 6001-1,4BD; and 4 hours at 121 C for 6001-XA.

Exposure Conditions

Each epoxy and urethane polymer film was divided into four portions and each of the four portions were placed in a different dessicator. In the four dessicators, the films were exposed to the following conditions:

- (1) 23 C, 0 Percent RH
- (2) 23 C, 95 Percent RH
- (3) 85 C, 0 Percent RH
- (4) 85 C, 95 Percent RH

Periodically, samples were removed for dielectric, chemiluminescence, spectral (IR and NMR), and hardness measurements. After a measurement was completed, the sample was returned to its original dessicator.

Hardness Measurements

ASTM Test D2240-68 procedures were followed. All samples were measured using either a Shore A-2 durometer or a Shore D durometer after conditioning the samples for one day or more at 23 C in a dry atmosphere. Samples were measured immediately before and after any test or exposure condition. For samples exposed to elevated temperatures, hardness measurements were made both while the sample was at an elevated temperature and after the sample had cooled to room temperature.

Dielectric Measurements

The dielectric measurement instrument used in this research is a General Radio 2990 automatic capacitance measuring system. This unit has three set frequencies of 120, 400, and 1000 cycle/sec. Specimens can be in film or powder form. Operation only requires putting the sample between aluminum sheets to which the electrical contacts are made. The capacitance, resistance or dielectric, and dissipation factor can be determined automatically as a function of temperature and frequency.

RESULTS

Epoxy Polymers

SCTH 235

The hardness and volume resistivity data for SCTH 235 are shown in Figures 1 and 2, respectively. The hardness data (Shore D) indicates slight initial softening of the samples exposed to only moisture or to only heat. However, this slight softening does not appear to be significant because the samples show little change in hardness in the period from 21 to 157 days. There was major softening of the sample exposed to both heat and moisture. At 41 days exposure (to heat and moisture) the hardness reached zero on the Shore D hardness scale. This sample showed visual evidence of flow at the end of 56 days and had completely liquified at 74 days exposure to both heat and moisture.

The dielectric measurements (Figure 2) indicate little change in resistivity for the SCTH 235 sample exposed to heat only. There is some loss of resistance for the sample exposed only to moisture, but this loss is small compared to the sample exposed to both heat and moisture. Thus, both the hardness and dielectric data indicate reversion occurring for the sample exposed to heat and moisture, while the volume resistivity data indicates the possibility of reversion beginning in the sample exposed to only moisture.

The infrared spectra closely correlate with these hardness and dielectric data. Figure 3 shows subtracted spectra of SCTH 235 after 26 days exposure. Only the sample exposed to both heat and moisture showed formation of the 1710 cm^{-1} carbonyl absorption (believed to be indicative of reversion). From Figures 1 and 2, at 26 days exposure, only the sample exposed to both heat and moisture shows appreciable softening or loss of resistivity.

Figure 4B shows the subtracted spectrum of the SCTH 235 sample after 60 days exposure to both heat and moisture. Just as for the sample exposed for 26 days, there is clear evidence of the formation of a 1710 cm^{-1} carbonyl absorption band. At 60 days exposure, this sample is soft and beginning to flow.

FIGURE 1. SHORE D HARDNESS VALUES, SCTH 235

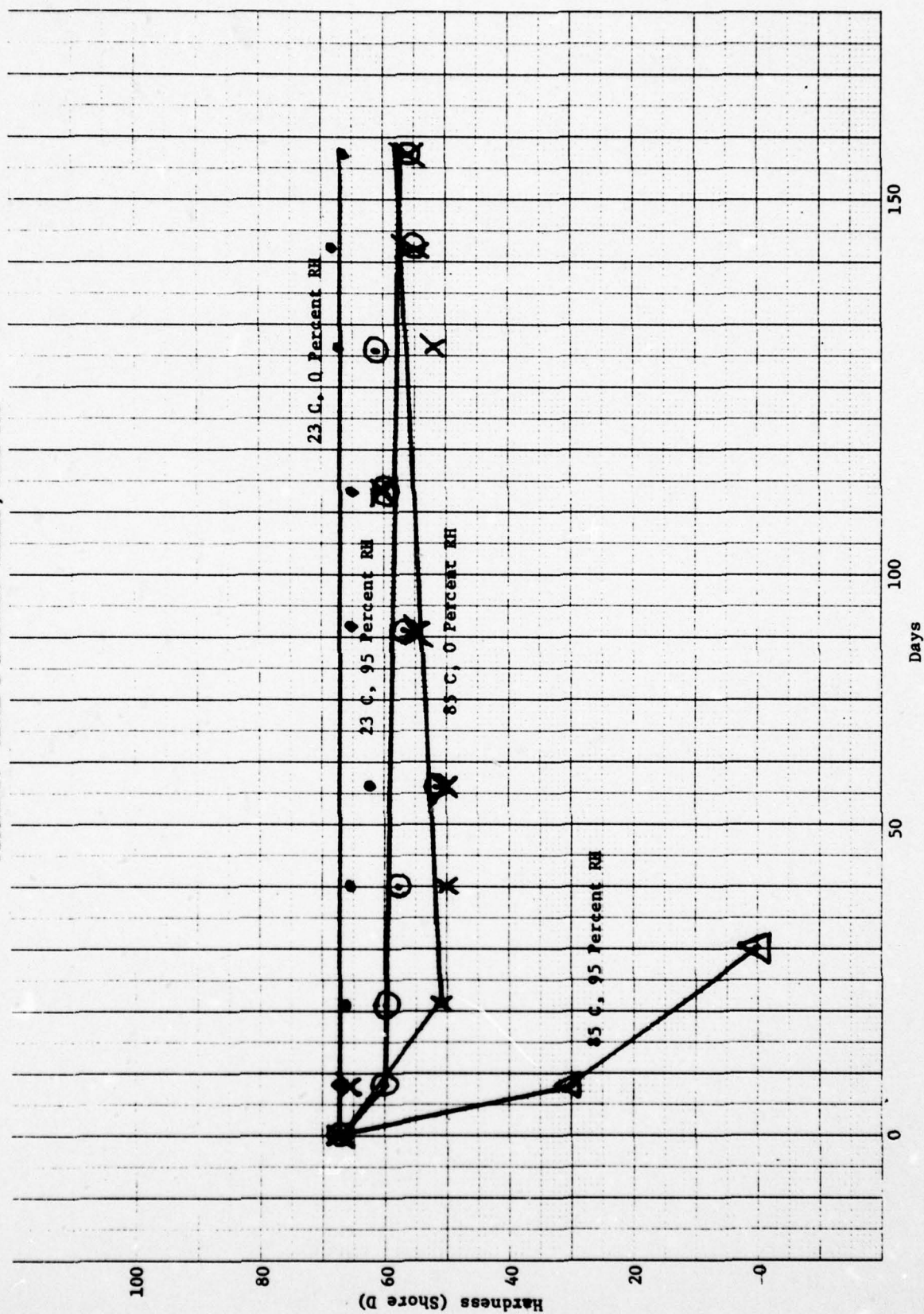
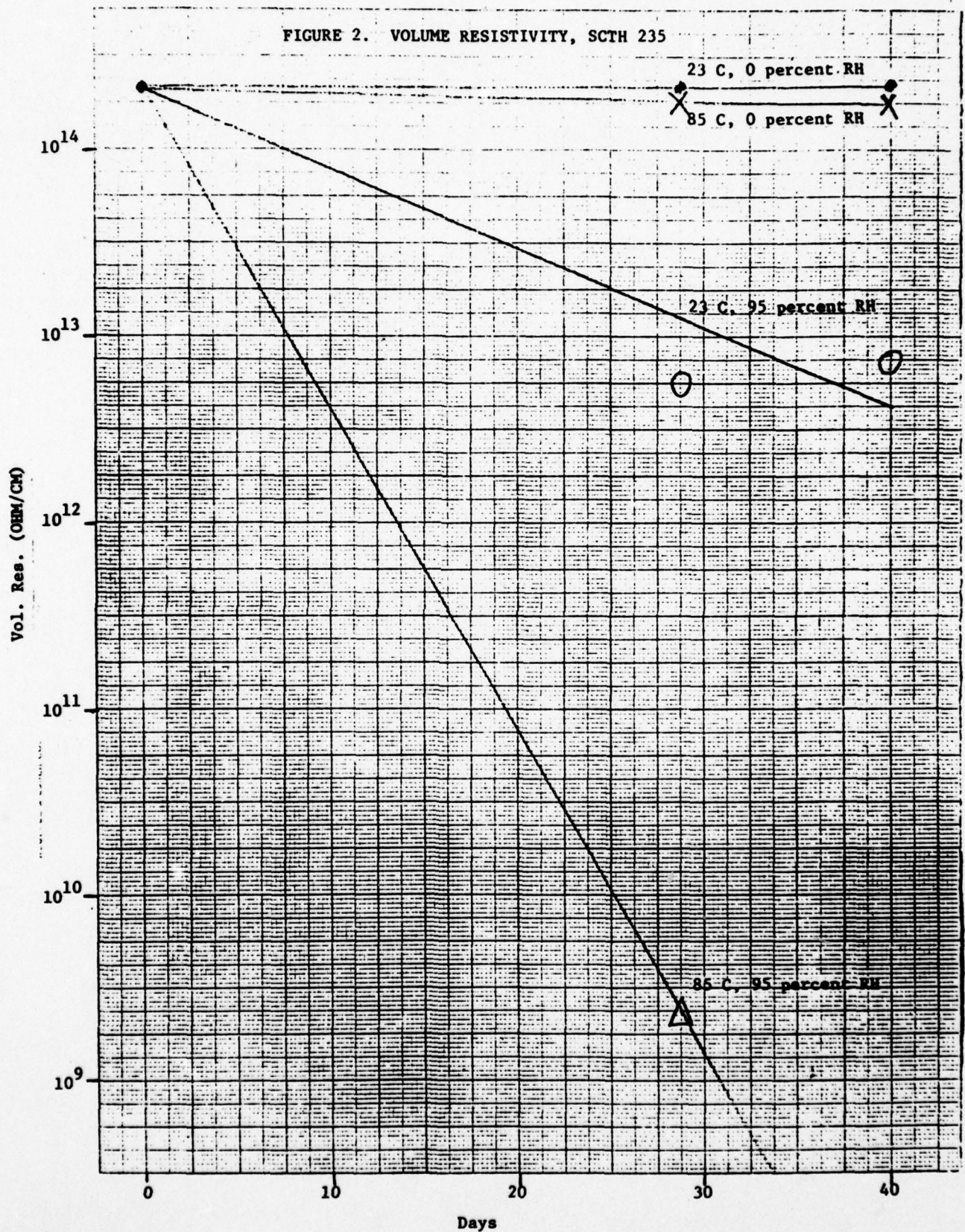


FIGURE 2. VOLUME RESISTIVITY, SETH 235



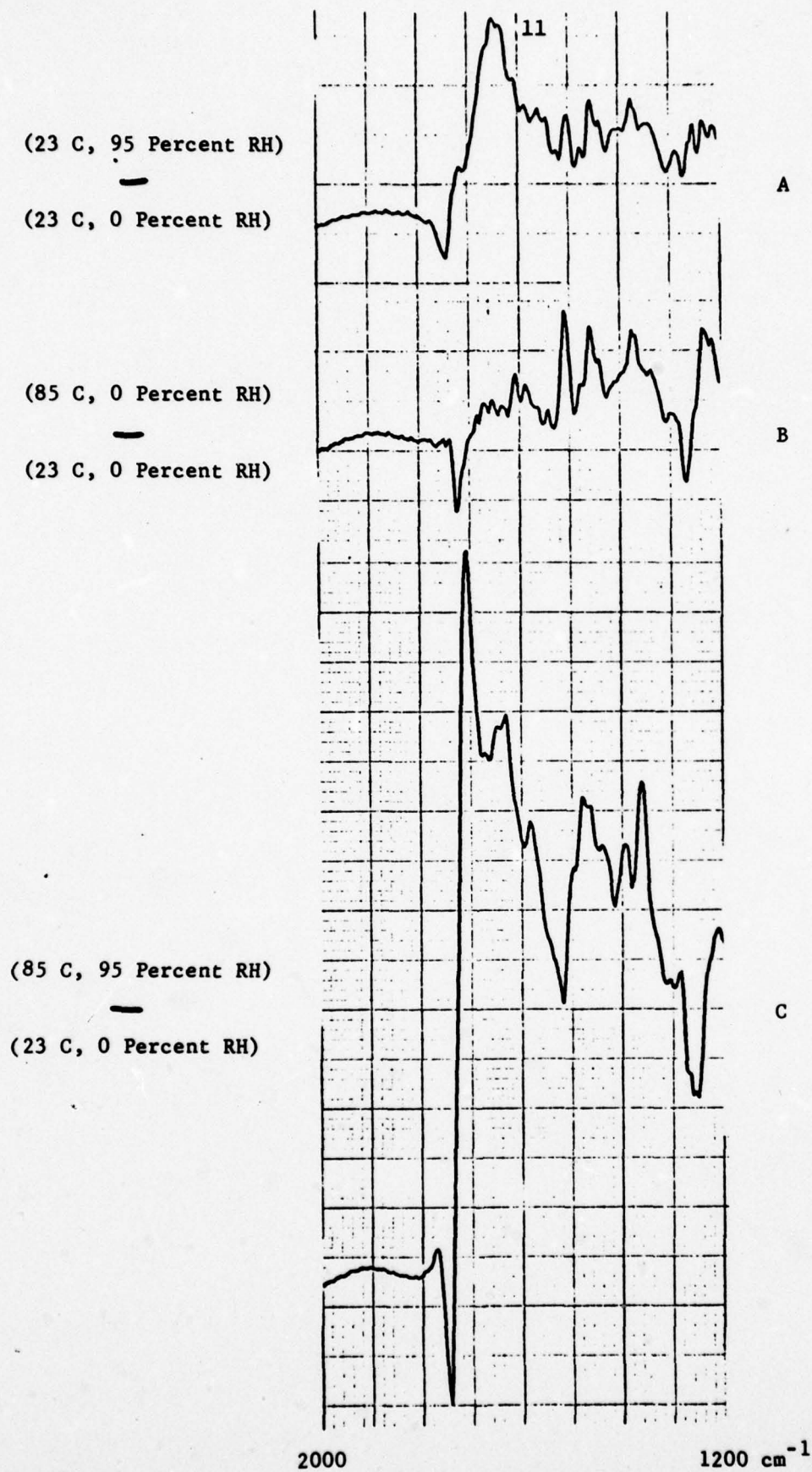
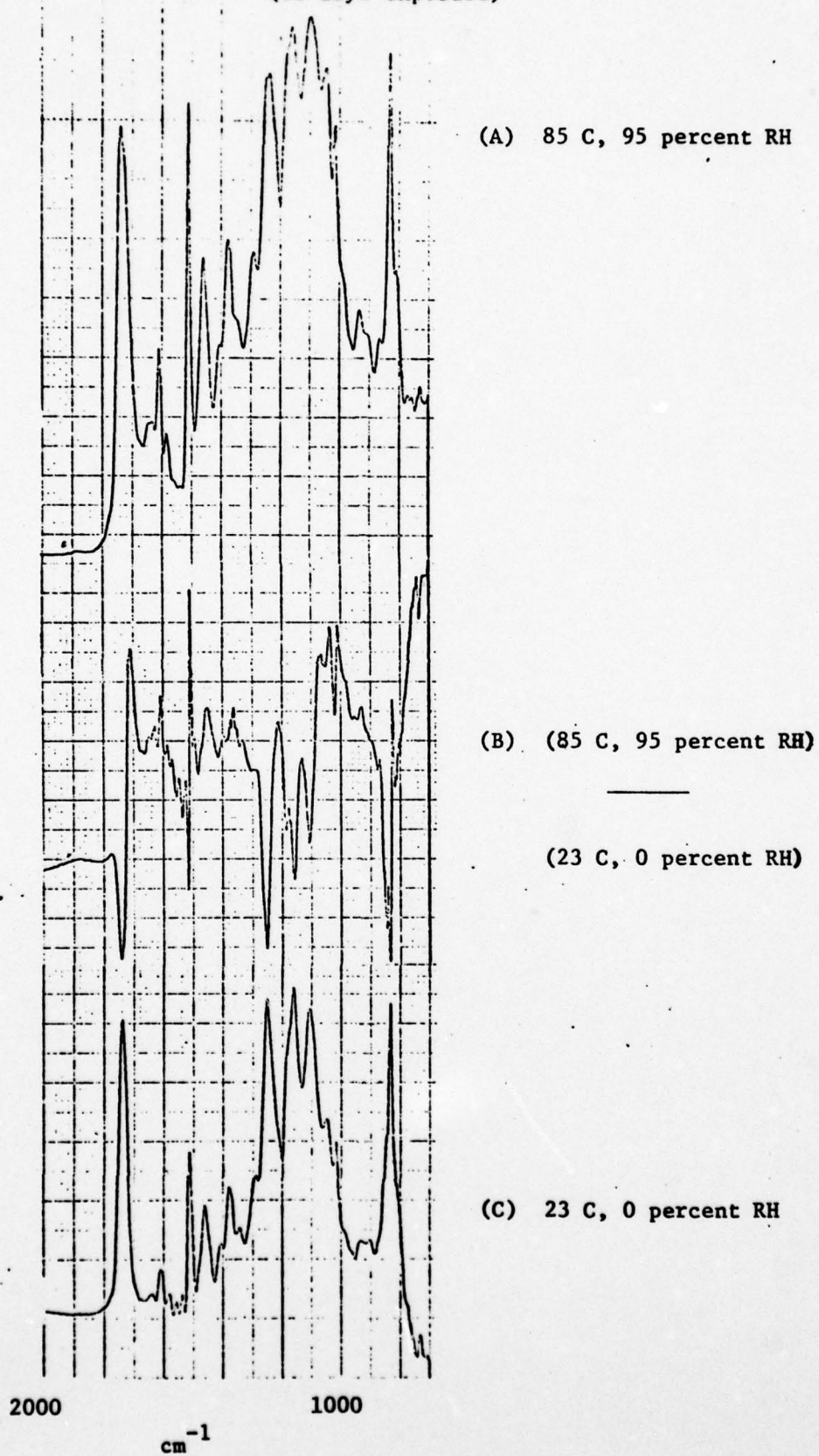


FIGURE 3. SUBTRACTED INFRARED SPECTRA OF SETH 235
(26 Days Exposure)
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FIGURE 4. INFRARED SPECTRA OF SCTH 235
(60 days exposure)



The subtracted infrared spectra, after 74 days exposure to the various exposure conditions, are shown in Figure 5. Here the sample exposed to both heat and moisture has liquefied, but the samples exposed to heat only or exposed to moisture only showed little signs of softening. The spectrum (Figure 5C) of the sample exposed to both heat and moisture shows major formation of 1710 cm^{-1} absorption. The spectra (Figure 5A and 5B) of the samples exposed to only moisture or to only heat show small signs of formation of 1710 cm^{-1} absorption. This could either be due to the beginning of the reversion process or to improper cancelling of absorption bands in the subtraction process (cancellation of the 1500 cm^{-1} C=C vibration is used as the criteria for subtraction). The dielectric data (Figure 2) at 41 days exposure indicate that reversion could be starting for the sample exposed to moisture, but without further data we cannot tell if reversion is starting for the heat exposed sample.

One of the benefits of the dedicated computer of FT-IR systems is that data can be stored and various subtractions carried out. The sample of SCTH 235 exposed to both heat and moisture showed signs of flow at 56 days exposure and had completely liquefied at 74 days exposure. Thus, using the 56 day exposure sample as the control sample for subtractions might reveal the changes due to melting or the final stages of the reversion process. Some of these subtractions are shown in Figure 6 and 7. All the spectra in these figures are for the sample exposed to both heat and moisture. Figure 6A shows the change one day (i.e., 57 days exposure - 56 days exposure) after signs of flow were detected. Figure 6B shows the changes after 4 days (60 days exposure - 56 days exposure). Both spectra indicate that the sample loses water (1630 cm^{-1}) absorption during the melting process. This loss of water can also be observed in Figure 7A which shows the spectral changes 18 days after flow was detected (when the sample completely liquefied). This loss of water could be due to many causes, among which is some degradation of the polymer due to prolonged exposure.

