

# ON INVESTIGATING THE MECHANISM OF WEATHERING OF CHLOROSULFONATED POLYETHYLENE ROOFING AND EXPLORING MAINTENANCE TECHNIQUES

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All roofs are subject to the degradation effects of weathering. Built-up roofing, the oldest roofing material, exhibits a classic form of weathering, exemplified by asphalt embrittlement, alligatoring, asphalt chalking, and splitting. These observations are symptomatic of the ultimate destruction of this type roof and signal the need for the building owner to maintain, repair, or replace the existing roof.

The rapid growth and acceptance of the newer thermoplastic and thermoset single-ply membranes has been accompanied by claims of increased longevity of these roofs. Although this statement may bring some argument, the fundamental presupposition is that these roofs will ultimately fail and must be maintained, repaired, or replaced.

This paper studies the weathering degradation mechanism of chlorosulfonated polyethylene (CSPE) roofing materials. Samples from an actual weathered roof were analyzed chemically and compared to an unweathered control. Surface chemistry characterization was conducted using electron spectroscopy for chemical analysis (ESCA), time-of-flight secondary ion mass spectrometry (TOF-SIMS), scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), and attenuated total reflectance infrared spectroscopy (ATR-IR). Bulk chemical analyses using fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC) were used to identify the compositional changes attributed to prolonged weathering. Dynamic mechanical thermal analysis (DMTA) was employed to evaluate functional changes in the membrane as a result of weathering. Based on this combined data, a mechanism for surface weathering is proposed.

A maintenance procedure, using 100 percent acrylic elastomeric coatings, is explored based on six years of actual field studies on coating aged weathered membranes in service. These field studies have demonstrated the improved life cycle advantage for these maintenance coatings without the need for removal and replacement of the membrane.

## KEYWORDS

Acrylic maintenance coating, CSPE, degradation mechanism, life cycle cost, roofing degradation, weathering.

## INTRODUCTION

Roofs are typically replaced for one of two reasons; either they fail because of improper design, faulty materials, incorrect

installation, abuse, or they simply wear out, hopefully after their predicted life expectancy. Unfortunately, very little has been written about the fundamental mechanism of how roofs degrade as a result of natural weathering.<sup>1</sup> In 1994, the authors conducted fundamental studies to elucidate the mechanism of asphalt roof degradation.<sup>2</sup> The study examined weathering effects on the chemistry of organic and glass felt membrane built-up roofs. The chemical and physical (reinforcing scrim) components of unweathered and weathered roofing materials were characterized and compared. The study also showed that a 100 percent acrylic elastomeric coating applied over the asphalt membranes demonstrated excellent durability and greatly prolonged the roof life.<sup>2</sup>

This paper is concerned with the normal aging of a class of thermoplastic single-ply membranes known as chlorosulfonated polyethylene (CSPE). This material is sometimes referred to as Hypalon®. Chlorosulfonated polyethylene has been used as a waterproofing and roofing material for almost 25 years. One major manufacturer claims to have manufactured over one billion square feet since 1975.<sup>3</sup>

Like asphalt degradation, few fundamental mechanistic studies have been published<sup>1</sup> that define a mechanism for CSPE roof membrane degradation. This paper compares the chemistry of new and weathered CSPE membranes and hypothesizes a mechanism for roof degradation. A life cycle cost analysis for the use of 100 percent acrylic elastomeric maintenance coatings over aged CSPE membranes is also discussed.

## FIELD OBSERVATIONS

Consultants and others conducting field surveys and roof inspections have observed the characteristic symptoms of roofing degradation. This degradation may be observed as surface checking or asphalt chalking on bitumen-surfaced membranes. It may be exemplified by coating erosion on sprayed-in-place polyurethane foam roofs. It may be cracking on some thermoplastic single-ply membranes. Simply put, each of these roofing materials exhibits its own characteristic symptoms of degradation. Obviously, when the degradation becomes severe and the watertight integrity of the membrane is compromised, the roof must be repaired, maintained, or replaced.

Chlorosulfonated polyethylene thermoplastic membranes exhibit classical symptoms of degradation, which include white chalking, surface checking, and cracking down to and

sometimes through the reinforcing scrim.<sup>4</sup> These observations are referred to as weathering, but the more sophisticated answer and the purpose of this paper is to describe the chemical and physical changes the membrane undergoes as a result of weathering factors such as sunlight (UV), heat, water, oxygen, thermal shock, and from these changes to elucidate the overall degradation mechanism of this roofing material.