FIGURE 5. SUBTRACTED INFRARED SPECTRA OF SETH 235
(74 days exposure)

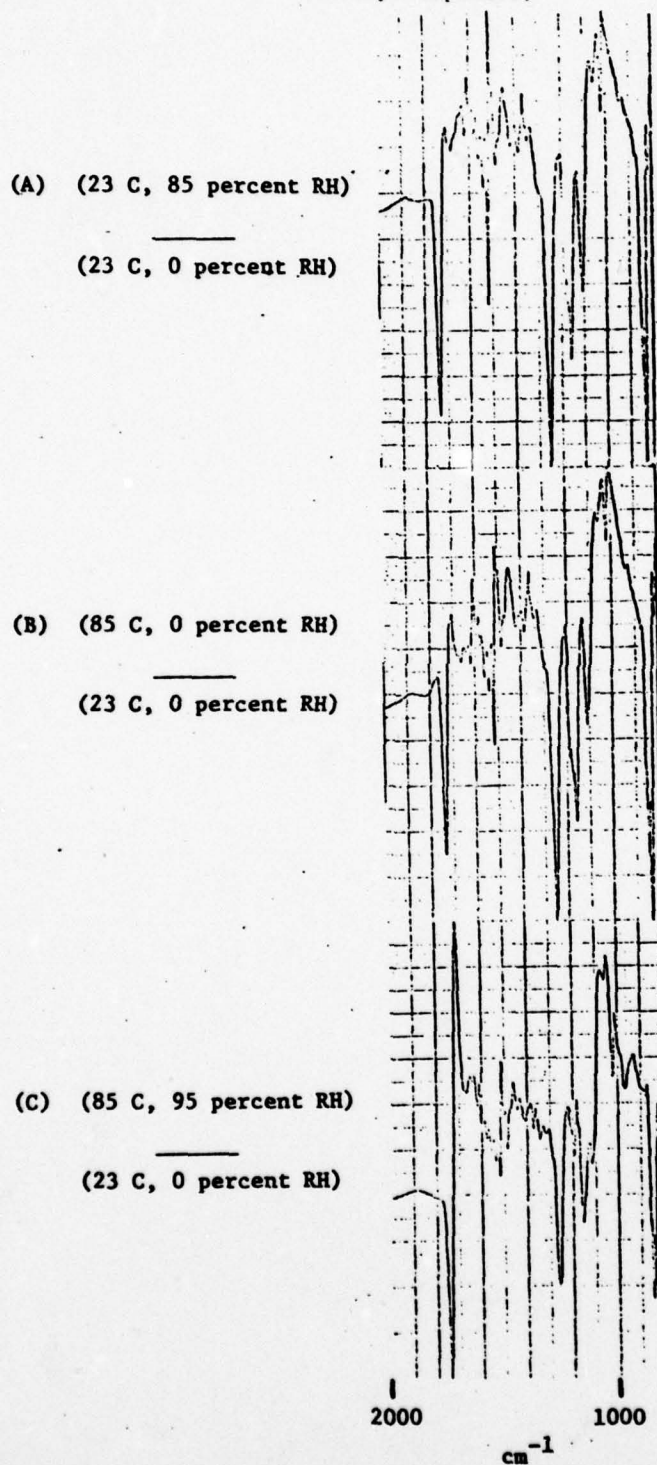


FIGURE 6. SUBTRACTED INFRARED SPECTRA OF SETH 235
(Exposed varying lengths of time at 85 C
and 95 percent RH)

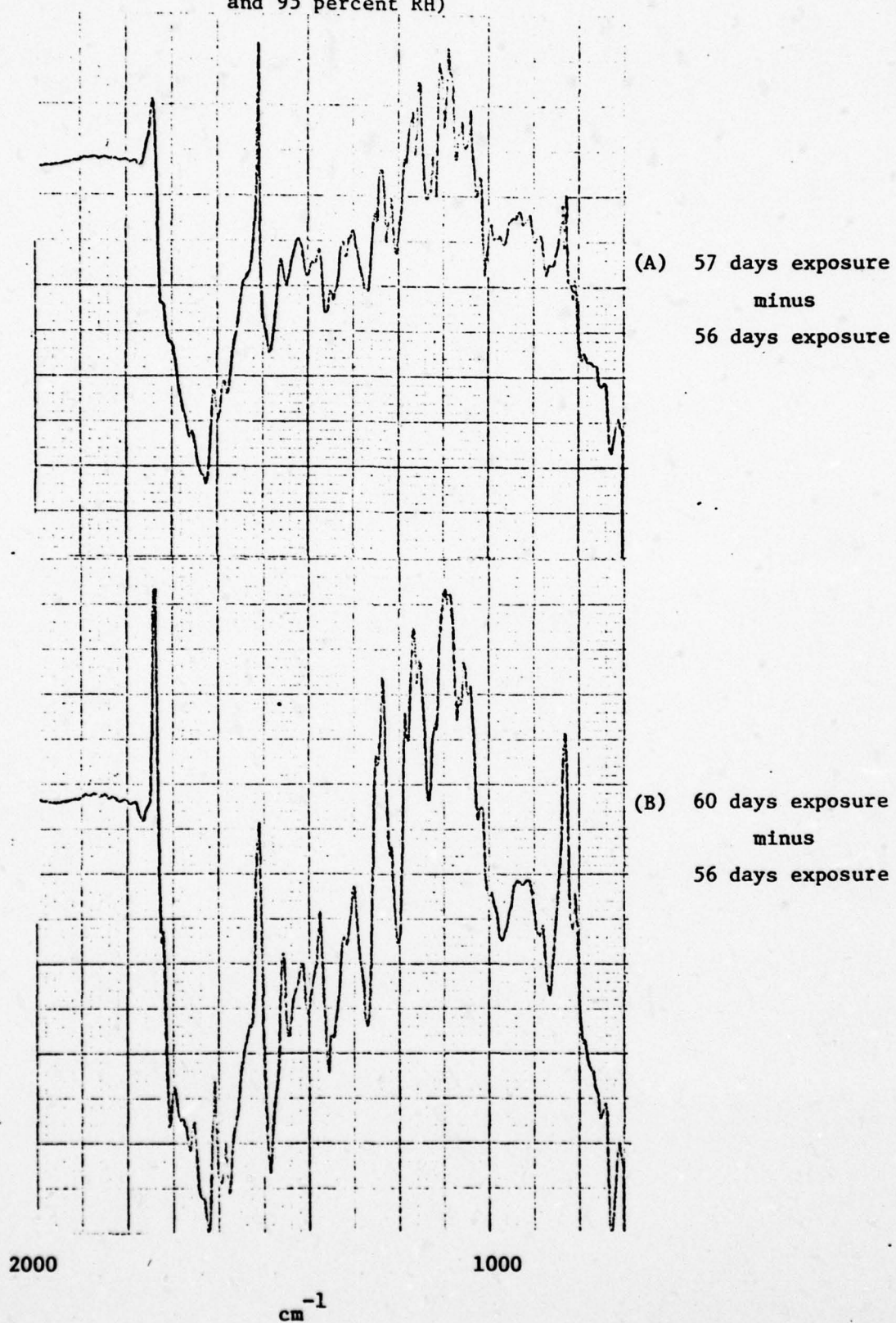
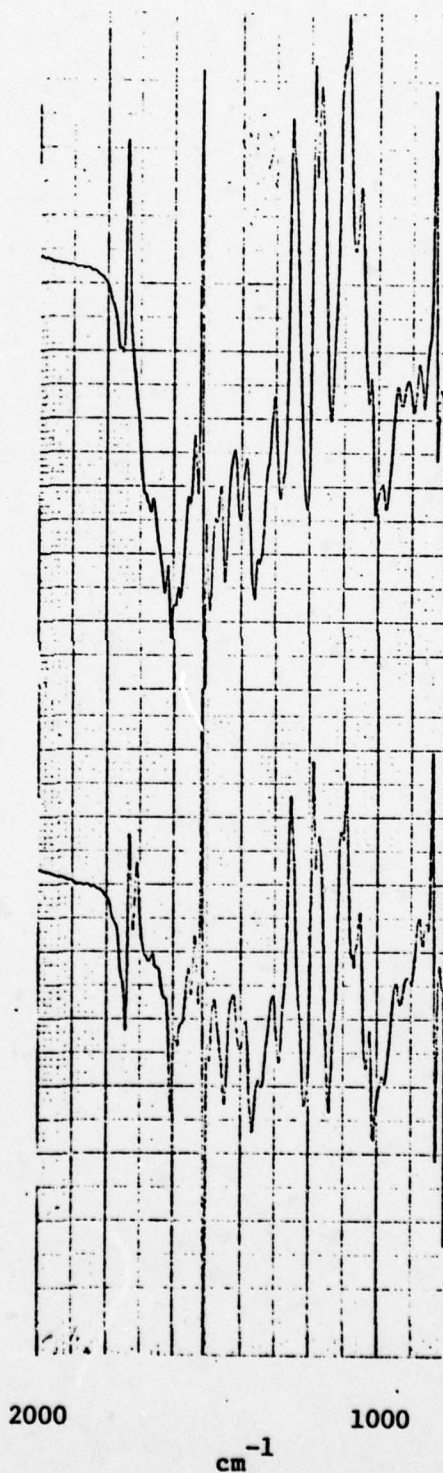


FIGURE 7. SUBTRACTED INFRARED SPECTRA OF SETH 235
(Exposed varying lengths of time at 85 C
and 95 percent RH)

(A) 74 days exposure
minus
56 days exposure

(B) 74 days exposure
minus
60 days exposure



Of interest is the spectrum of Figure 7B which shows the result of subtracting the spectrum 4 days after flow was detected from the spectrum 18 days (liquid) after flow commenced. Here there is only slight evidence for the broad H_2O band in the 1600 cm^{-1} region which possibly indicates that most of the water is lost when the polymer first becomes soft enough to flow. This spectrum also clearly shows the increase of 1710 cm^{-1} absorption as a separate band. This definitely establishes that the 1710 cm^{-1} absorption originates from a new chemical species and is not just a shifting of the original epoxy carbonyl frequency.

The samples exposed to only moisture or to only heat showed little evidence for softening (Figure 1) even after 157 days exposure. This is confirmed by the infrared spectrum shown in Figure 8 which shows the the subtracted spectrum of the sample exposed (for 186 days) to only heat. Here there are only small changes in the carbonyl region of the spectrum and these changes only indicate a lose of 1740 cm^{-1} absorption and a gain of 1720 cm^{-1} absorption, not formation of a new species near 1710 cm^{-1} . Thus the infrared spectrum of this sample does not show any evidence of reversion.

SCTH 3

Hardness and dielectric data for SCTH 3 are shown in Figures 9 and 10, respectively. The patterns of these curves are similar to the hardness and dielectric data obtained for SCTH 235. Only the sample exposed to both heat and moisture showed much softening and loss of electric properties, but the sample exposed to moisture gave evidence for some change in resistivity.

The subtracted infrared spectra (Figure 11) of the SCTH 3 samples after 4 days exposure show formation of a 1710 cm^{-1} carbonyl band for the sample exposed to both heat and moisture, but no 1710 cm^{-1} absorption is observed for the samples exposed to moisture or exposed to heat. These effects are even more dramatically shown in Figure 12. This figure shows a similar subtracted set of spectra of SCTH 3 samples after 28 days exposure (after the temperature-moisture exposed sample

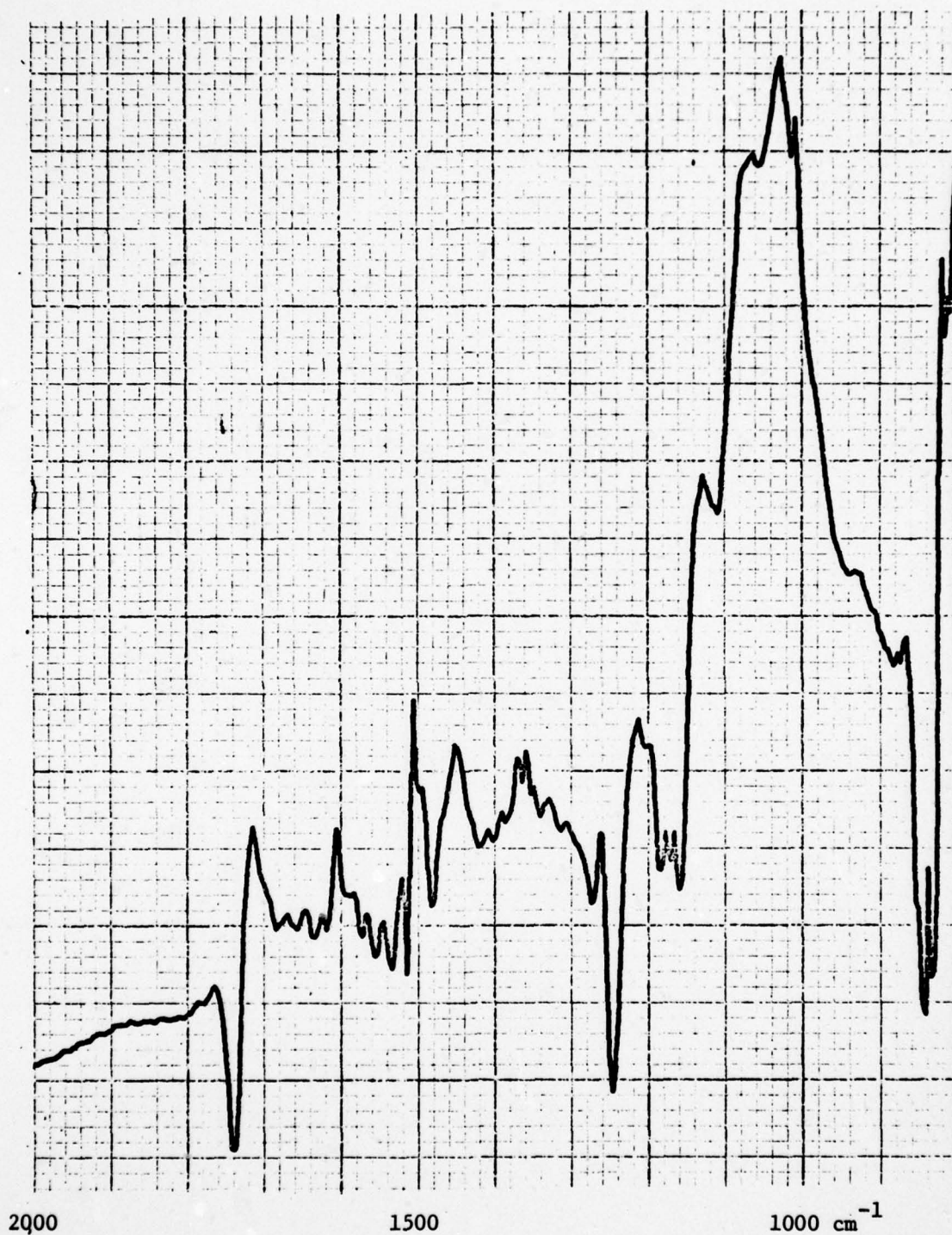


FIGURE 8. SUBTRACTED INFRARED SPECTRUM OF SCTH 235 EXPOSED 186 DAYS
(85 C, 0 PERCENT RH - 23 C, 0 PERCENT RH)

FIGURE 9. SHORE D HARDNESS VALUES (SCTH3)

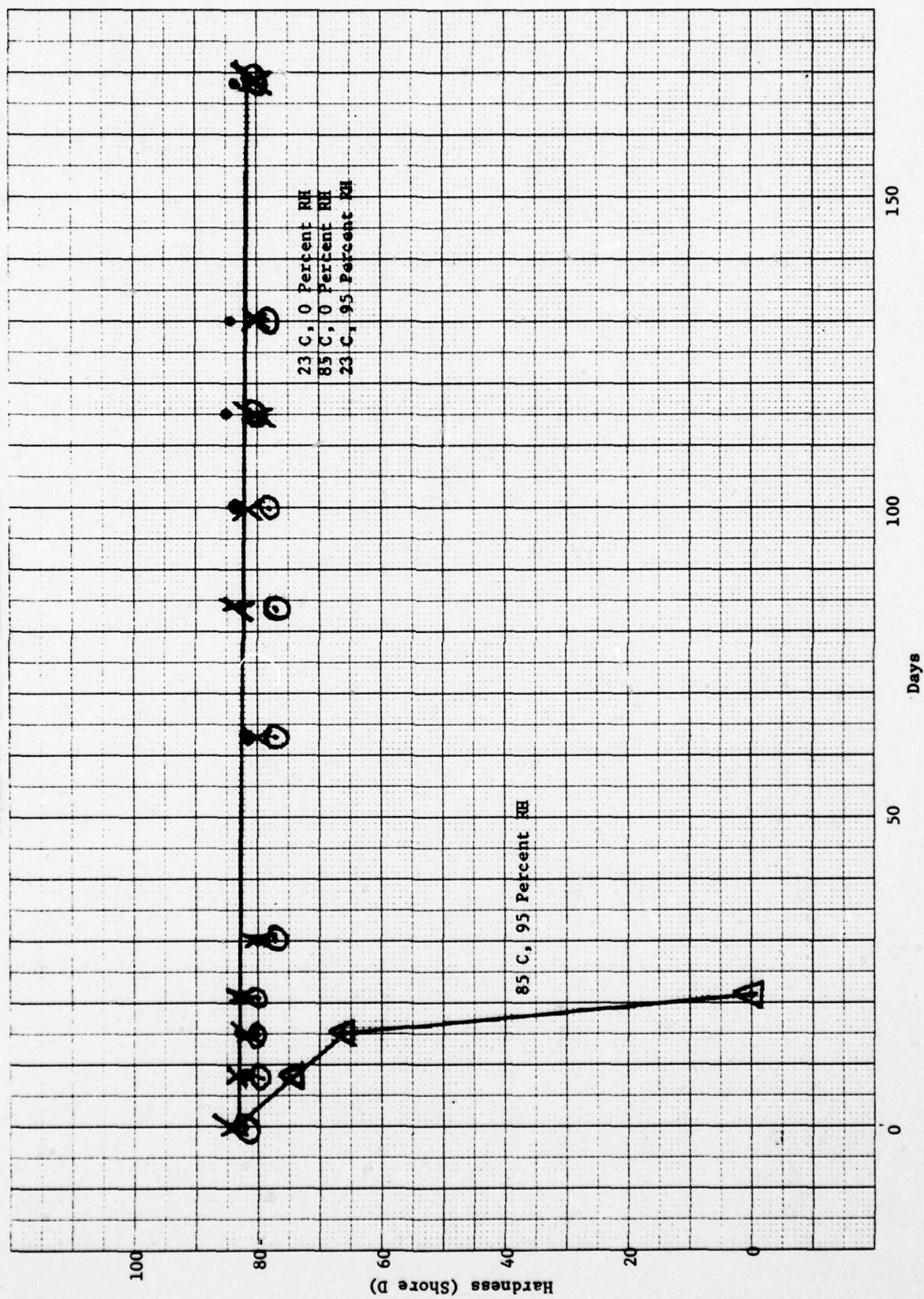


FIGURE 10. VOLUME RESISTIVITY, SCTH 3

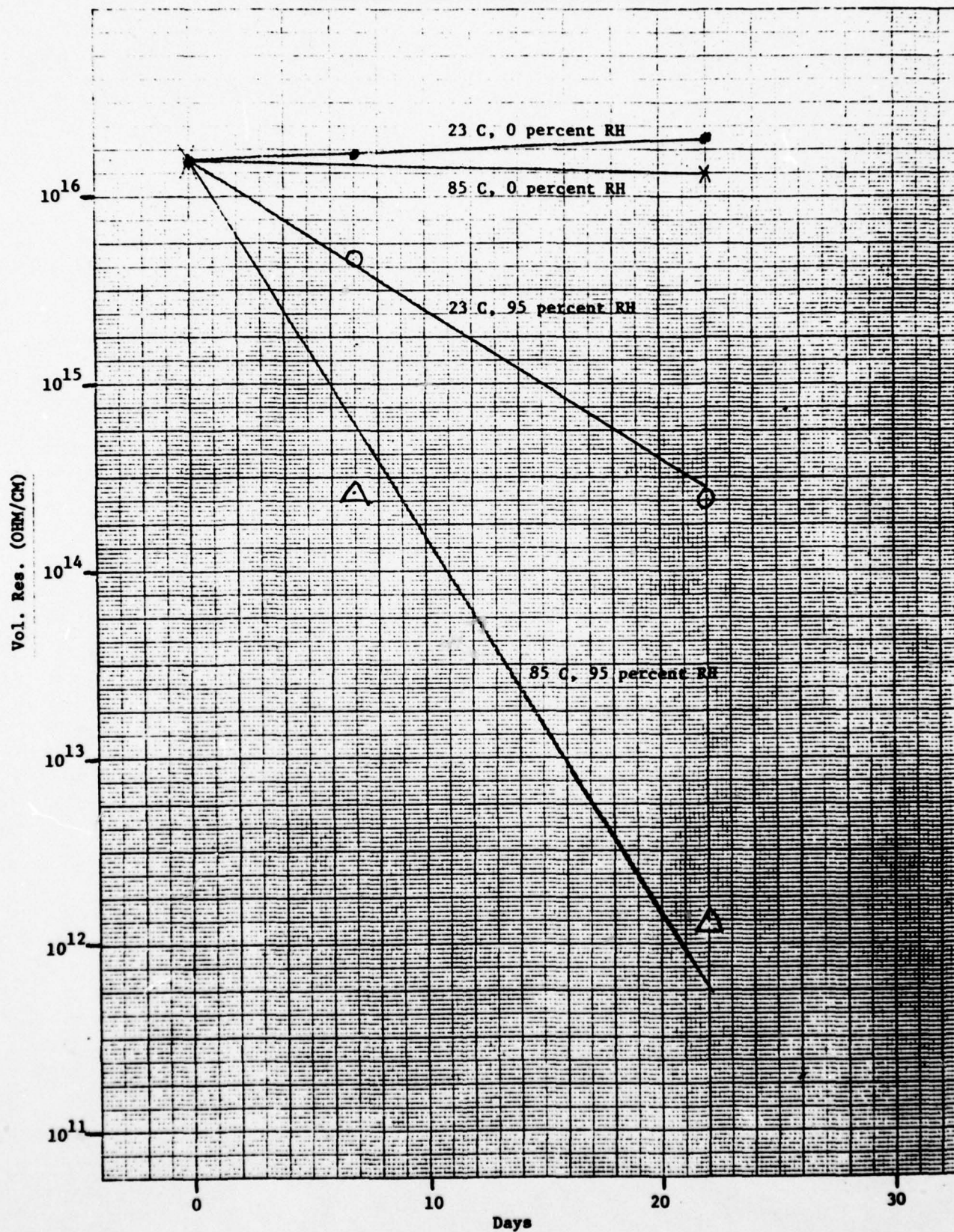


FIGURE 11. SUBTRACTED INFRARED SPECTRA OF SCTH 3
(4 Days Exposure)

(23 C, 95 Percent RH)

(23 C, 0 Percent RH)

A

(85 C, 0 Percent RH)

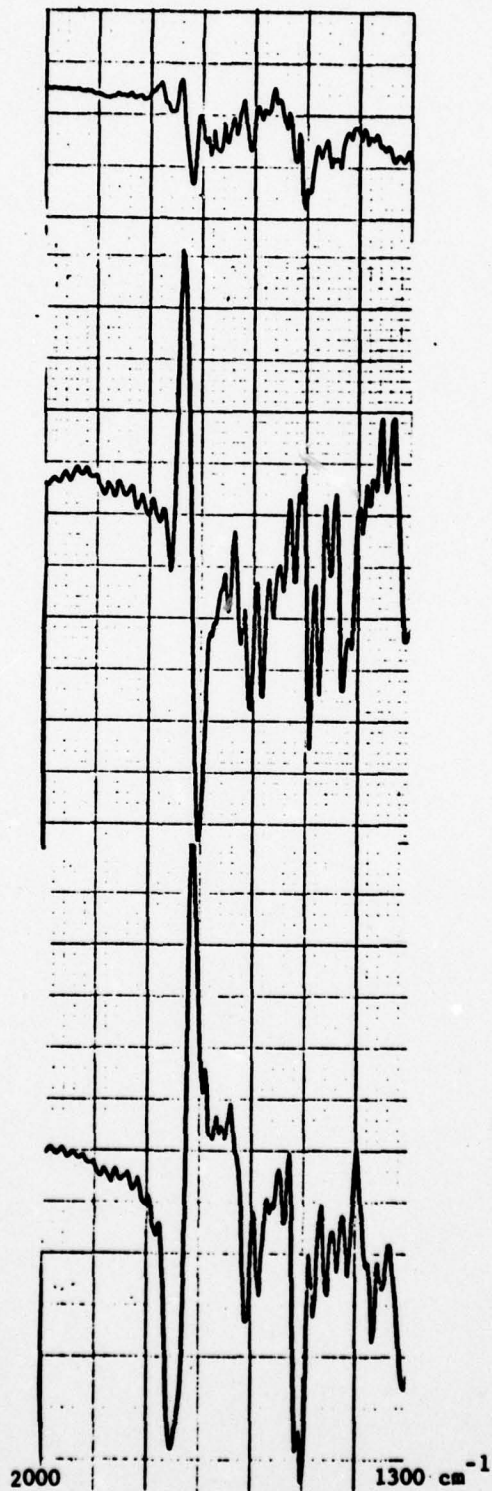
(23 C, 0 Percent RH)

B

(85 C, 95 Percent RH)

(23 C, 0 Percent RH)

C



(A) 23 C, 95 percent
RH

23 C, 0 percent
RH

(B) 85 C, 0 percent
RH

23 C, 0 percent
RH

(C) 85 C, 95 percent
RH

23 C, 0 percent
RH

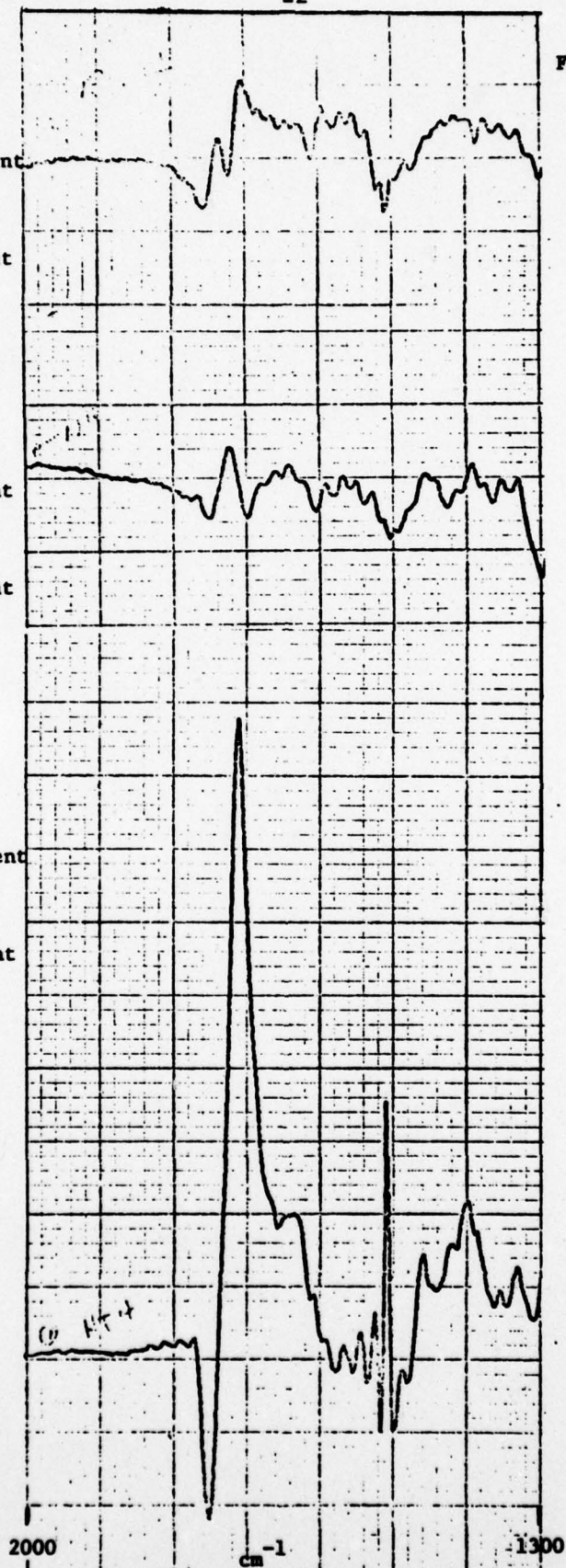


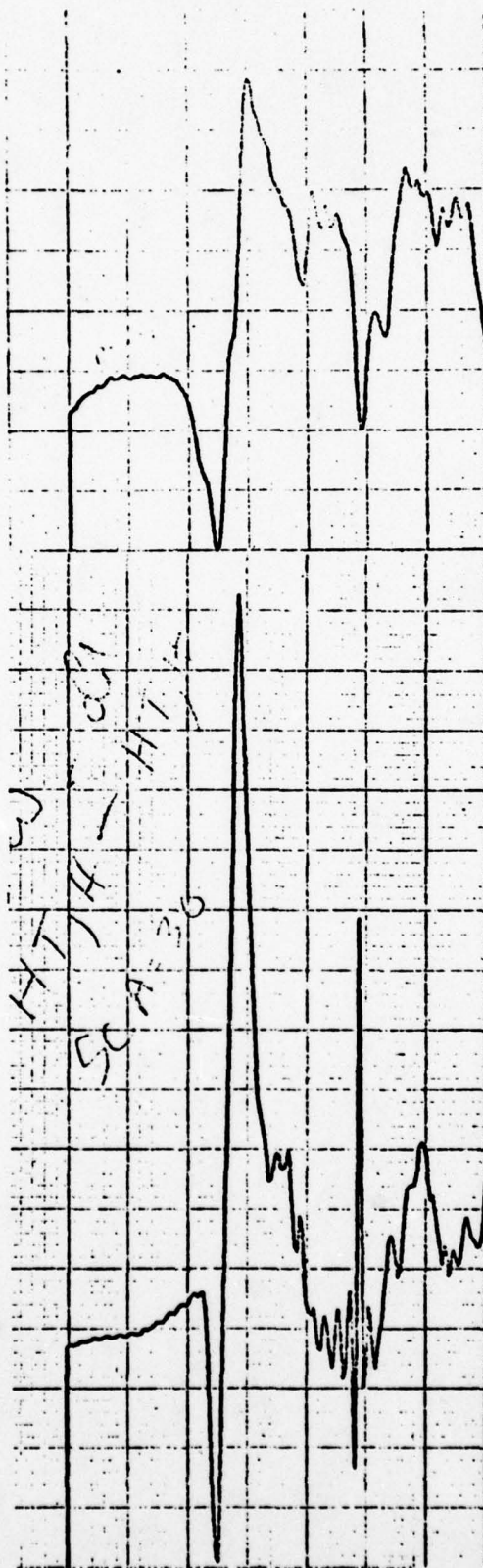
FIGURE 12. SUBTRACTED
INFRARED SPECTRA
OF SCTH 3
(28 days ex-
posure)

had liquefied). Here only the sample exposed to both heat and moisture gives major changes (formation of 1710 cm^{-1} absorption) upon exposure. However, while small, the sample exposed to moisture gives some evidence for a band at 1710 cm^{-1} . In order to verify this 1710 cm^{-1} band in the moisture exposed sample, we subtracted the 4-day exposure samples from the corresponding 28-day exposure samples. These subtracted spectra are shown in Figure 13 for the sample exposed to moisture (Figure 13A) and for the sample exposed to temperature and moisture (Figure 13B). Figure 13A demonstrates that 1710 cm^{-1} absorption is formed in the moisture exposed sample between 4 and 28 days exposure. While small compared to the moisture and temperature exposed sample, 1710 cm^{-1} absorption is definitely formed in the sample exposed to just moisture. The hardness data (Figure 9) does not show appreciable softening for the sample exposed to moisture for 28 days. This could mean that observation of 1710 cm^{-1} absorption is not an indication of reversion. However since the dielectric data (Figure 10) shows some loss of electrical properties for the moisture exposed sample, we feel that the dielectric and infrared techniques are more sensitive indicators of reversion than Shore A or D hardness measurements.

Figure 14 shows that no infrared evidence of reversion is detected unless softening or loss of electric properties is observed. This figure gives a subtracted spectrum of the sample exposed (for 189 days) to only heat. No softening or loss of electrical properties has been detected for this sample (Figures 9 and 10) and correspondingly, no absorption at 1710 cm^{-1} can be seen. Instead there is a loss of infrared absorption near this frequency which may result from prolonged exposure to heat.

Further evidence for reversion in the moisture exposed SCTH 3 sample comes from the measurements of the dissipation factor as shown in Figures 15 through 20. These figures show the change in dissipation factor between samples exposed for approximately 1 week (7 to 10 days) and those exposed for approximately 3 weeks (20 to 23 days). Figures 15 and 16 show that there is not much change in the magnitude of the dissipation factor in this time period for the heat exposed sample. However,

FIGURE 13. SUBTRACTED INFRARED SPECTRA OF SCTH 3 (Exposed varying lengths of time)



(A) 23°C, 95 percent RH,
28 days exposure

4 days exposure

(B) 85°C, 95 percent RH,
28 days exposure

4 days exposure

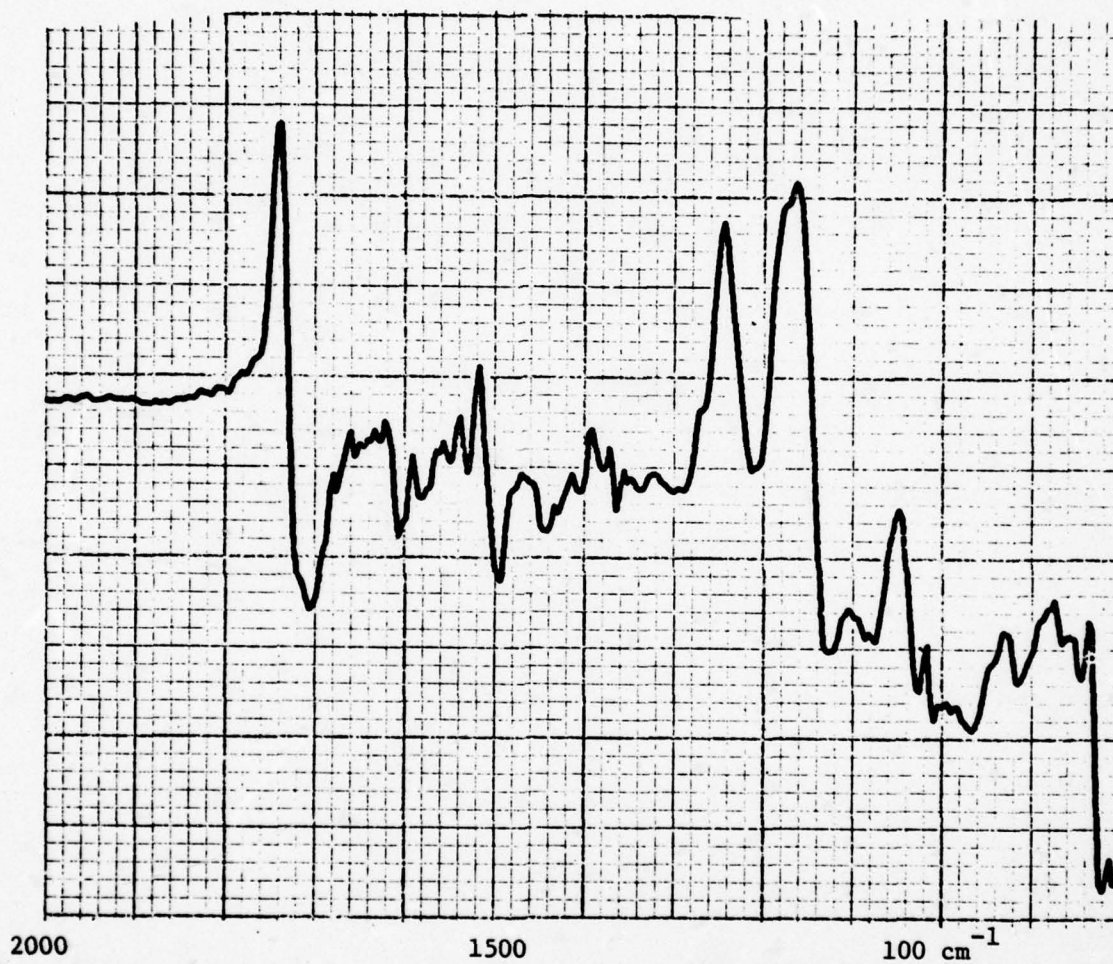


FIGURE 14. SUBTRACTED INFRARED SPECTRUM OF SCTH 3 EXPOSED 189 DAYS
(85 C, 0 PERCENT RH - 23 C, 0 PERCENT RH)