Typical thermoplastic single-ply roof membranes based on CSPE polymer contain several other ingredients in addition to the polymer. These ingredients may include but are not limited to  $\text{CaCO}_3$  (filler),  $\text{TiO}_2$  (whitening and UV resistance),  $\text{MgO}$  (crosslinking and color stability), processing aids, antistat and antioxidant compounds, and epoxy-based curing agents.<sup>5</sup> Tribasic lead maleate ( $\text{C}_4\text{H}_2\text{O}_7\text{Pb}_4 \cdot \text{H}_2\text{O}$ ) is sometimes used in roofing sheets requiring increased water resistance.<sup>6</sup>

## EXPERIMENTAL

All analyses were conducted on two samples: an exposed portion of CSPE membrane, hereafter referred to as weathered, and the portion of membrane beneath the top layer on the same roof, hereafter referred to as protected. It is assumed for these analyses the protected area is completely unexposed, and thus, it is used as the unweathered control. The samples were obtained from a low-slope commercial roof on an industrial building in the Philadelphia, Pennsylvania, area. The roof design consisted of lightweight bar joist construction under a fluted steel deck. Polyisocyanurate board stock insulation was mechanically fastened to the deck. The CSPE single-ply was also mechanically fastened through the insulation into the deck. Field seams were heat-welded.

## MICROSCOPIC ANALYSES

Scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) was used to quantify the differences between these samples. The samples were first given a light conductive coating of carbon and then imaged in a Jeol 840 using a 20.0 KeV beam. Both samples were analyzed at low magnification (20x) and higher magnification (500x).

The weathered and protected CSPE membrane samples were also examined using optical microscopy (OM) at 63x magnification.

## SURFACE ELEMENTAL ANALYSES

### Electron Spectroscopy for Chemical Analysis (ESCA)

The ESCA experiments were performed on a VG ESCA/SIMSLAB MkII instrument equipped with a hemispherical analyzer.  $\text{Al K}_\alpha$  X-rays ( $h\nu = 1486.6 \text{ eV}$ ) were used as the excitation source. The source was operated at 290W, 14.5kV, and 20mA. A take-off angle of 75 degrees was used. All survey (elemental) scans were collected using a pass energy of 100eV and a step size of 0.5 eV/step. All high-resolution scans were collected using a pass energy of 20eV and a step size of 0.1 eV/step. Binding energies were referenced to the carbon 1s Chx component set at 284.6 eV.

### Secondary Ion Mass Spectrometry (SIMS)

SIMS involves mass analyzing the molecular ions that are sputtered from a solid surface, thus providing detailed, surface-specific, compositional information. SIMS detects molecular species, as well as all elements and their isotopes emanating from the top one to two monolayers of a solid.

The sputtering of the molecular and elemental species is

achieved by bombardment of the sample with a primary ion beam of kilovolt energy. To minimize damage to organic surfaces, a low primary ion dose, less than  $10^{13}$  ions/ $\text{cm}^2$ , was utilized. This minimizes the depletion of molecular information because the probability that a primary ion will strike the same molecule on the surface twice during the analysis is minimal. Therefore, molecular information can be obtained by SIMS because structural and bonding information is not compromised by the primary ion beam. Although the analysis is restricted to solids, all materials—whether insulators or conductors—can be examined without pretreatment.

The SIMS experiments were performed on a Physical Electronics, PHI-Evans TFS-2000 TOF-SIMS instrument. The primary ion beam was generated from a  $^{69}\text{Ga}^+$  liquid metal ion gun with an energy of 15kV. The nominal size of the analysis regions varied between 120  $\mu\text{m}^2$  and 180  $\mu\text{m}^2$ . The secondary ions were all accelerated to a constant kinetic energy by the application of 8000 volts prior to entering the drift tube. Typical ion doses were on the order of  $10^{12}$  ions/ $\text{cm}^2$ , ensuring that the data were collected within the static limit (i.e., less than 1 percent of a monolayer was sputtered). Therefore, all molecular fragments are indicative of species existing on the surface prior to analysis. Under these conditions, the sampling depth of TOF-SIMS is approximately one monolayer for molecular fragment ions and about one to three monolayers for atomic species.

## SOLVENT EXTRACTION AND BULK COMPOSITIONAL ANALYSIS

A preweighed, 25 mm by 25 mm (1 inch by 1 inch) piece of each sample was extracted 72 hours in about 10 g tetrahydrofuran (JT Baker Analyzed, HPLC grade, unstabilized). Samples were centrifuged approximately 30 minutes at 8000 rpm to facilitate separation of the soluble fraction (soluble polymer and other organics) from the insoluble fraction (insoluble polymer, pigments, fillers, and scrim). Total weight percent of soluble fraction was determined gravimetrically; total insolubles were determined by difference. The THF extracts were analyzed to determine composition using a Mattson Galaxy 5000 FTIR spectrometer with DTGS detector. Spectral data collection parameters:  $\text{N}_2$  purge, DTGS detector, 32 co-added scans, 4  $\text{cm}^{-1}$  resolution, triangular apodization.