FIGURE 15. DISSIPATION FACTOR MEASUREMENTS, SCTH 3, 8 DAYS AT 85 C, 0 PERCENT RH

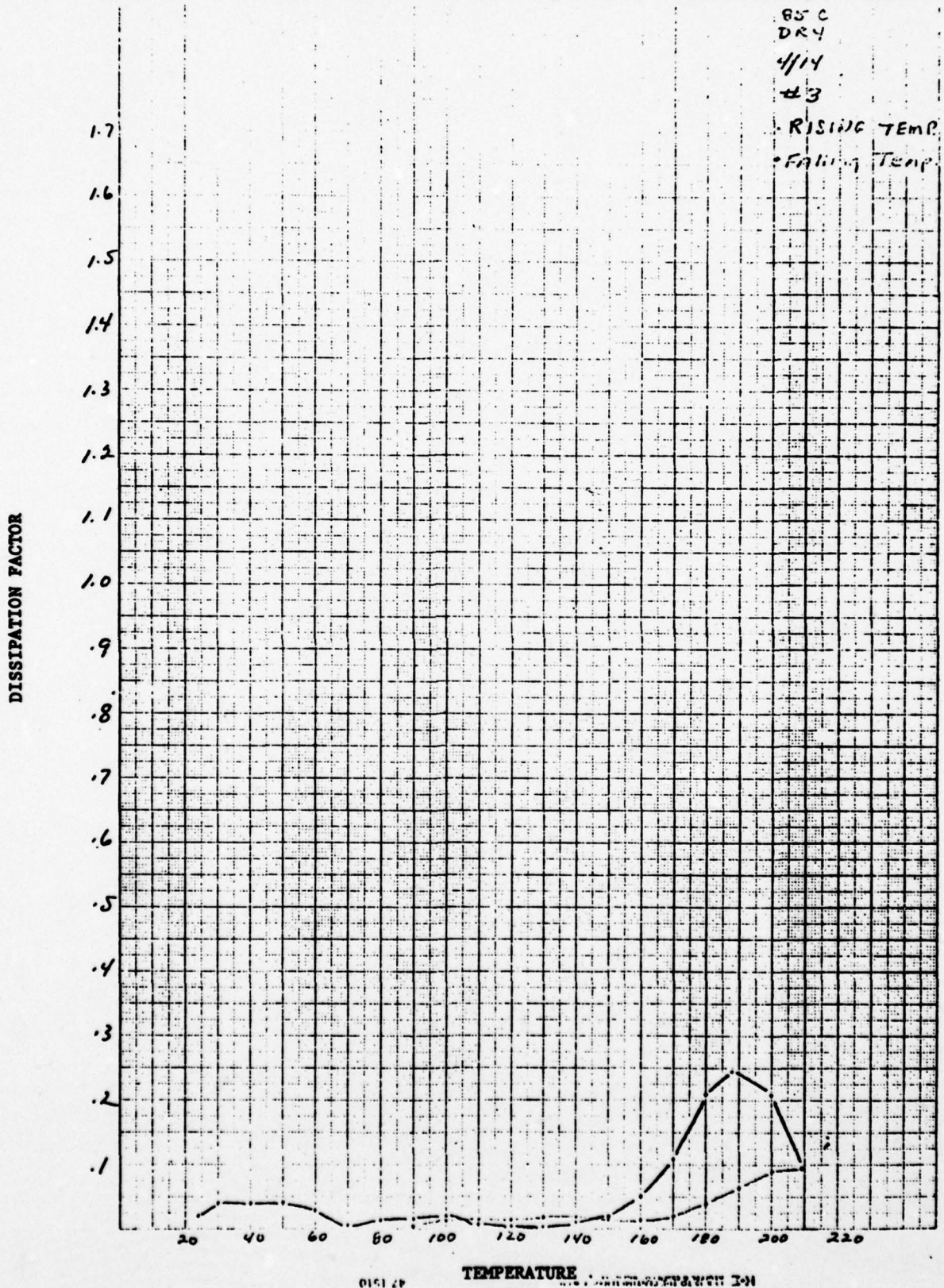


FIGURE 16. DISSIPATION FACTOR MEASUREMENTS, SCTH 3, 22 DAYS AT 85 C, 0 PERCENT RH

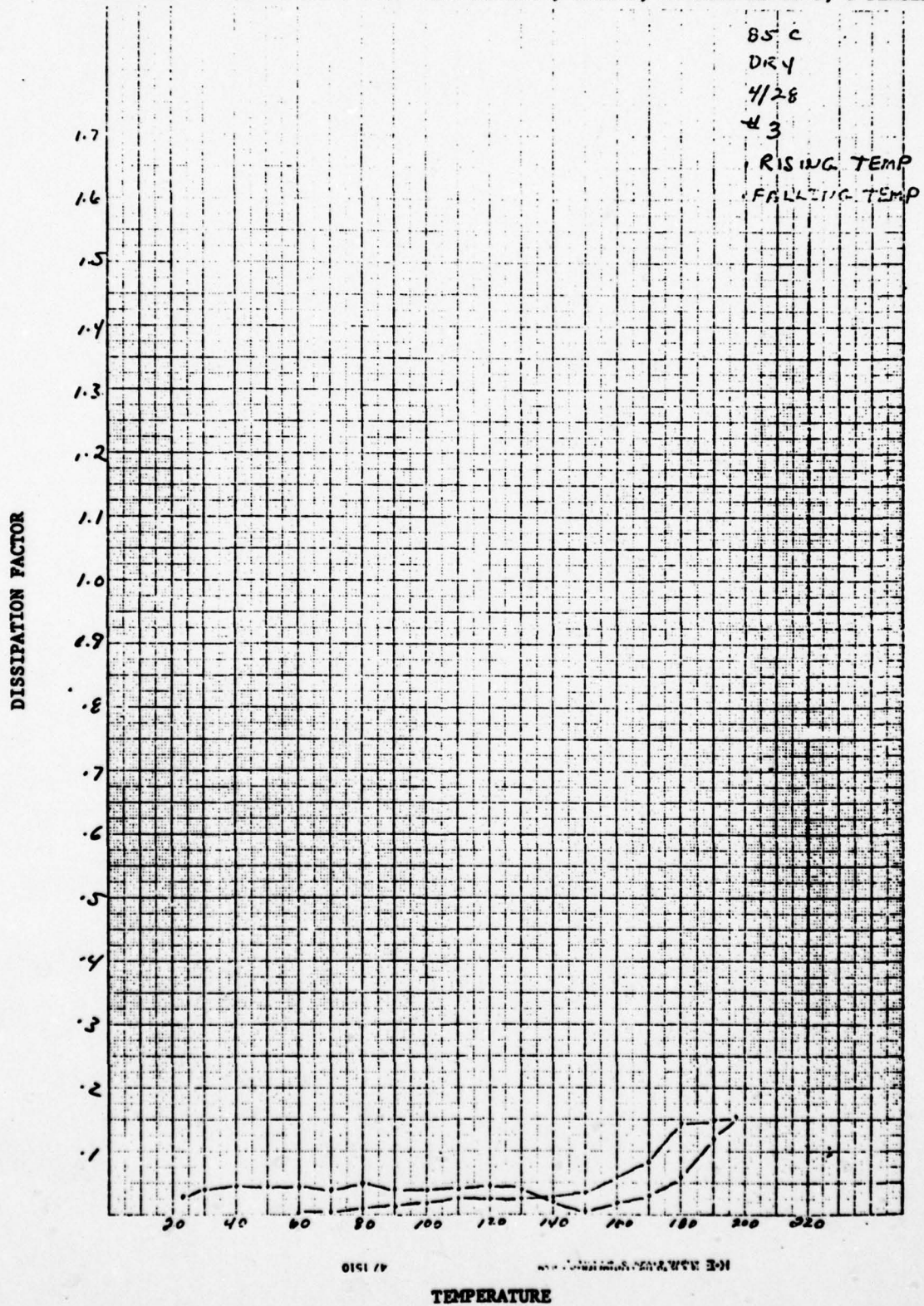
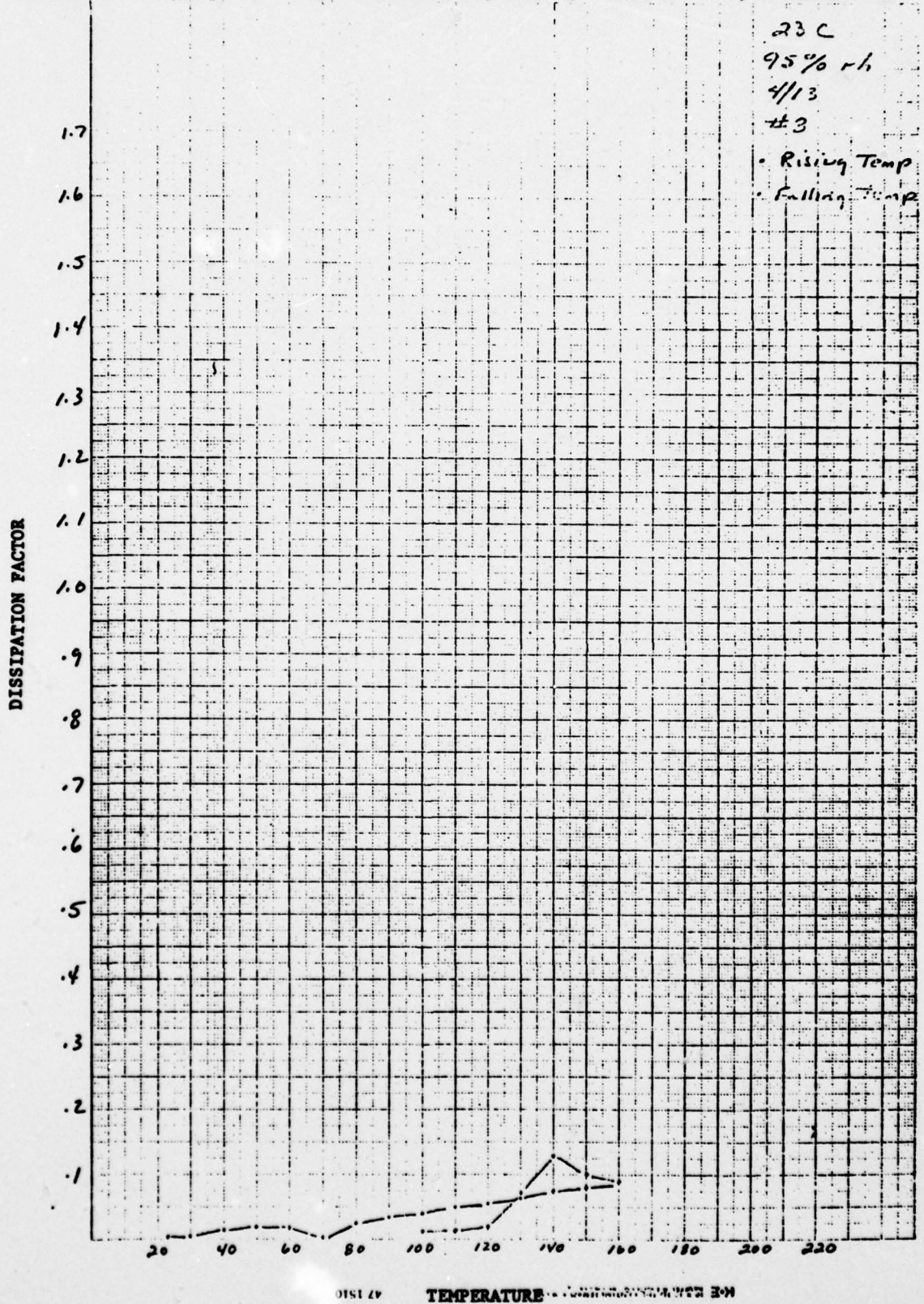


FIGURE 17. DISSIPATION FACTOR MEASUREMENTS, SCTH 3, 7 DAYS AT 23 C, 95 PERCENT RH



BATTLE - COLUMBUS

FIGURE 18. DISSIPATION FACTOR MEASUREMENTS, SCTH 3, 23 DAYS AT 23 C, 95 PERCENT RH

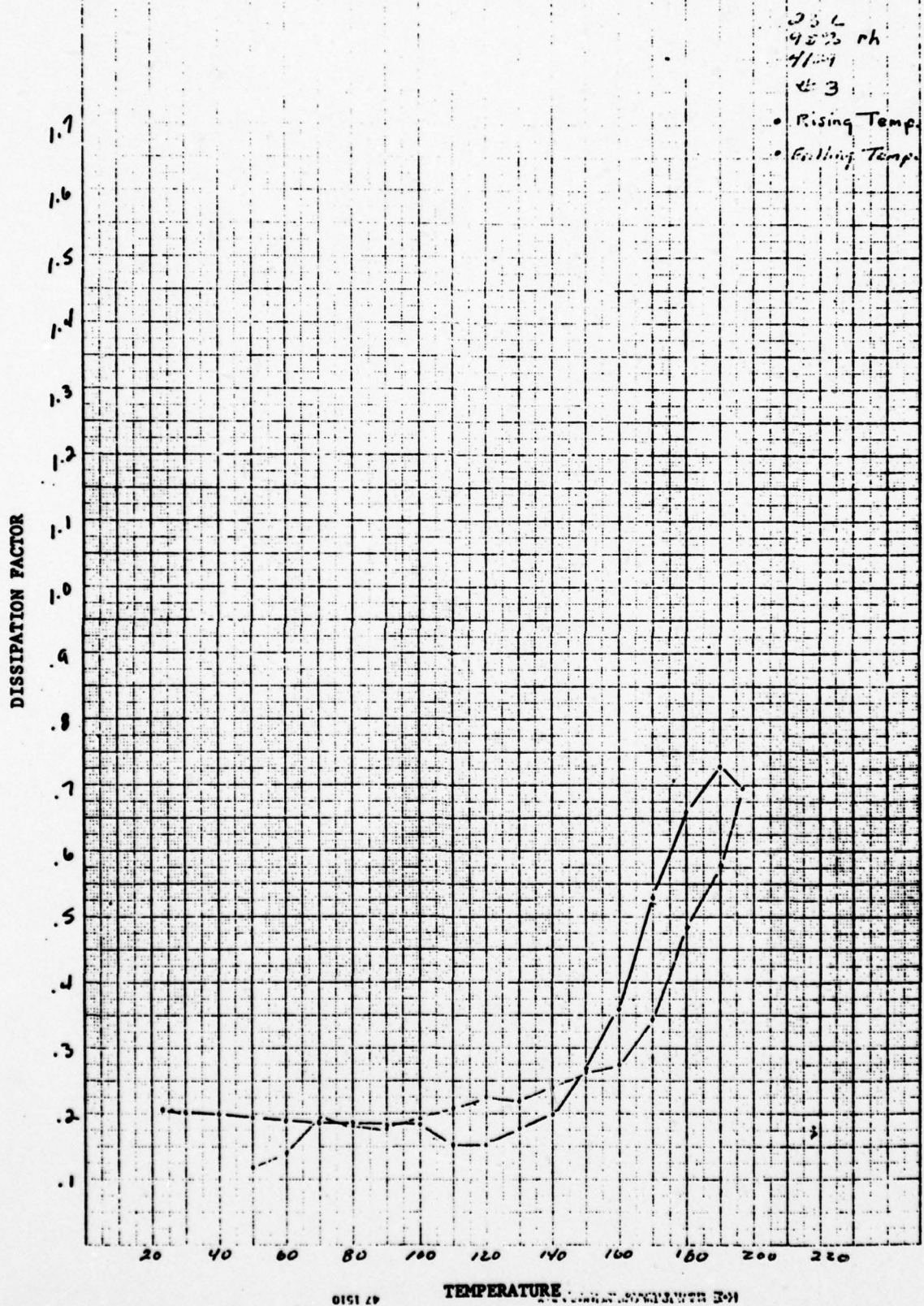


FIGURE 19. DISSIPATION FACTOR MEASUREMENTS, SCTH 3, 7 DAYS AT 85 C, 95 PERCENT RH

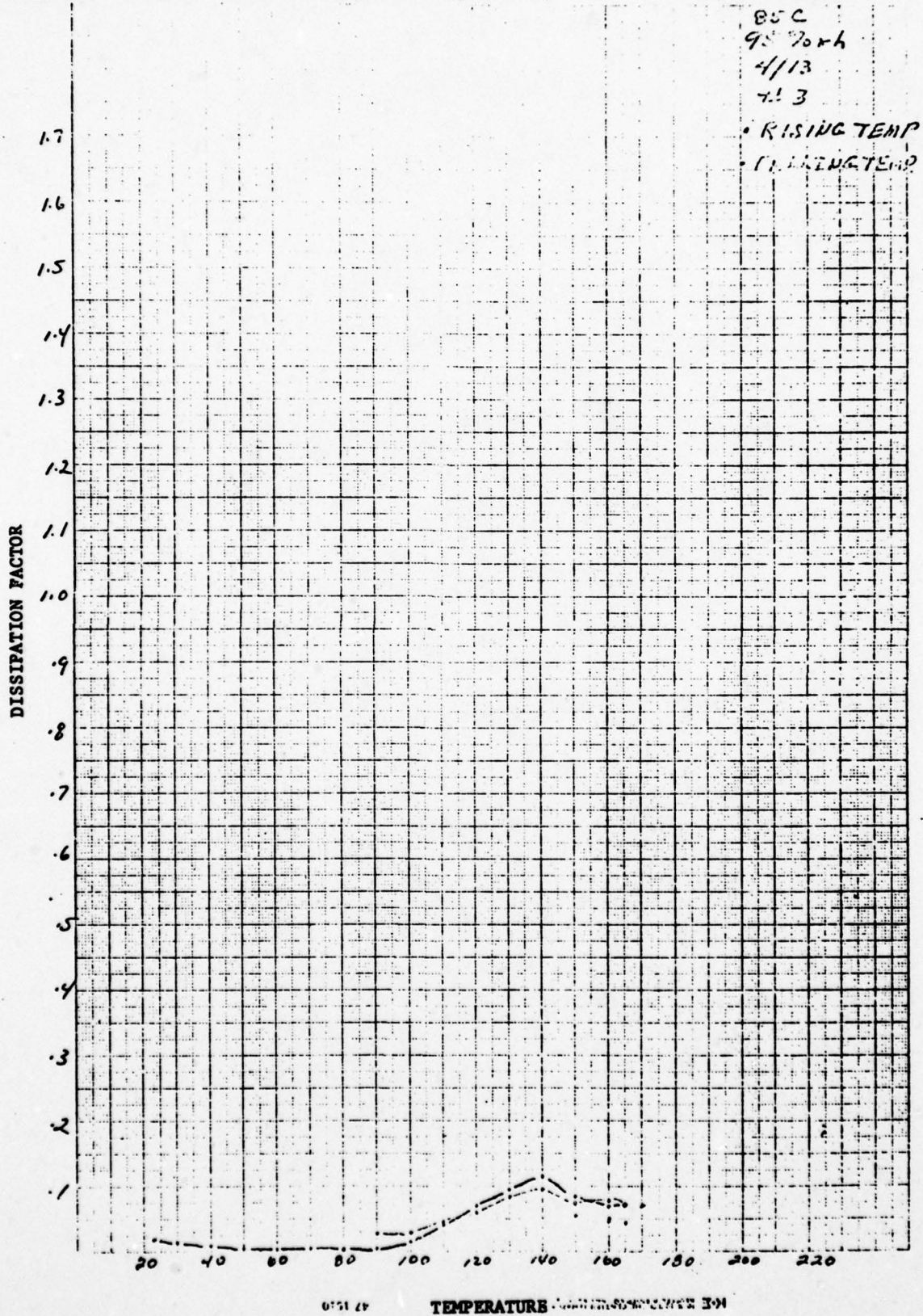
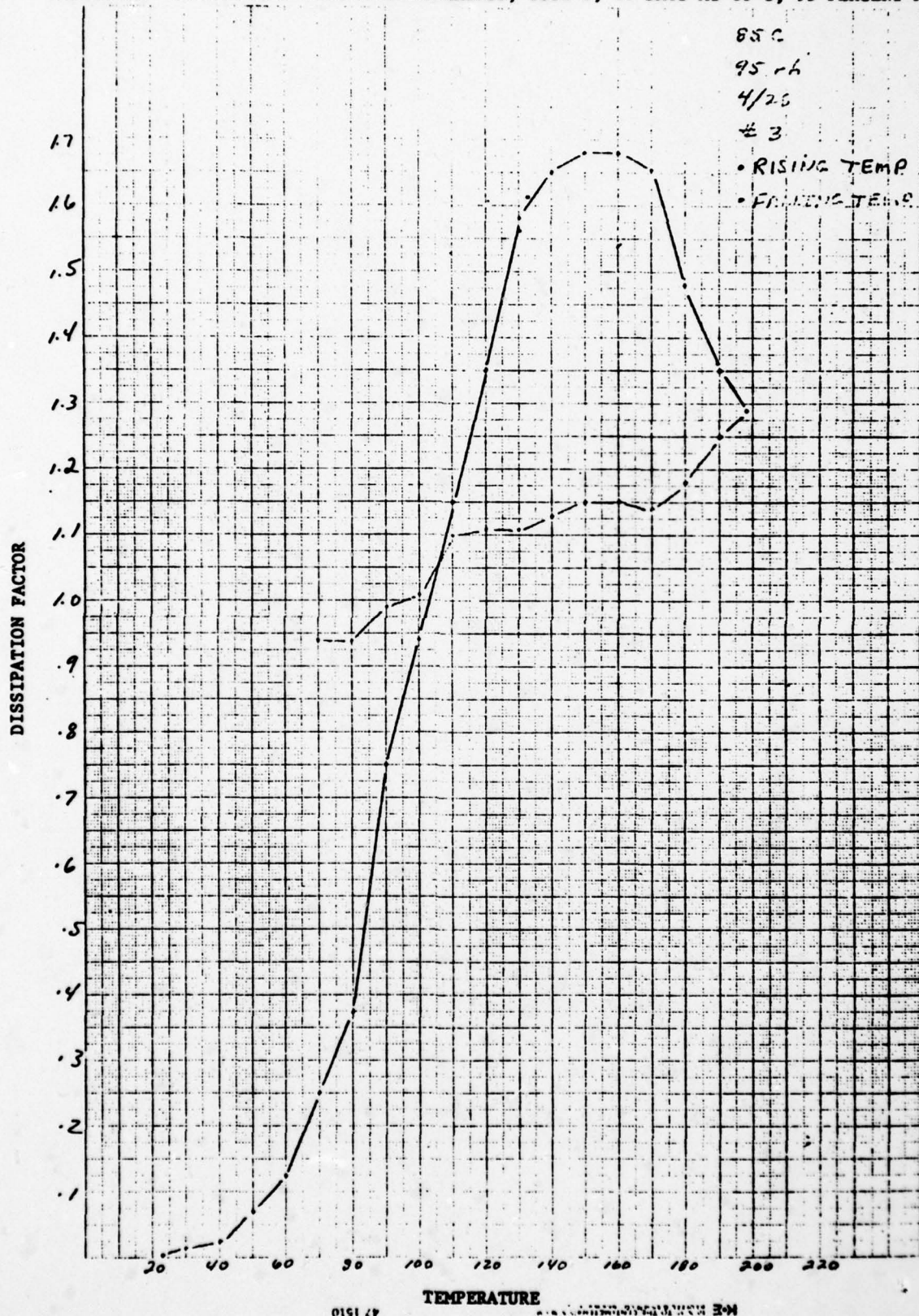


FIGURE 20. DISSIPATION FACTOR MEASUREMENTS, SCTH 3, 20 DAYS AT 85 C, 95 PERCENT RH



there are major changes in the magnitude of the dissipation factor for the moisture and heat exposed sample between 1 and 3 weeks exposure (Figures 19 and 20). For the moisture exposed sample (Figures 17 and 18), the changes in the magnitude of the dissipation factor are intermediate between those of the heat exposed sample and those of the heat and moisture exposed sample. Thus, some of the same changes that take place in the moisture and heat exposed sample are beginning to occur in the moisture exposed sample as evidenced by resistivity, dissipation factor, and infrared measurements.

Urethane Polymers

SCTH 226

The hardness and dielectric data for this polyester urethane (SCTH 226) are given in Figures 21 and 22 respectively. Figure 21 shows that (up to 62 days exposure) there is a slight softening for both of the samples exposed to moisture. However, after 62 days exposure, the sample exposed to only moisture maintains a relatively constant hardness value. On the other hand, the sample exposed to both heat and moisture softened rapidly (after 62 days) until it became almost liquid at 100 days exposure. The sample exposed to just heat indicates a slight hardening effect - likely due to further curing or loss of moisture.

Both of the samples exposed to moisture show about equal (small) losses in resistivity (Figure 22) up to 62 days exposure. After 62 days exposure, however, the sample exposed to only moisture maintains a constant resistivity value, while the sample exposed to both heat and moisture is beginning to exhibit large losses of resistivity. As with the hardness measurements (Figure 21), the heat exposed sample exhibits an increase in resistivity.

Infrared spectra of SCTH 226 after 7 days exposure are shown in Figure 23. A subtracted spectrum for the heat and moisture exposed sample is given in Figure 23B. This subtracted spectrum shows fairly good cancellation of the carbonyl absorption near 1740 cm^{-1} and shows that the

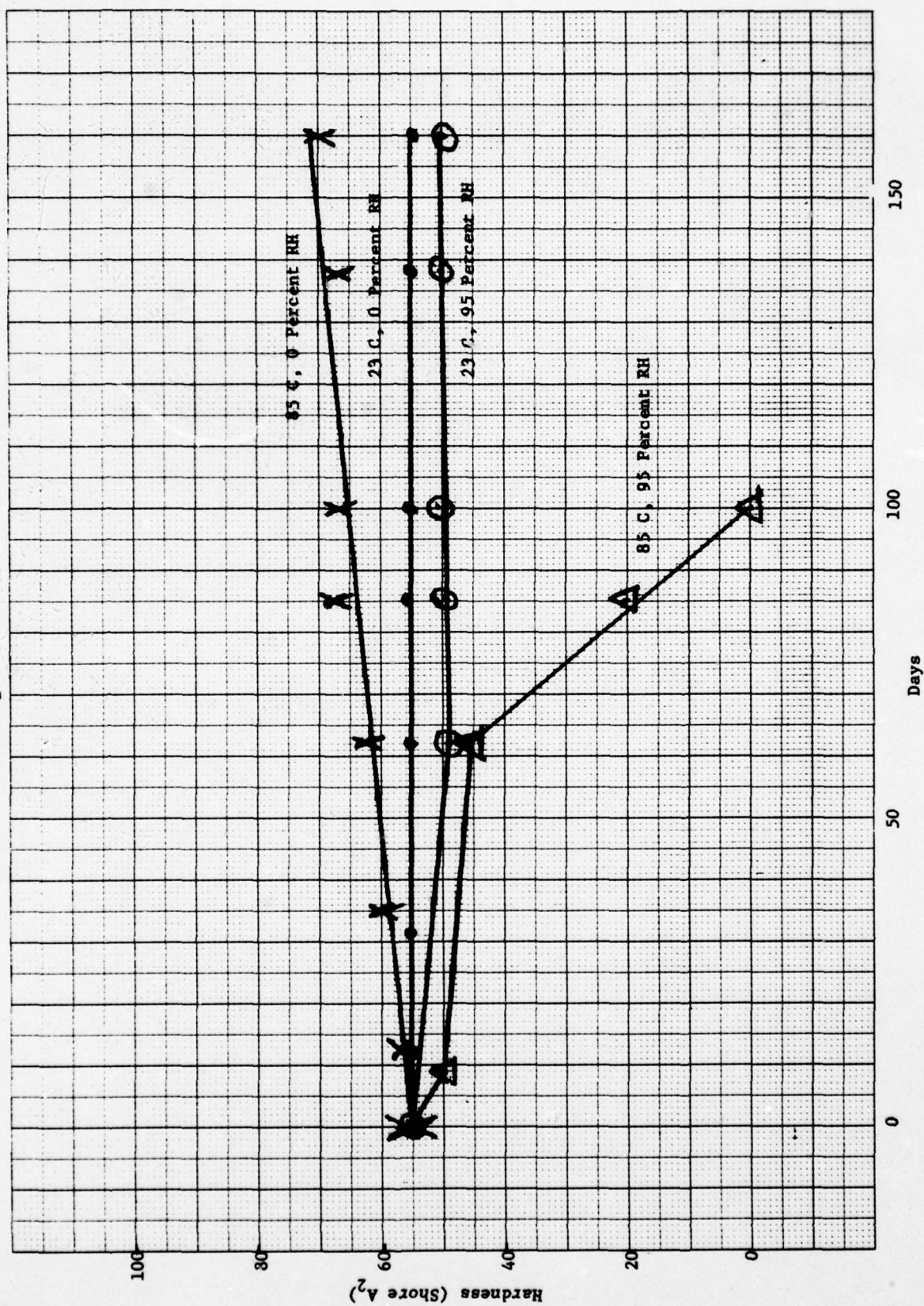
FIGURE 21. SHORE A₂ HARDNESS VALUES, SC7H 226

FIGURE 22. VOLUME RESISTIVITY, SCTH 226

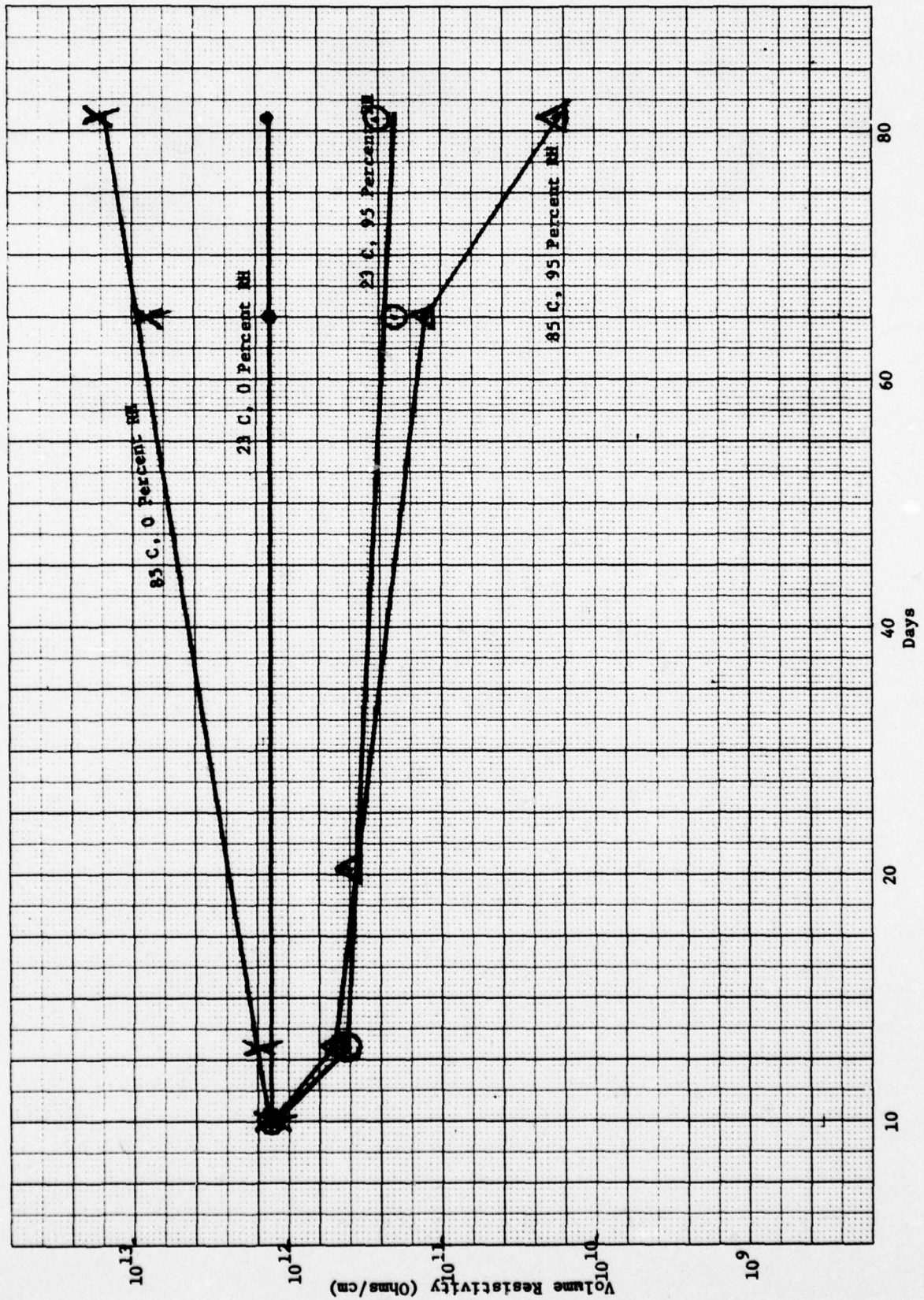


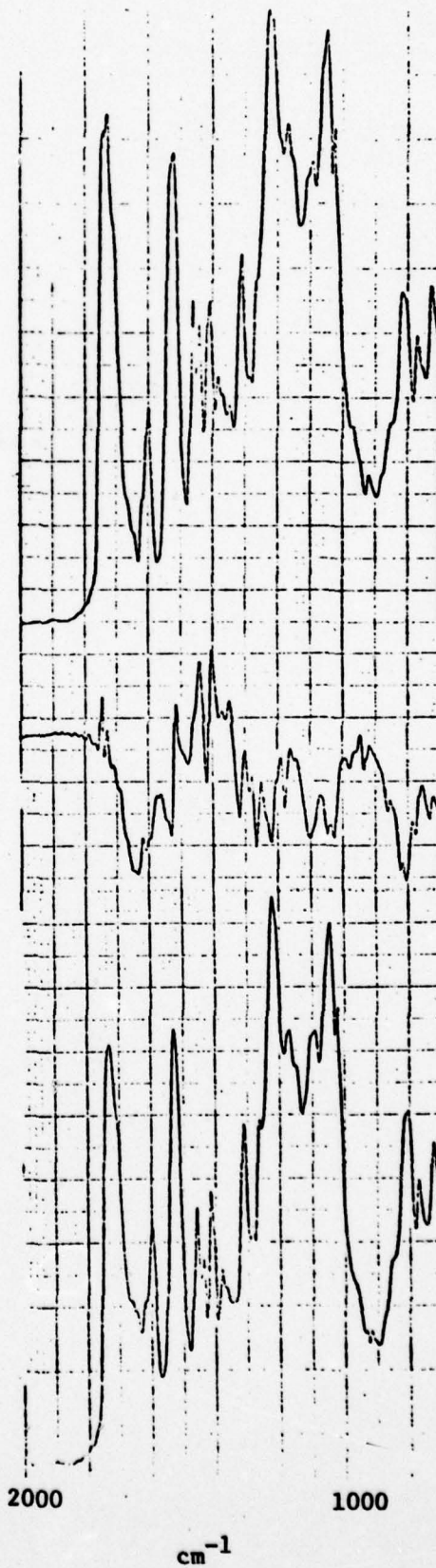
FIGURE 23. INFRARED SPECTRA OF SETH 226
(7 days exposure)

(A) 23 C, 0 percent RH

(B) 85 C, 95 percent RH

—
23 C, 0 percent RH

(C) 85 C, 95 percent RH



major effect of the 7 days exposure is loss of water (1630 cm^{-1}). No other major changes are observed.

However, after 62 days exposure, there are major changes in the carbonyl spectral region of the sample exposed to moisture and heat. This can be observed in Figure 24 which shows the subtracted spectra of the SCTH 226 samples exposed to the various conditions for 62 days. In Figure 24C (sample exposed to both heat and moisture) there is formation of carbonyl absorption near 1700 cm^{-1} and loss of carbonyl absorption at 1740 cm^{-1} . Very little change in the carbonyl spectral region is seen for the sample exposed to just heat for 62 days (Figure 24B), but small changes (similar to those observed in Figure 24C) can be observed in the carbonyl region of the sample exposed to moisture only (Figure 24A). While the hardness data (Figure 21) does not show evidence for much softening, the dielectric data does indicate some loss of electrical properties for the samples exposed to moisture for 62 days.

The above listed data for SCTH 226 is similar to some of the data for the epoxy polymers and is very encouraging. It is the first indication that reversion in urethane polymers might be detected. However, these initial results must be interpreted (and possibly tempered) with the following two observations:

- (1) Changes have been observed in the SCTH 226 sample exposed to neither heat nor moisture, i.e., the sample stored at 23 C and 0 percent RH (the control sample).
- (2) There is some evidence for inhomogeneity in the SCTH 226 film.

For the epoxy polymers, there is little or no change in the control samples (23 C and 0 percent RH) with time. This is not the case for the polyester urethane (SCTH 226) as shown in Figure 25. This figure shows the result of subtracting the spectrum of the control sample (shortly after the film was prepared or at zero exposure time) from the spectrum of the control sample after 62 days at 23 C and 0 percent RH. This subtracted spectrum shows differences in the carbonyl (1700 cm^{-1}) spectral region which are due to either:

FIGURE 24. SUBTRACTED
INFRARED SPECTRA OF SCTH 226
(62 days exposure using 0
days exposure control sample)

(A) 23 C, 95 percent RH

23 C, 0 percent RH

(B) 85 C, 0 percent RH

23 C, 0 percent RH

(C) 85 C, 95 percent RH

23 C, 0 percent RH

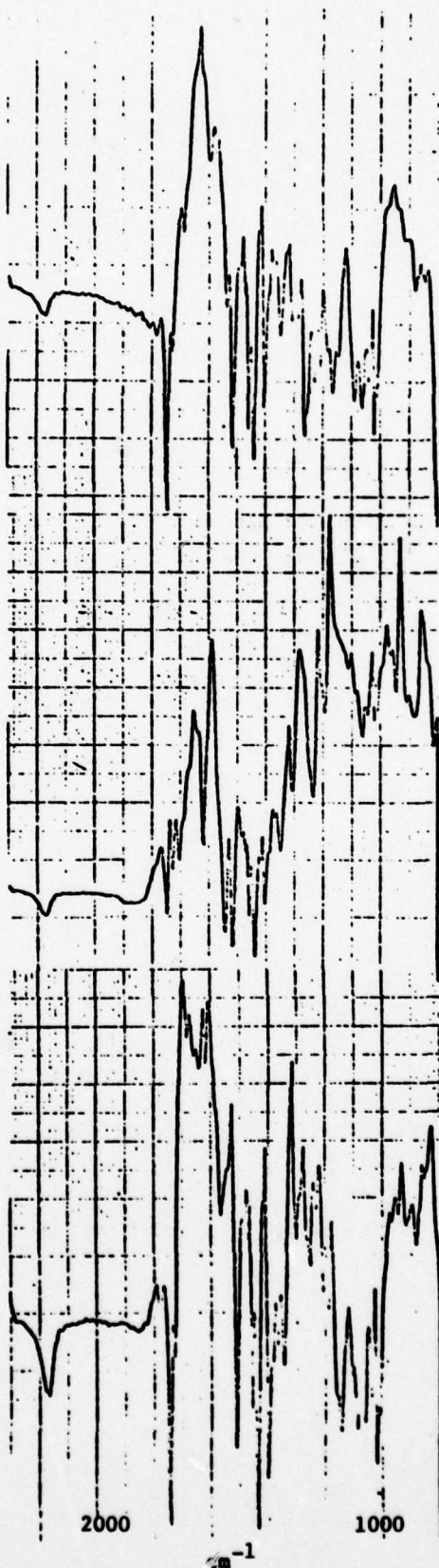
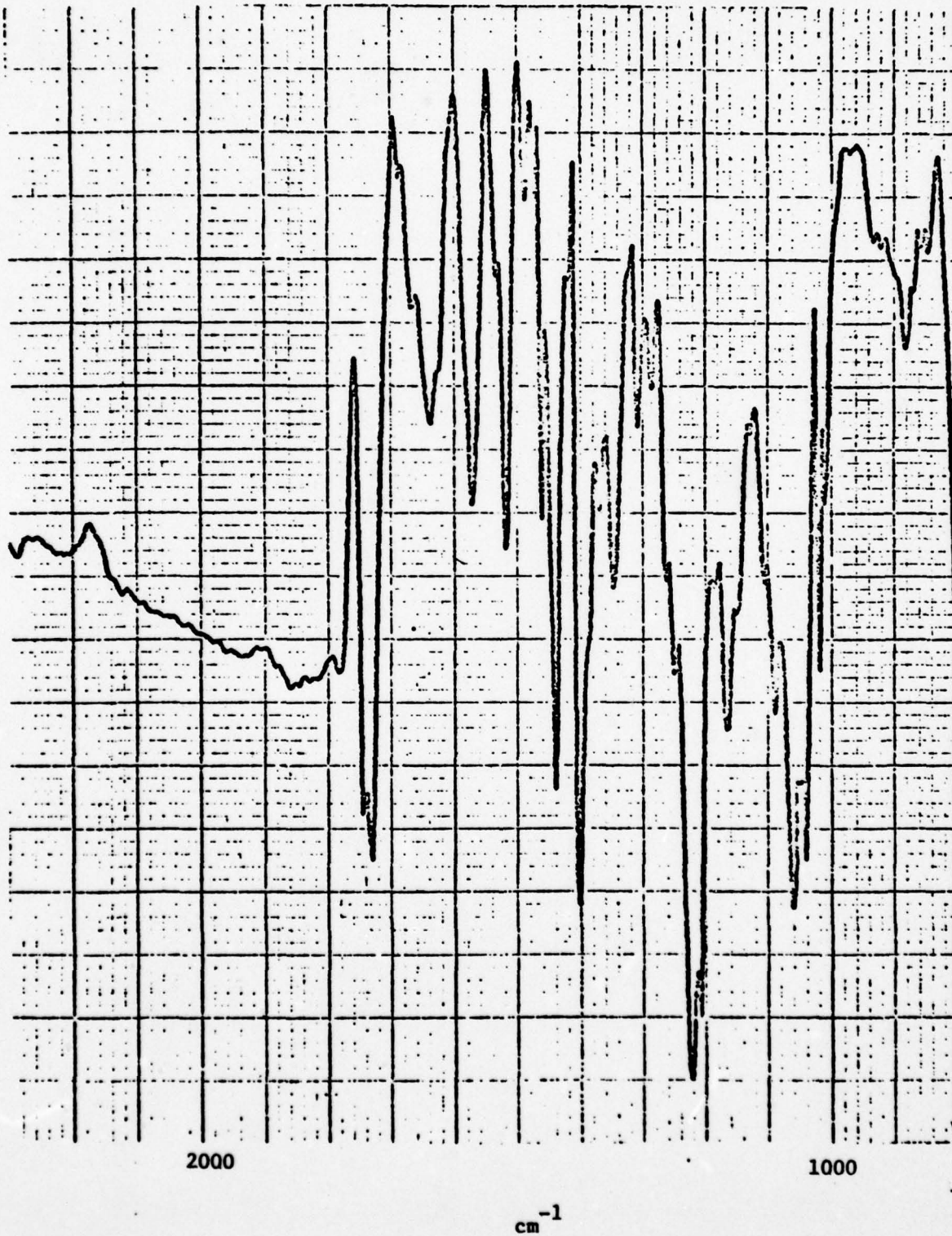


FIGURE 25. SUBTRACTED INFRARED SPECTRUM OF SCTH 226
(23 C, 0 percent RH) (62 days exposure - 0 days exposure)



- (1) formation of 1760 and 1695 cm^{-1} bands with increasing time, or
- (2) band broadening of the carbonyl absorption with increasing time resulting in "wings" on the subtracted spectra in the carbonyl region.

Of the two possibilities, band broadening is considered the most likely, but this can only be definitely established by following future changes in the control sample. The exact reason for these changes is not as important as the fact that the changes in the control sample could alter the subtracted spectra of the samples exposed to various conditions. This alteration of the subtracted spectra can be observed by comparison of the subtracted spectra of Figure 24 with those of Figure 26. Figure 24 shows the results of 62-day exposure at various conditions using the zero time control sample in each subtraction process. Figure 26 shows these same results when the control sample stored at 23 C and 0 percent RH for 62 days was used in each subtraction process.

In Figure 26C, the sample exposed to both heat and moisture still shows formation of one type of carbonyl absorption and loss of another type. However, in this case the newly formed carbonyl absorbs near 1710 cm^{-1} (as opposed to 1700 cm^{-1} as seen in Figure 24C). The sample exposed to moisture only shows a dispersion type subtracted carbonyl infrared band (i.e., resulting from a frequency shift rather than formation of a new carbonyl species).

Thus the infrared results on the urethane samples exposed to various conditions depend on which control sample is used. In either case, the spectra of the sample exposed to both heat and moisture shows formation of a new carbonyl species. However, the exact frequency (and the nature of the carbonyl group) cannot be precisely determined at this time. It is also difficult to ascertain how much of the change is due to reversion and how much of the change is due to the process that causes the changes (with time) in the control sample. The change in the control sample might be related to curing since the sample exposed to heat shows an increase in both hardness and volume resistivity.

FIGURE 26. SUBTRACTED INFRARED SPECTRA OF SETH 226 (62 days exposure using 62 days exposure control sample)

(A) 23 C, 95 percent RH

23 C, 0 percent RH

(B) 85 C, 0 percent RH

23 C, 0 percent RH

(C) 85 C, 95 percent RH

23 C, 0 percent RH

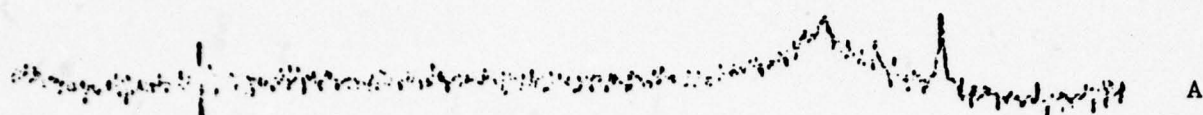


The second caution to be observed in the interpretation of the polyester polyurethane (SCTH 226) data is the possibility of non-homogeneous films. This possibility of non-homogeneity has been raised by some of the NMR data as shown in Figure 27. This figure shows the C^{13} -NMR spectra for 2 pieces of the control sample (Figures 27A and 27B) and for the 2 moisture exposed samples (Figures 27C and 27D). As can be seen, the differences between the 2 control samples are as large as the differences between either control sample and the samples exposed to moisture. The differences between the 2 control samples could be due to either non-homogeneity in the film or to the NMR technique itself. We have had problems with a silicone grease contaminant (see following paragraphs on polyether urethane samples) in the initial urethane film preparation, but this problem has subsequently been resolved. Infrared measurements of several urethane control samples have not shown significant differences. Thus it is more likely to have difficulties associated with obtaining NMR spectra of solids rather than film homogeneity. We do not have "magic angle" NMR equipment so obtaining NMR spectra of solids requires critical positioning of the sample, a large number of scans, and depends on the molecular mobility of the sample. Even then signal-to-noise ratio is not high (as can be seen in Figure 23). However, until film homogeneity is thoroughly evaluated, the possibility of lack of film homogeneity must be kept in mind when evaluating the exposure data on urethane samples.

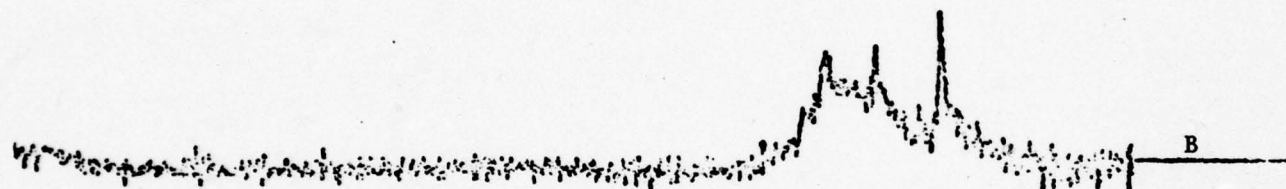
Chemiluminescence data obtained on samples of SCTH 226 after 4 days exposure are shown in Figure 28. This data appears to be completely random and shows no correlation with possible softening or dielectric data trends. While this may indicate that chemiluminescence cannot be used to detect reversion, the possibility of film non-homogeneity must also be kept in mind.

As with the epoxy samples, we can use the storage capability of the FT-IR computer to help offset possible problems with either film inhomogeneity or changes in the control sample. This is illustrated in Figure 29. This figure gives subtracted spectra of the sample exposed to both heat and moisture for various periods of time. Thus Figure 29A

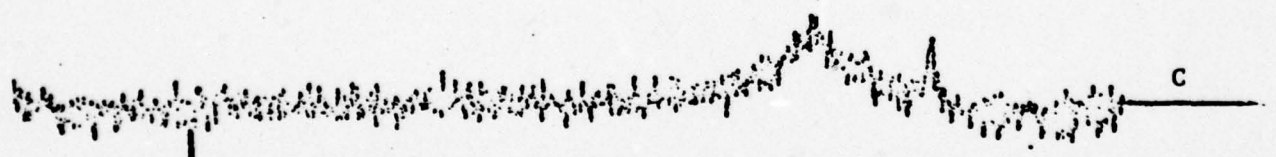
FIGURE 27. NUCLEAR MAGNETIC RESONANCE (C^{13}) SPECTRA
OF SETH 226 (7 days exposure)



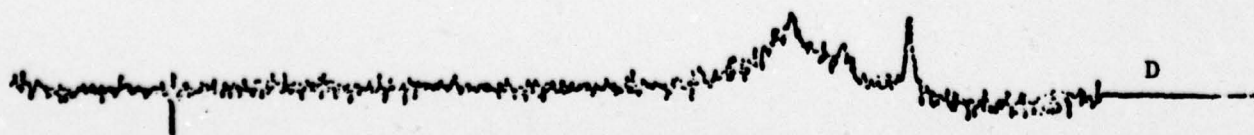
Control Sample 1, 23 C, 0 percent RH



Control Sample 2, 23 C, 0 percent RH

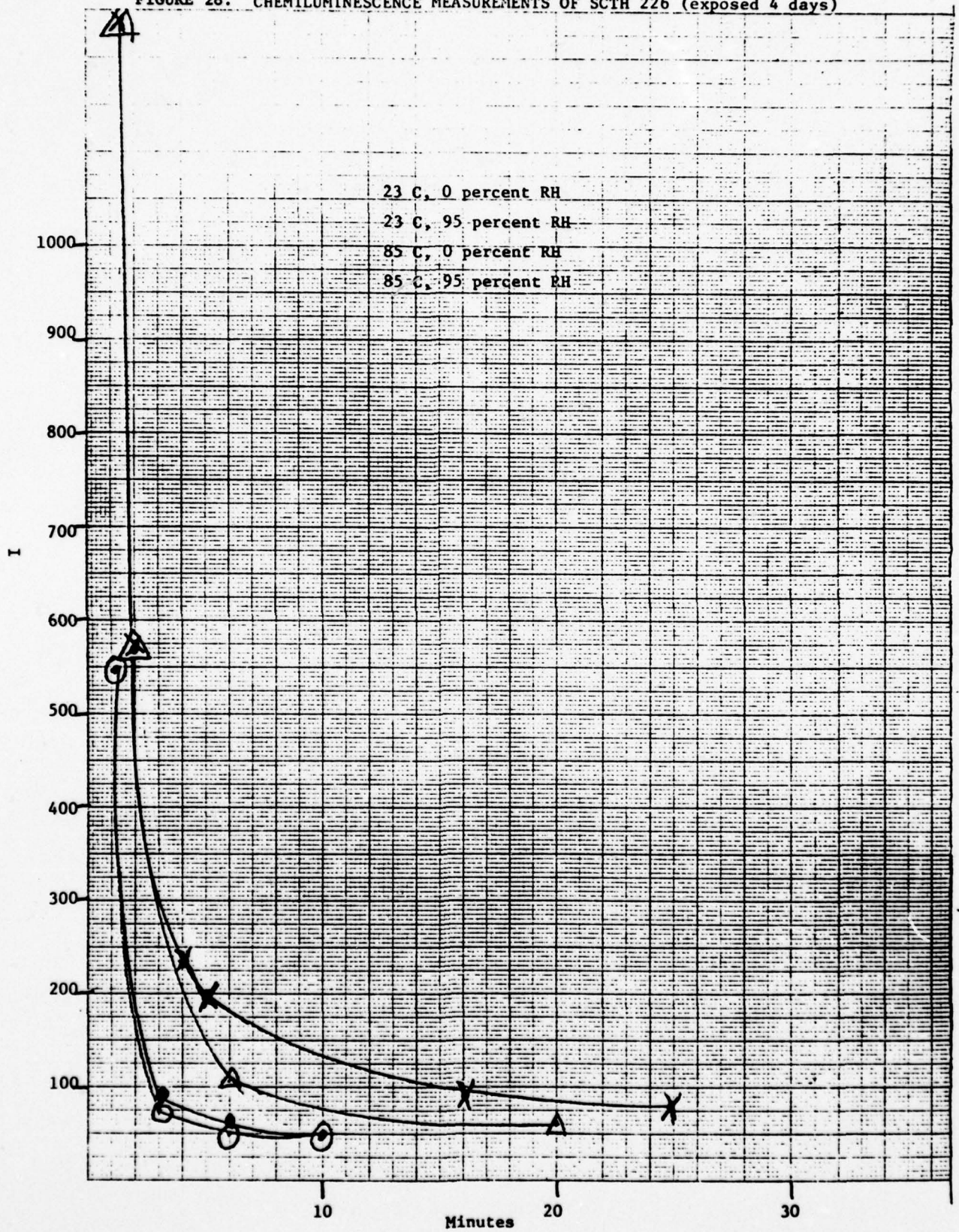


23 C, 95 percent RH



85 C, 95 percent RH

FIGURE 28. CHEMILUMINESCENCE MEASUREMENTS OF SETH 226 (exposed 4 days)



A. 101 Days Exposure
minus
62 Days Exposure

B. 129 Days Exposure
minus
101 Days Exposure

C. 164 Days Exposure
minus
129 Days Exposure

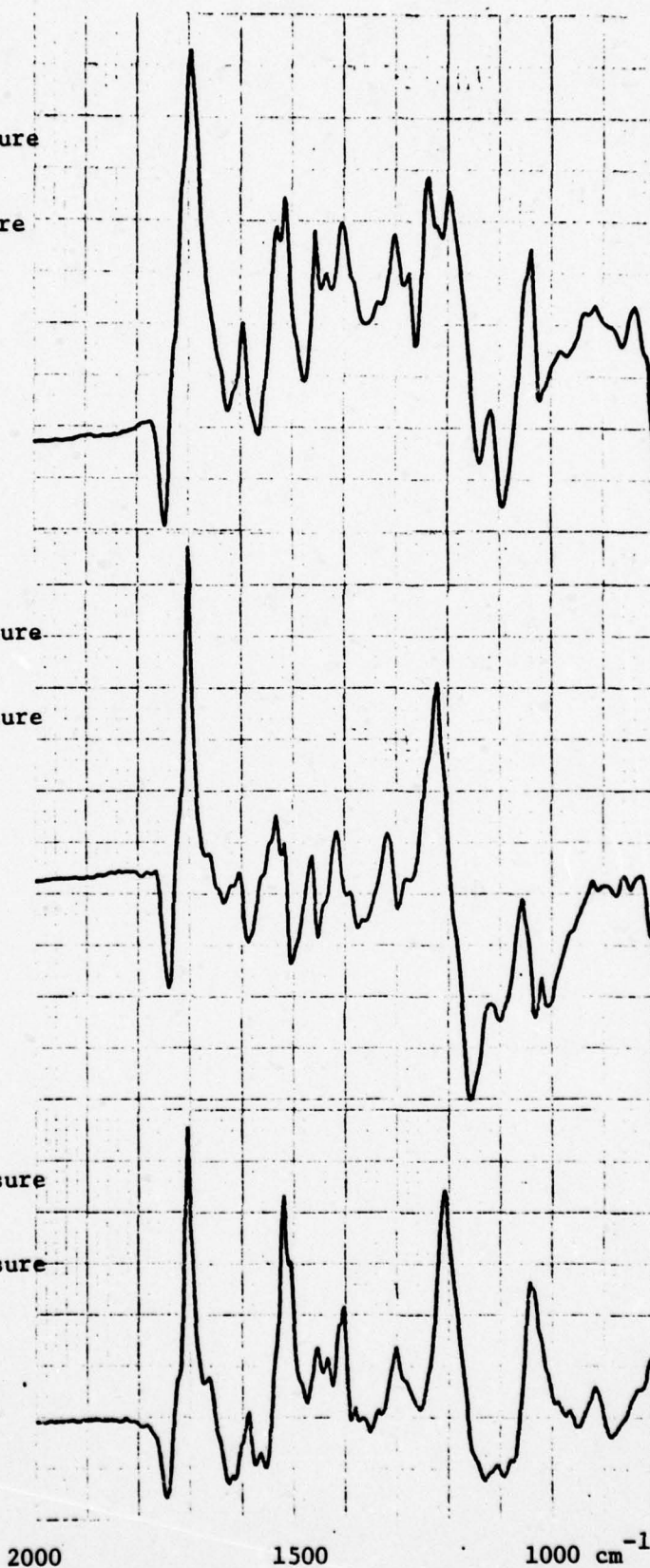


FIGURE 29. SUBTRACTED INFRARED SPECTRA OF SCTH 226
(Exposed Varying Lengths of Time at 85 C and
95 Percent RH)

shows the changes in this sample occurring between 62 and 101 days exposure, Figure 29B gives the changes between 101 and 129 days exposure, and Figure 29C indicates the changes occurring between 129 and 164 days exposure. Since all the spectra used for the subtractions of Figure 29 were run on the same sample of film, this eliminates (or greatly minimizes) the possibility of film inhomogeneity. It also eliminates changes in the control sample since spectra of the control sample were not used in the subtraction procedure.

During the period between 62 and 101 days, the SCTH 226 exposed to both heat and moisture changed from a semi-hard solid to nearly liquid (Figure 21) and exhibited large losses in resistivity. Thus the subtracted spectrum of Figure 29A indicates the structural changes that occur as the sample softens and loses resistivity. Note the intense, positive absorption band near 1700 cm^{-1} indicating either formation of a new carbonyl species or a low frequency shift of the original carbonyl species near 1735 cm^{-1} . We believe this represents formation of a new carbonyl species (since there is an inflection point near 1720 cm^{-1}), but this cannot be definitely established at the present time. Regardless of the origin of the infrared band, there is strong absorption near 1700 cm^{-1} which appears as the sample becomes softer (Figure 24) and finally liquifies (Figure 29A).

Spectra were also obtained in the sample after 129 and 164 days exposure to heat and moisture. In each case the viscous liquid sample was allowed to harden (by cooling) enough to obtain the infrared spectra. The changes in the sample due to exposure between 101 and 164 days are shown in Figures 29B and 29C. These subtracted spectra show a continuation of the results shown in Figure 29A, i.e., with increasing time of exposure there continues to be absorption near 1700 cm^{-1} .

The results shown in Figure 29 are encouraging since these spectra give strong indications that reversion in urethane polymers can be detected in samples where the possibility of film inhomogeneity and the changes in the control samples are greatly minimized. However, other urethanes need to be studied in order to be certain that the infrared, dielectric, and hardness results will correlate for urethanes in general.

HXUR 3113

The hardness and dielectric data for the polyether urethane (HXUR 3113) are shown in Figures 30 and 31, respectively. As with the previous polymers, the sample exposed to both heat and moisture shows the most softening while both the samples exposed to moisture indicate loss of electrical properties. The reason for the differences in hardness between the various samples at zero time appears to be related to the presence of a silicone grease impurity. Both of the samples which were exposed to moisture have more of this silicone grease surface impurity than the other two samples. Note that the infrared spectra in Figure 32 have been cut off below 1300 cm^{-1} because the bands due to silicone grease obscure the bands due to the urethane from 1260 to 800 cm^{-1} . Polyether urethanes are not commonly used as potting compounds and this sample was studied only as a guide to urethane behavior. For these reasons it was not deemed to be advisable to go through the effort to remove the silicone impurity (as done for the polyester urethanes) and repeat the experiments.

The subtracted infrared spectra due to the various exposure conditions (72-days exposure) are given in Figure 32. The HXUR 3113 sample exposed to heat alone shows few spectral changes (Figure 32B), when compared to the control sample, as would be expected from the hardness and dielectric data. The spectrum (Figure 32A) of the sample exposed to moisture indicates formation of a 1640 cm^{-1} band (H_2O) and a 1570 cm^{-1} (?) band. The effects of moisture and heat are shown (Figure 32 C) by the formation of a 1635 cm^{-1} (H_2O) and loss of a 1530 cm^{-1} (urethane amide II vibration) band. Figure 32D shows the subtraction of the spectrum of the sample exposed only to moisture from that of the sample exposed to both heat and moisture. This subtracted spectrum shows that the effect of heat and moisture over moisture alone is that additional carbonyl (1735 cm^{-1}) is formed when both heat and moisture are used. These spectra demonstrate that differences can be observed for the samples exposed to various conditions, but as yet there is no correlation of spectra data with hardness or dielectric data.

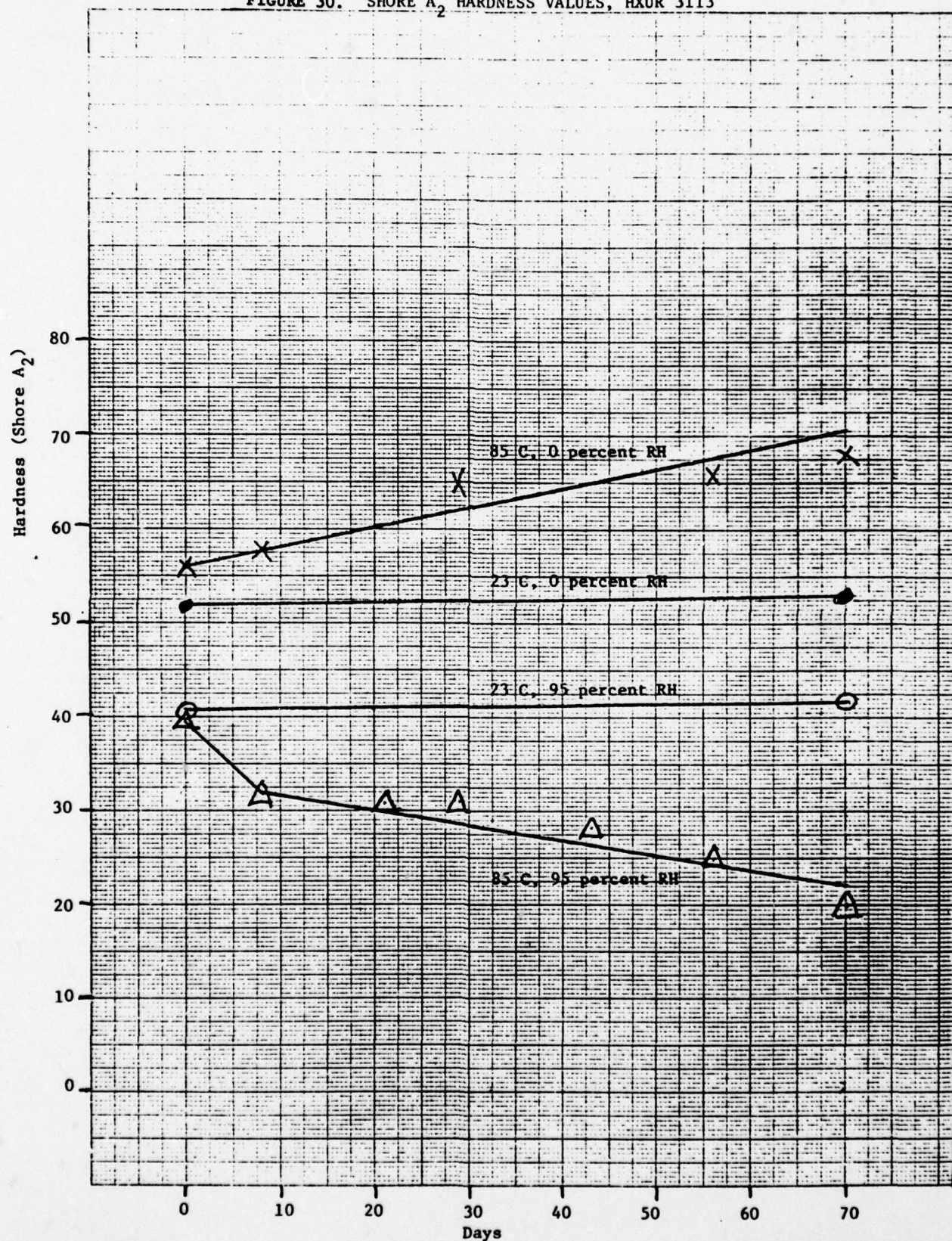
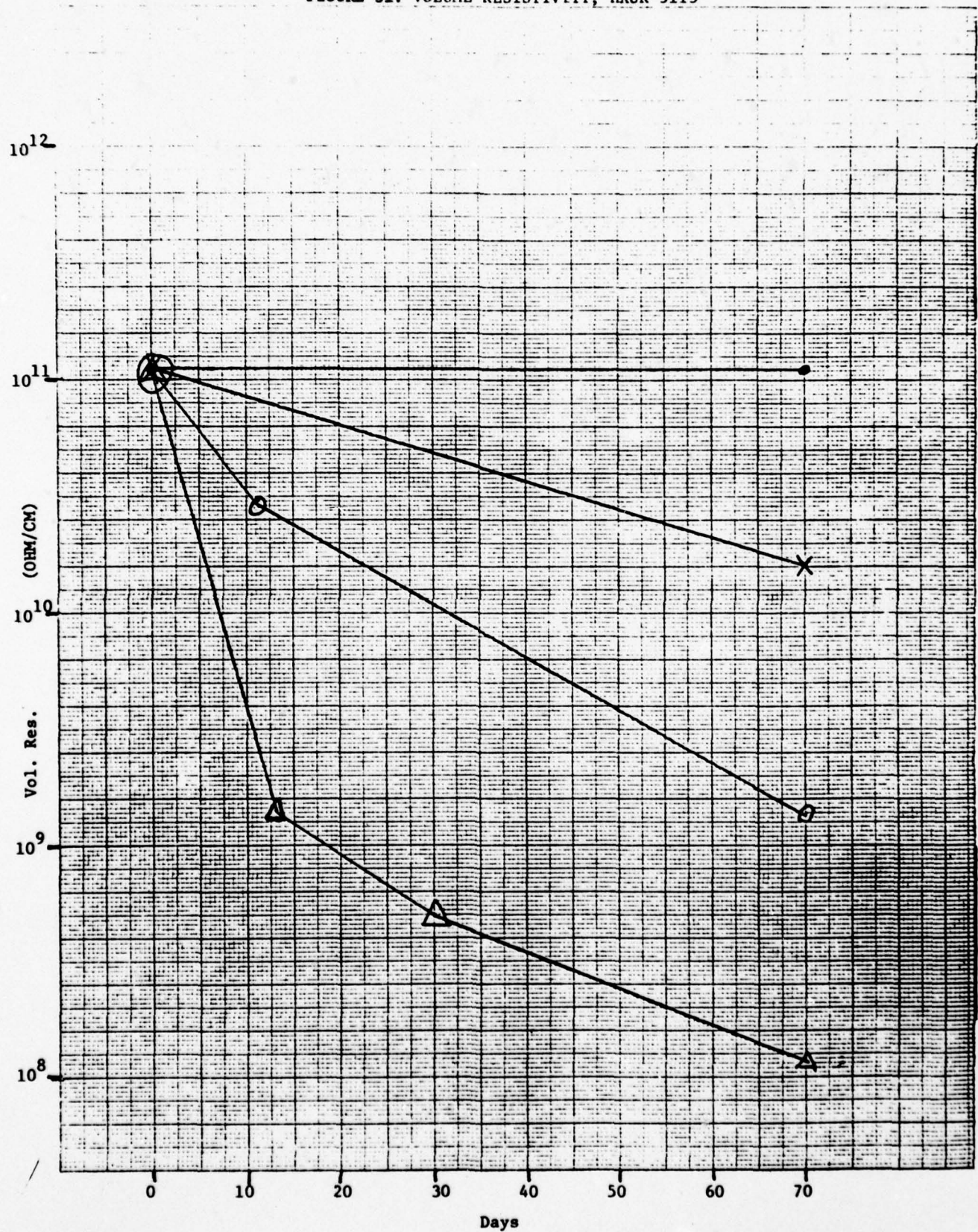
FIGURE 30. SHORE A₂ HARDNESS VALUES, HXUR 3113

FIGURE 31. VOLUME RESISTIVITY, HXUR 3113



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FIGURE 32. SUBTRACTED INFRARED SPECTRA OF HXUR 3113
(72 days exposure)

(A) 23 C, 95 percent RH

——
23 C, 0 percent RH

(B) 85 C, 0 percent RH

——
23 C, 0 percent RH

(C) 85 C, 95 percent RH

——
23 C, 0 percent RH

(D) 85 C, 95 percent RH

——
23 C, 95 percent RH



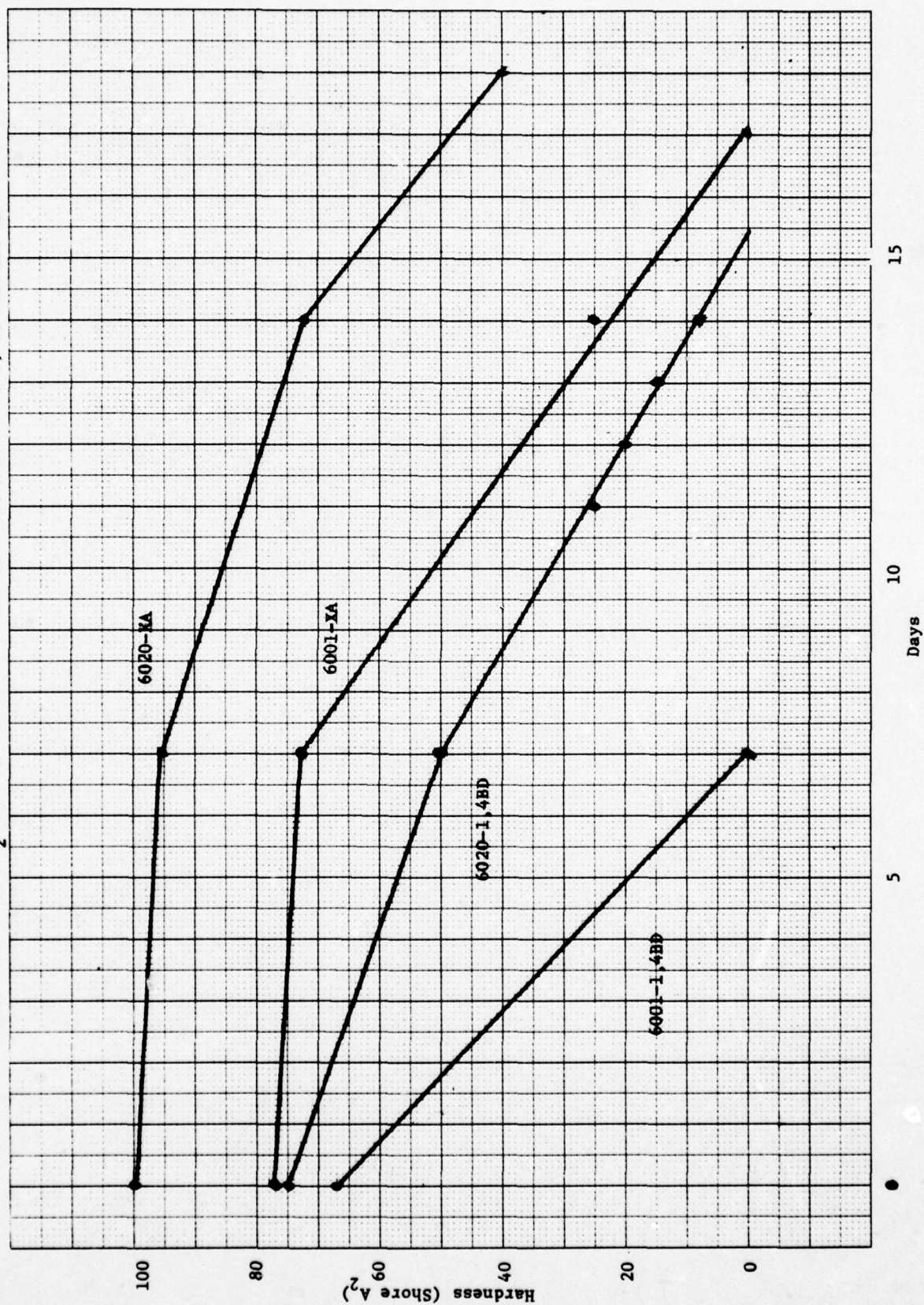
6001-1,4BD

Figure 33 gives hardness data for the four polyester urethanes: 6001-1,4BD; 6020-1,4BD; 6001-XA; and 6020-XA. As can be seen in Figure 33 only two points were obtained for the softening of 6001-1,4BD, so the slope of the softening curve may not be correct as indicated. However, the most important point is that when the second measurement was made (7-days exposure), the sample had already become a liquid. While 6001-1,4BD clearly liquifies before the other three urethanes; 6020-1,4BD and 6001-XA show similar softening behavior to each other - becoming very soft or liquid between 15 and 17 days exposure. 6020-XA, on the other hand; has softened, but not become a liquid after 18 days exposure. Thus the chemical changes observed in these four urethanes as a result of exposure should provide definitive information as to which of the changes are directly related to the reversion process.

While these four urethane samples should provide valuable information about the chemical changes which indicate reversion, it is important to remember that there were questions raised about the data obtained from another polyesterurethane (SCTH 226). These questions concerned the possibility of either film inhomogeneity or of changes in the control sample with time. These questions must be resolved in order for urethane data to be meaningful.

For the 6001 and 6020 urethanes, the possibility of film inhomogeneity was checked by obtaining several infrared spectra (at different parts of the film) on each film prepared. All of the spectra on the same film were identical (to the limits of the infrared instrument). Thus film inhomogeneity does not appear to be a problem with these urethanes.

The only evidence for inhomogeneity came from the NMR measurements of SCTH 226 (Figure 27). These measurements indicated differences between two pieces of the control sample of SCTH 226. These small differences could result from difficulties in obtaining NMR spectra of solids rather than film inhomogeneity. This possible explanation of the NMR data, coupled with the fact that the infrared measurements do not

FIGURE 33. SHORE A₂ HARDNESS VALUES FOR URETHANES EXPOSED TO 85 C, 95 PERCENT RH

indicate inhomogeneity, strongly indicates that film inhomogeneity need not be a major concern.

The changes (with time) in the control sample of 6001-1,4BD are shown in Figure 34. Note that on the spectrum of Figure 34 (and the spectra of all succeeding figures) there is a "5X" or a "2X" in the lower right hand corner of the spectrum. This number indicates the ordinate scale expansion factor used to plot the spectra in the figures. The amount of scale expansion is listed because the relative magnitude of the changes (as well as the type of changes) can be important for the 6001 and 6020 urethanes.

Figure 34 shows the changes that take place in the control sample of 6001-1,4BD as a result of 19 days exposure to 23 C and 0 percent RH. While there are some changes (carbonyl vibration near 1740 cm^{-1} and bands in the $1000\text{ to }1200\text{ cm}^{-1}$ range) in the control sample, these changes are relatively small especially when compared to the changes observed in the control sample of SCTH 226 (Figure 25). Remember that the spectrum of Figure 34 (6001-1,4BD) is 5X scale expanded while the spectrum of Figure 25 (SCTH 226) is only 2X scale expanded. At 2X scale expansion the changes in the control sample of 6001-1,4BD would be even smaller. Thus changes in the control sample of 6001-1,4BD should not present a major problem in relating observed changes to the reversion process.

Figure 35 shows the changes in 6001-1,4BD as a result of 11 days (Figure 35A) and 19 days (Figure 35B) exposure to both temperature and humidity. By 11 days the sample had already melted and Figure 35A shows the appearance of carbonyl absorption near 1700 cm^{-1} and H_2O absorption near 1630 cm^{-1} . As the sample became more liquid between 11 and 19 days exposure, the amount of 1700 cm^{-1} absorption greatly increased (Figure 35B) in relation to the H_2O band at 1630 cm^{-1} . (Note the difference in scale expansion factors between Figures 35A and 35B.) Thus for 6001-1,4BD, a carbonyl band appears as the sample melts and there is pick-up of water. As the sample became more liquid, the magnitude of the 1700 cm^{-1} carbonyl absorption increases and there appears to be a loss of H_2O . The appearance of absorption near 1700 cm^{-1} as this urethane liquifies agrees with the changes observed as SCTH 226 softens and gives further evidence that the appearance of 1700 cm^{-1} absorption can be used to detect reversion.

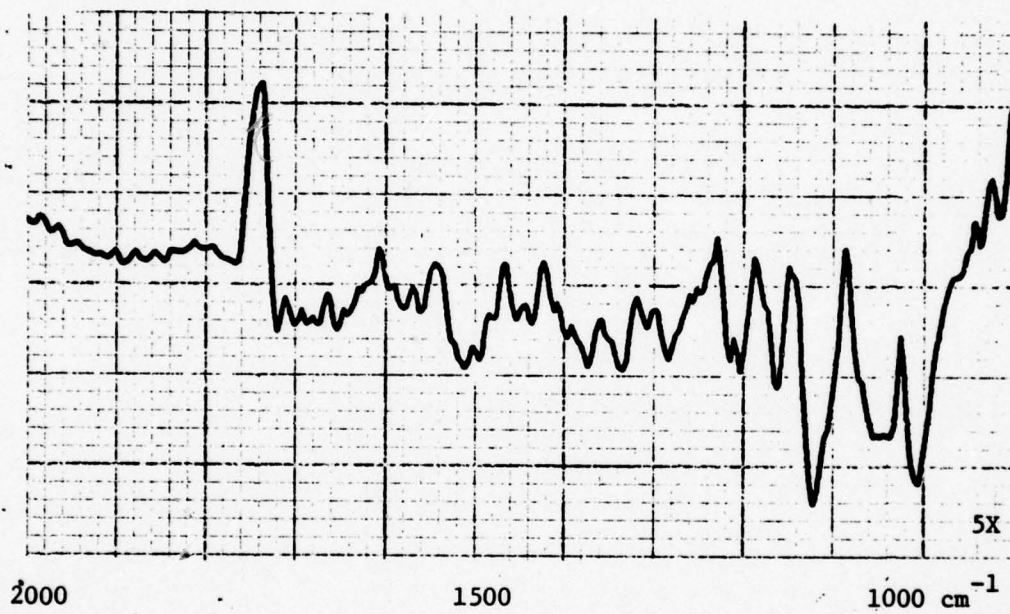
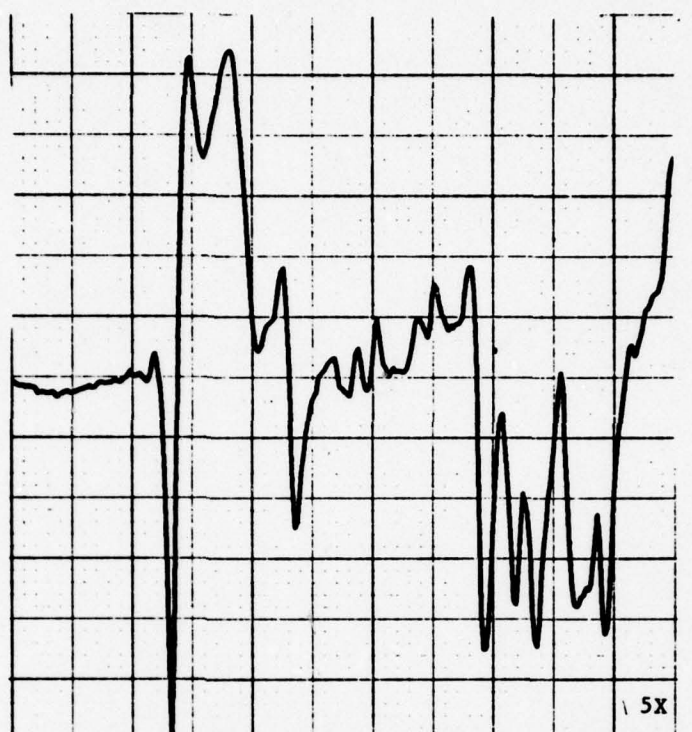


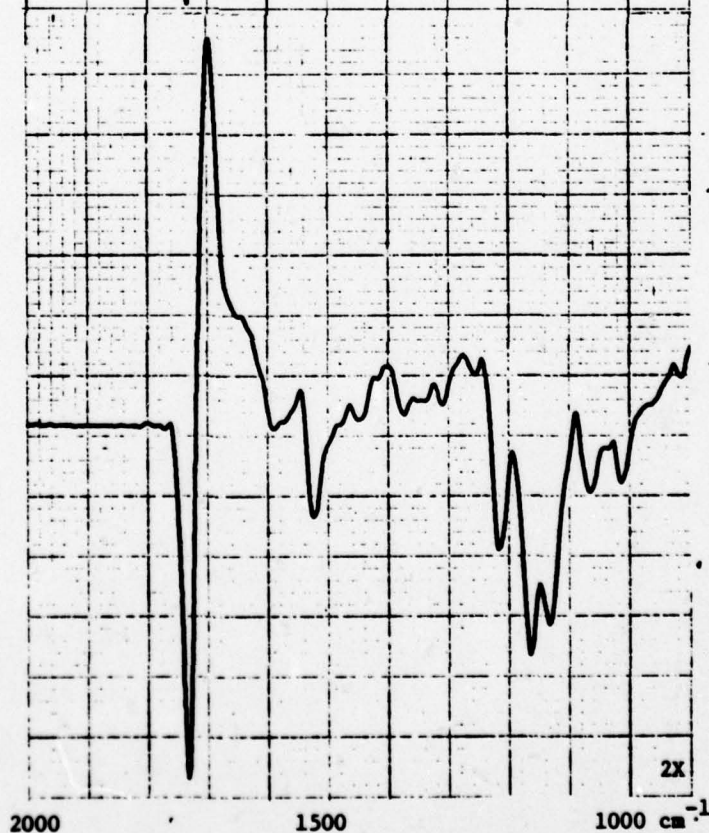
FIGURE 34. SUBTRACTED INFRARED SPECTRUM OF 6001-1,4BD
(23 C, 0 percent RH)
19 Days Exposure - 0 Days Exposure

FIGURE 35. SUBTRACTED INFRARED SPECTRA OF 6001-1,4BD
(85 C, 95 Percent RH - 23 C, 0 Percent RH)

A. 11 Days
Exposure



B. 19 Days
Exposure



6020-1,4BD

From the hardness data of Figure 33, it can be seen that 6020-1,4BD had slightly softened after 7 days exposure to both temperature and humidity. The sample became still softer after 11 days exposure and had completely melted by the time it had been exposed for 19 days.

The spectral changes corresponding to these exposure times are seen in Figure 36. After 7 days exposure (Figure 36A) there is some apparent increase in 1700 cm^{-1} absorption and a gain in H_2O (1630 cm^{-1}). However from the shape of absorption in the $1700\text{--}1760\text{ cm}^{-1}$ region, it is probable that the carbonyl changes are really due to band broadening, i.e., after 7 days exposure the carbonyl absorption near 1735 cm^{-1} had broadened as compared to the carbonyl vibration of the control sample. After 11 days exposure (Figure 36B) there is an increase in the original carbonyl band (1735 cm^{-1}) of the urethane and an increase in H_2O content. However, when the sample melted (19 days exposure, Figure 36C), there is a major increase in 1700 cm^{-1} absorption. These changes are emphasized in Figures 37A and 37B (which are at the same scale expansion factors). Figure 37 also completely eliminates any worry about changes in the control sample since the subtractions only involve the spectra of exposed samples (and do not involve the control sample). This figure shows that the main change between 7 and 11 days exposure (when the sample was softening, but had not melted) is a gain in the ester carbonyl band near 1735 cm^{-1} . However, between 11 and 19 days exposure (when the sample melted), Figure 37C shows a major gain in 1700 cm^{-1} absorption. Here the 1700 cm^{-1} absorption is only observed when the sample melts.

6001-XA

For this polyester urethane, the hardness data (Figure 33) indicates some softening after 11 days exposure to both temperature and humidity. At 17 days exposure the sample began to melt. Figure 38 shows the spectral changes corresponding to these exposure times. The soft film (Figure 38A) after 11 days exposure shows some gain in 1700 cm^{-1}

FIGURE 36. SUBTRACTED INFRARED SPECTRA OF 6020-1,4BD
(85 C, 95 Percent RH - 23 C, 0 Percent RH)

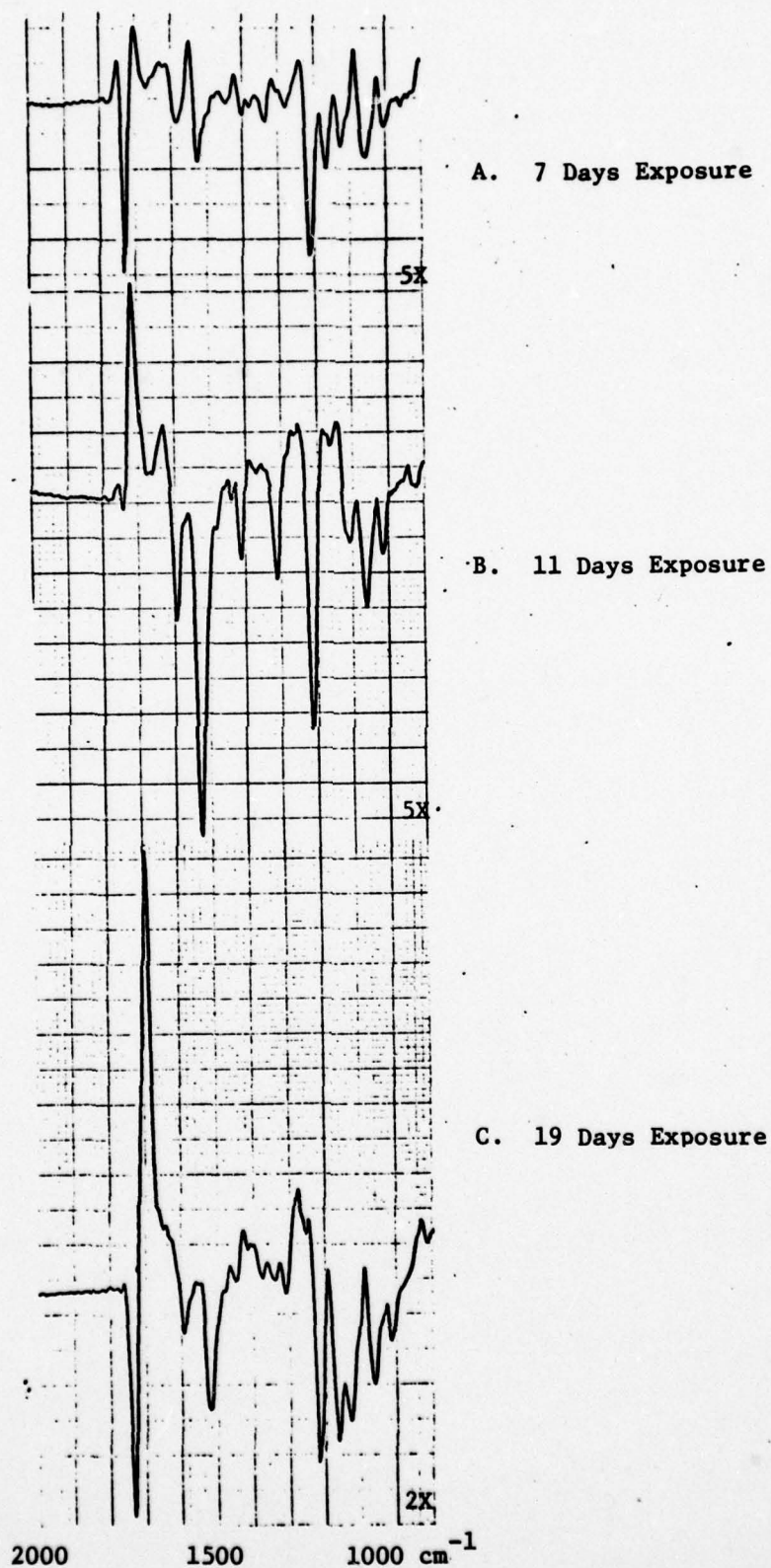


FIGURE 37. SUBTRACTED INFRARED SPECTRA OF 6020-1,4BD
(85 C, 95 Percent RH)

A. 11 Days Exposure

7 Days Exposure

B. 19 Days Exposure

11 Days Exposure

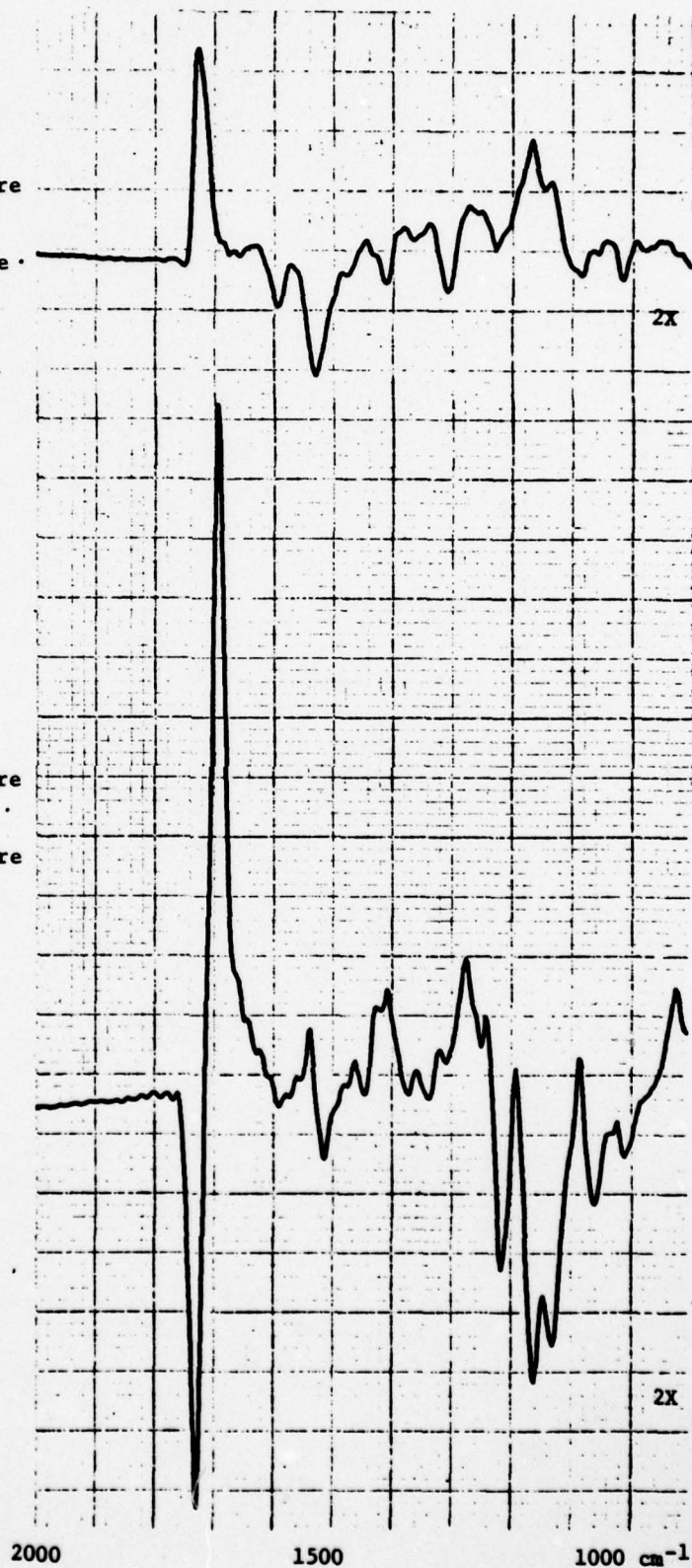
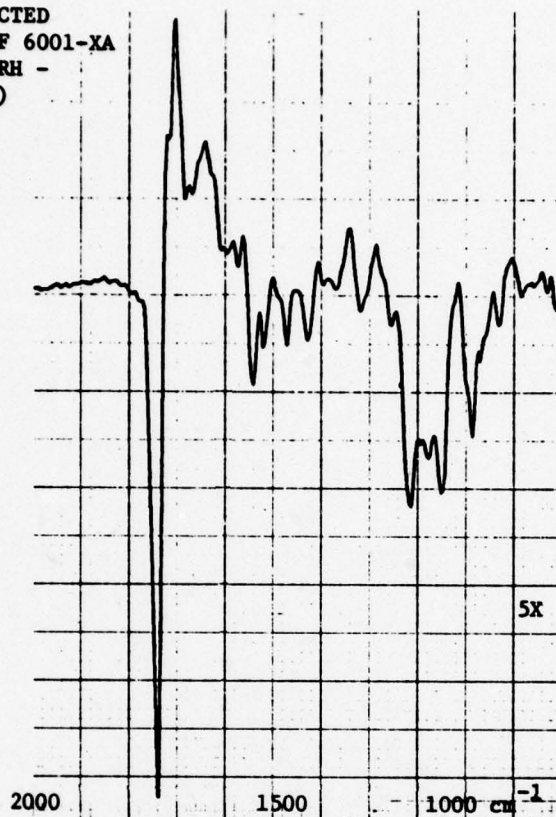
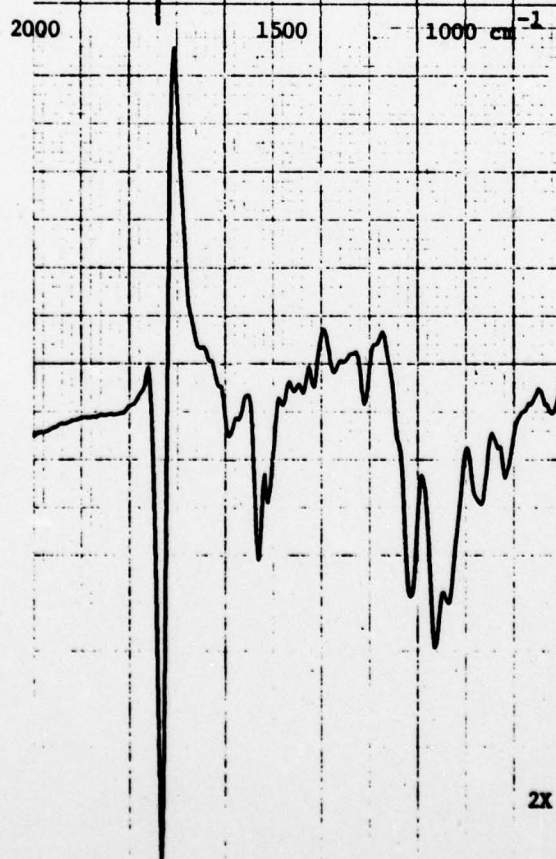


FIGURE 38. SUBTRACTED
INFRARED SPECTRA OF 6001-XA
(85 C, 95 Percent RH -
23 C, 0 Percent RH)



A. 11 Days Exposure



B. 19 Days Exposure

absorption and an increase in water content (1630 cm^{-1}). The inflection point at 1720 cm^{-1} indicates that there is a low frequency shift of the 1735 cm^{-1} ester carbonyl and that the 1700 cm^{-1} band is the formation of a new chemical species. After 19 days exposure, the liquid sample indicates a major increase in 1700 cm^{-1} absorption (Figure 38B). Again notice the differences in scale expansion factors which show that the changes observed in Figure 38B are much greater than those seen in Figure 38A.

Figure 39A demonstrates that there are no detectable changes in the control sample as a result of 19 days exposure at 23 C and 0 percent RH. The changes between 11 and 19 days exposure to both temperature and humidity (as the sample melts) are shown in Figure 39B. This spectrum clearly shows the gain in absorption near 1700 cm^{-1} as the sample becomes a liquid.

The reasons why a small amount of 1700 cm^{-1} absorption is seen after 11 days exposure (Figure 38A) and before the sample melts is not known at the present time. Such absorption is not seen in urethane 6020-1,4BD (Figures 36A and 36B) until the sample melts. Perhaps (as will be discussed later) this has to do with the different curing agents used. In any event a major gain in 1700 cm^{-1} absorption is observed when 6001-XA melts. However it is also important to note that the 1700 cm^{-1} absorption appearing when 6001-XA softens is really above 1700 cm^{-1} (i.e., is near 1705 cm^{-1}). For 6001-1,4BD and for 6020-1,4BD, this absorption appears below 1700 cm^{-1} (i.e., near 1698 cm^{-1}). This will be discussed in more detail in succeeding sections.

6020-XA

The hardness data (Figure 33) indicate that 6020-XA had slightly softened after 11 days exposure to temperature and moisture. The sample became softer after 19 days exposure, but it had not melted. The infrared spectra (Figure 40) corresponding to these exposure times do not show formation of 1700 cm^{-1} absorption after 11 days exposure (Figure 40A) but this 1700 cm^{-1} absorption is present after 19 days exposure (Figure 40B).

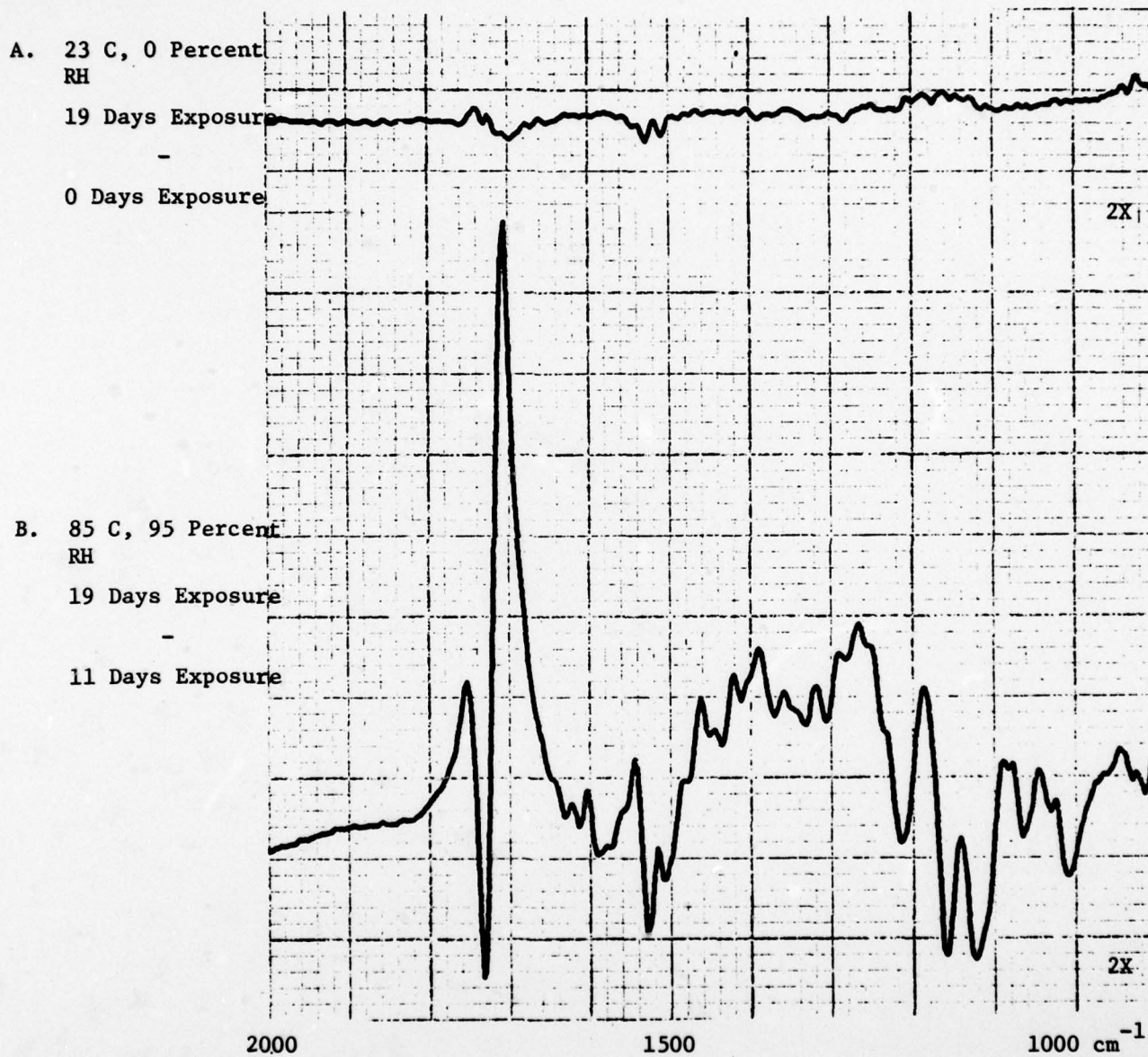
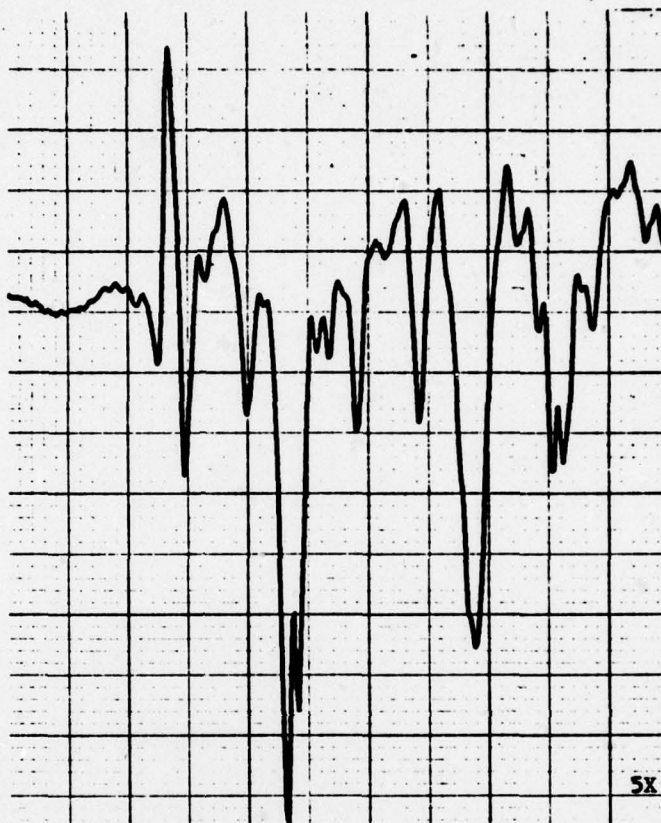


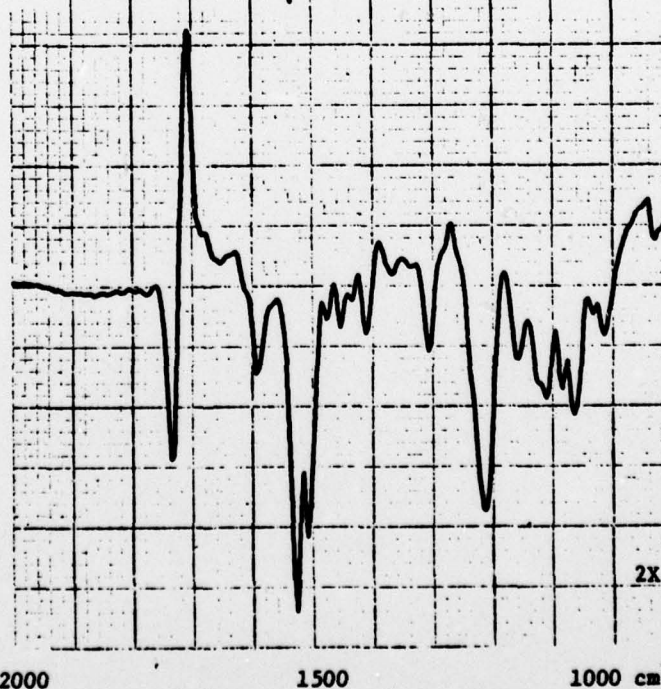
FIGURE 39. SUBTRACTED INFRARED SPECTRA OF 6001-XA

FIGURE 40. SUBTRACTED INFRARED SPECTRA OF 6020-XA
(85 C, 95 Percent RH - 23 C, 0 Percent RH)

A. 11 Days
Exposure



B. 19 Days
Exposure



2000

1500

1000 cm⁻¹

That this absorption is formed between 11 and 19 days exposure is demonstrated in Figure 41. This figure shows the result of subtracting the spectrum after 11 days exposure from the spectrum obtained after 19 days exposure. In addition, Figure 41 shows that this absorption is at 1710 cm^{-1} , an even higher frequency than observed in 6001-XA (Figures 38 and 39). This high frequency may indicate that the exact carbonyl frequency is related to softening and is shifting to lower frequencies as the sample softens. However more data is needed to verify this speculation.

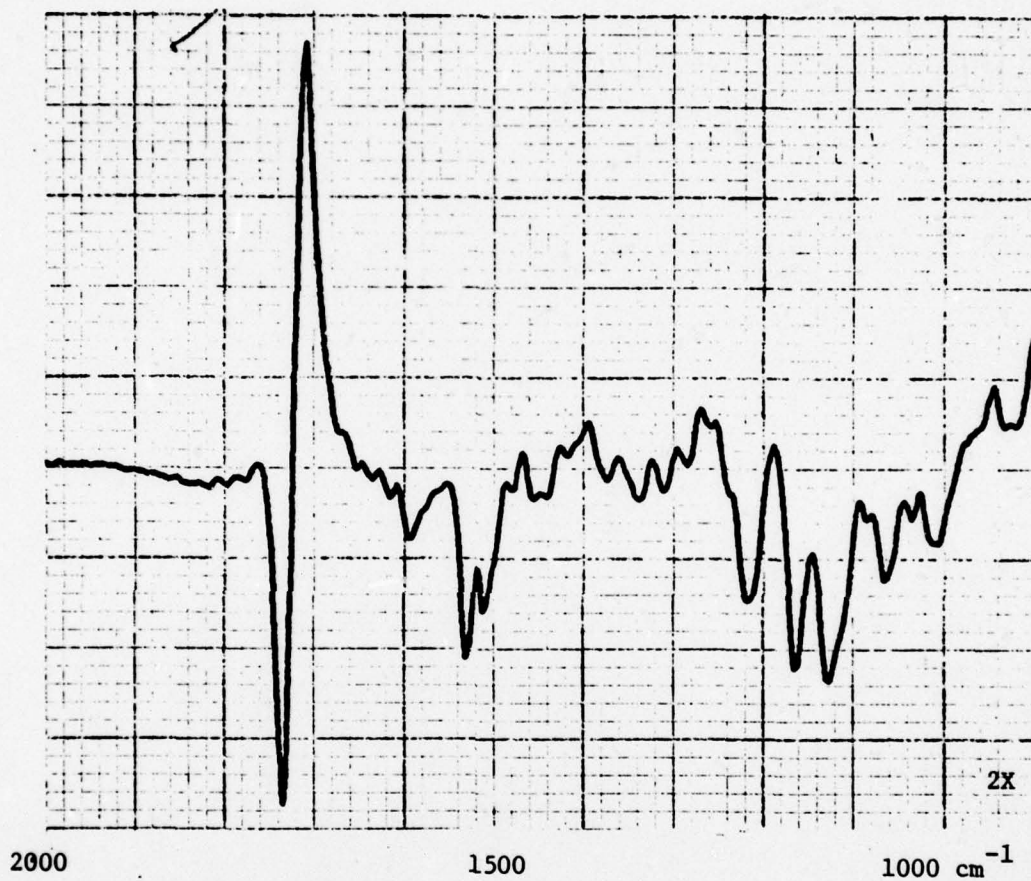


FIGURE 41. SUBTRACTED INFRARED SPECTRUM OF 6020-XA
(85 C, 95 Percent RH)
19 Days Exposure - 11 Days Exposure

DISCUSSIONEpoxy Polymers

For the two epoxy systems studied (SCTH 235 and SCTH 3), the formation of a 1710 cm^{-1} infrared band closely correlates with softening of the polymers and with loss of electrical properties. During the first year of research on this program, another epoxy polymer (SCTH 280) showed formation of 1710 cm^{-1} infrared absorption as the sample softened. Thus, all three epoxy systems studied showed a correlation between softening and formation of 1710 cm^{-1} infrared absorption. The combination of infrared spectroscopy and dielectric measurements, backed up by hardness data appears to be a promising means of detecting and predicting reversion in epoxy polymers.

It is of interest to note (especially when considering the behavior of urethane polymers) that for epoxys, the 1710 cm^{-1} infrared absorption can be detected as the sample softens). This can be observed in Figure 11C. In one case (Figure 13C), the 1710 cm^{-1} band can be detected even before there are signs of softening (but where there is some loss of electrical properties). This behavior would seem to indicate that the formation of 1710 cm^{-1} infrared absorption is a sensitive means of detecting the onset of reversion. If this is true, it may be possible to use the formation of this infrared band as a means of predicting service life of epoxy polymers.

Just as important is the fact that the 1710 cm^{-1} band is never observed when there are no indications of reversion (i.e. no indications of either softening or loss of electrical properties). This enhances the reliability of using the 1710 cm^{-1} absorption for detecting reversion.

Figures 6 and 7 demonstrate the changes in an epoxy system from the point where the sample is beginning to flow until the sample completely liquifies (i.e. as the sample melts). These figures

show that the sample loses water as it melts (as it softens). This is contrary to the normal behavior where substances become hard as they lose water. As yet, it is not possible to explain the loss of water, but it might be important to the mechanism of reversion especially since urethanes first seem to gain and then lose water during softening.

Polyester Urethane Polymers

For the five polyester urethane systems studied, infrared absorption in the 1700 cm^{-1} spectral region has been observed and the formation of this absorption shows a correlation with softening. From this standpoint, the urethane data are very encouraging. However, there are some inconsistencies in the urethane data that were not apparent in the data on epoxy systems. These questions about the urethane data need to be resolved before the 1700 cm^{-1} absorption can be reliably used as a means of predicting reversion. These inconsistencies can be deduced from Table 1.

For SCTH 226 the 1700 cm^{-1} absorption was observed even though the sample had only slightly softened (45-Shore A_2). However, this sample was beginning to show a loss in volume resistivity so this may be another case where the infrared and the dielectric measurements are more sensitive indicators of reversion than hardness measurements.

For 6001-XA, the 1700 cm^{-1} absorption also appears before the sample had melted (but had softened to Shore A_2 values between 30 and 45). However, the 1700 cm^{-1} absorption was not observed in a sample of 6020-1,4BD that had softened to a Shore A_2 value of 25. The 1700 cm^{-1} band did appear when 6020-1,4BD melted.

There are several possible explanations for this behavior, but with the limited data available it is difficult to select the proper explanation. In the urethanes using a 1,4 BD curing agent, the 1700 cm^{-1} absorption does not appear until the samples melt. For the urethanes using an XA curing agent, the 1700 cm^{-1} band can be detected during the softening process. This may indicate that depending on the particular urethane system (or rather the particular curing agent), the 1700 cm^{-1} absorption may show varying degrees of sensitivity to the reversion process.

Another explanation for the 6020-1,4 BD behavior is that more than one factor contributes to the softening process. For both the epoxys and the urethanes, the appearance of 1700 cm^{-1} absorption seems to correlate better with loss of electrical properties than with softening. Such may be the case for the 6001 and 6020 urethanes, but this cannot be established until dielectric measurements are obtained.

For all the epoxys, the 1700 cm^{-1} absorption always appeared at 1710 cm^{-1} . From Table 1 it can be seen that the exact frequency of the 1700 cm^{-1} absorption varies from urethane system to urethane system. This indicates a difference in the structures giving rise to the 1700 cm^{-1} absorption (which may explain why there could be varying degrees of sensitivity to the reversion process). For the limited number of urethanes studied the exact frequency of the 1700 cm^{-1} band seems to depend on the curing agent used. This in turn indicates that the curing agent may take part in the reaction which produces the structure giving rise to the 1700 cm^{-1} absorption.

The data in Table 1 indicate some inconsistencies in the urethane data, but this table also shows that there is a correlation between the appearance of the 1700 cm^{-1} absorption and the reversion process. The data also indicate that with additional measurements (including dielectric data) that information can be obtained on relating the effects of different structural features on the reversion process.

It is of interest to note that (Figure 33) for the 6001 and 6020 urethanes there is a direct relationship between initial hardness and length of exposure time before melting occurs. This correlation seems to be more dependent on the curing agent used than on the prepolymer used (although 6020 urethanes do not soften as fast as the corresponding 6001 urethane).

Most of the research covered in this report utilized hardness, dielectric, and infrared measurements because these techniques seem to best follow and detect the reversion process. NMR measurements are difficult to obtain on the solid urethane films and impossible

TABLE 1. RELATIONSHIP OF APPEARANCES OF 1700 cm^{-1} INFRARED ABSORPTION OF URETHANES TO SAMPLE CONDITION AND TIME OF EXPOSURE AT 85 C, 95 PERCENT RH

Urethane	Exposure Time (Days)	IR Band $\sim 1700\text{ cm}^{-1}$	Frequency (cm^{-1})	Physical Condition
SCTH 226	62	Yes	1700	Slightly soft - 45A ₂ Some loss of vol. res.
	100	Yes	1700	Liquid
6001-1,4BD	11	Yes	1698	Liquid
6020-1,4BD	11	No	--	Soft - 25A ₂
	19	Yes	1698	Liquid
6001-XA	11	Yes	1705	Soft - 45A ₂
	19	Yes	1705	Liquid
6020-XA	11	No	--	Hard - 80 A ₂
	19	Yes	1705	Soft - 32 A ₂

(with our instrument) to obtain on the epoxys. From the results on SCTH 226 (Figure 27) it is now believed that differences caused by the NMR technique (for solids) are as great as the differences caused by the various exposure conditions. The chemiluminescence measurements, on the other hand, are very sensitive to changes in the polymers caused by the various exposure conditions. However these measurements (such as seen in Figure 28) do not show any correlation with softening or reversion. Thus it appears as if the chemiluminescence technique is sensitive to many types of changes and, as yet, it has not been possible to isolate the changes due to reversion from those due to other causes (such as curing, oxidative degradation, etc.) This does not mean that NMR and chemiluminescence will not be used in future research. Rather it means that the use of these two techniques will be used where there is a need for more specific information such as establishing rates of reversion between two similar polymers.

The preceding data and conclusions indicate that the goals of future research should center about studies of urethanes with varying types of both prepolymers and curing agents. This should start with additional work on the 6001 and 6020 urethanes, but then move onto other urethane systems.

For the 6001 and 6020 urethanes there is need to get IR and hardness data on 6001-1,4 BD as it softens and on 6020-XA as it melts. Dielectric data should be obtained on all four systems.

The information obtained from more complete studies of the 6001 and 6020 urethanes will help in both the selection of other urethanes to be studied and the extent of the information that will be needed.

When it is definitely established that absorption in the 1700 cm^{-1} infrared region can be used to detect reversion, some of the research effort should shift to techniques for predicting service life of the polymer systems from the combination of infrared and dielectric measurements.

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