Attenuated total reflectance (ATR) infrared analysis of the membrane surface was accomplished using the Mattson Galaxy 5000 FTIR spectrometer fitted with a Split Pea™ accessory (Harrick). The Split Pea is a single-bounce ATR with a silicon crystal, which has a 300- $\mu\text{m}$ -diameter sampling area. Sensitivity of the ATR method (depth of penetration) is dependent upon wavelength and the refractive indices of the sample and the silicon crystal. For these experiments, the calculated depth of penetration was approximately 1  $\mu\text{m}$ . Spectral data collection parameters:  $\text{N}_2$  purge, DTGS detector, 256 co-added scans, 4  $\text{cm}^{-1}$  resolution, triangular apodization.

All infrared spectral data was analyzed using the WinFirst™ software package (ATI Mattson, Version 2.0, 1994).

## RHEOLOGICAL PROPERTIES OF THE MEMBRANE

Dynamic mechanical thermal analysis (DMA) was performed using a Rheometrics DMTA Mk II (originally a Polymer Laboratories instrument). The geometry employed was single cantilever, and the sample dimensions were roughly 10 mm

by 20 mm (.04 inches by .08 inches). A temperature ramp was performed from -25°C (-13°F) to 100°C (212°F) at a ramp rate of 2°C/min (3.6°F/min). During the ramp, a dynamic oscillation at a frequency of 1 Hz and very small strain was imposed on the sample, and the modulus and damping (tan delta) was measured.

### MOLECULAR WEIGHT CHARACTERIZATION

The THF extracts of each sample were also analyzed by gel permeation chromatography (GPC) with differential refractive index detection. Samples were filtered through 1.0  $\mu\text{m}$  glass filters and injected 100  $\mu\text{l}$  on a column set consisting of one each of 100Å, 10<sup>5</sup>Å, and 10<sup>6</sup>Å Ultrastaygel columns (Waters); the calibrated molecular weight range of this column set is approximately 200 to 2 x 10<sup>6</sup> daltons.

### RESULTS AND DISCUSSION

#### *Microscopic Analyses*

At low magnification (20x), the weathered surface is covered with an extensive network of cracks. The unweathered surface does not appear to contain any cracking. At higher magnification (500x), it is obvious the weathered surface has developed pinholes and has loosely held particulates, probably pigment and filler, on the surface. The unweathered surface has few pinholes and the particles at the surface are contained within the binder film. These features—the cracking, pinholing, and particulates (pigment/filler) on the surface—are consistent with weathering caused by binder erosion.

Energy dispersive spectroscopy (EDS) analysis of the unweathered chlorosulfonated polyethylene indicates the presence of elements associated with the binder (Cl) and pigments (Al, Si, Ca, and Ti) on the surface. For the weathered sample, the ratios of these elements have changed dramatically, with an increase in some of the pigment elements (Al, Si, and Ti) and a decrease in the binder element (Cl). These changes would be indicative of a change in the binder-to-pigment ratio, consistent with a loss of binder.

Low magnification (63x) optical microscopy shows extensive cracking on the surface of the weathered chlorosulfonated polyethylene. In cross section, it can be seen that some of the cracks in chlorosulfonated polyethylene sample extend all the way through the membrane to the reinforcing scrim (Figure 1). The top and edge views of the protected CSPE membrane show no cracking at the same magnification (Figure 2).

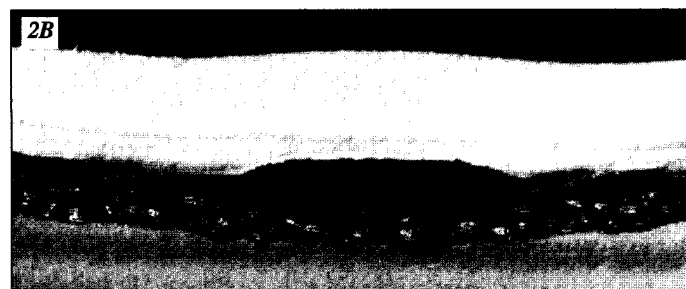
#### **Surface Elemental Analyses**

##### *Electron Spectroscopy for Chemical Analysis (ESCA)*

Both the weathered and protected surfaces of the CSPE sheet were examined. The weathered side was analyzed in triplicate and the protected surface in duplicate. The ESCA results can be found in Table 1. Chlorine and sulfur from the CSPE polymer are observed to decrease upon exposure, indicative of polymer degradation. Likewise, the carbon and nitrogen levels also decrease on weathering. The nitrogen detected, caused by amide functionality, may arise from material post-added to the formulation. Coincident with polymer degradation, the titanium, magnesium, silicon, aluminum, and oxygen levels on the exposed surface all increase because of exposure of filler/pigment particles.



**Figures 1A and 1B.** Optical micrograph (63x) of weathered CSPE single-ply roof membrane: 1A surface view, 1B cross-sectional view.



**Figures 2A and 2B.** Optical micrograph (63x) of protected CSPE single-ply roof membrane: 2A) surface view, 2B) cross-sectional view.

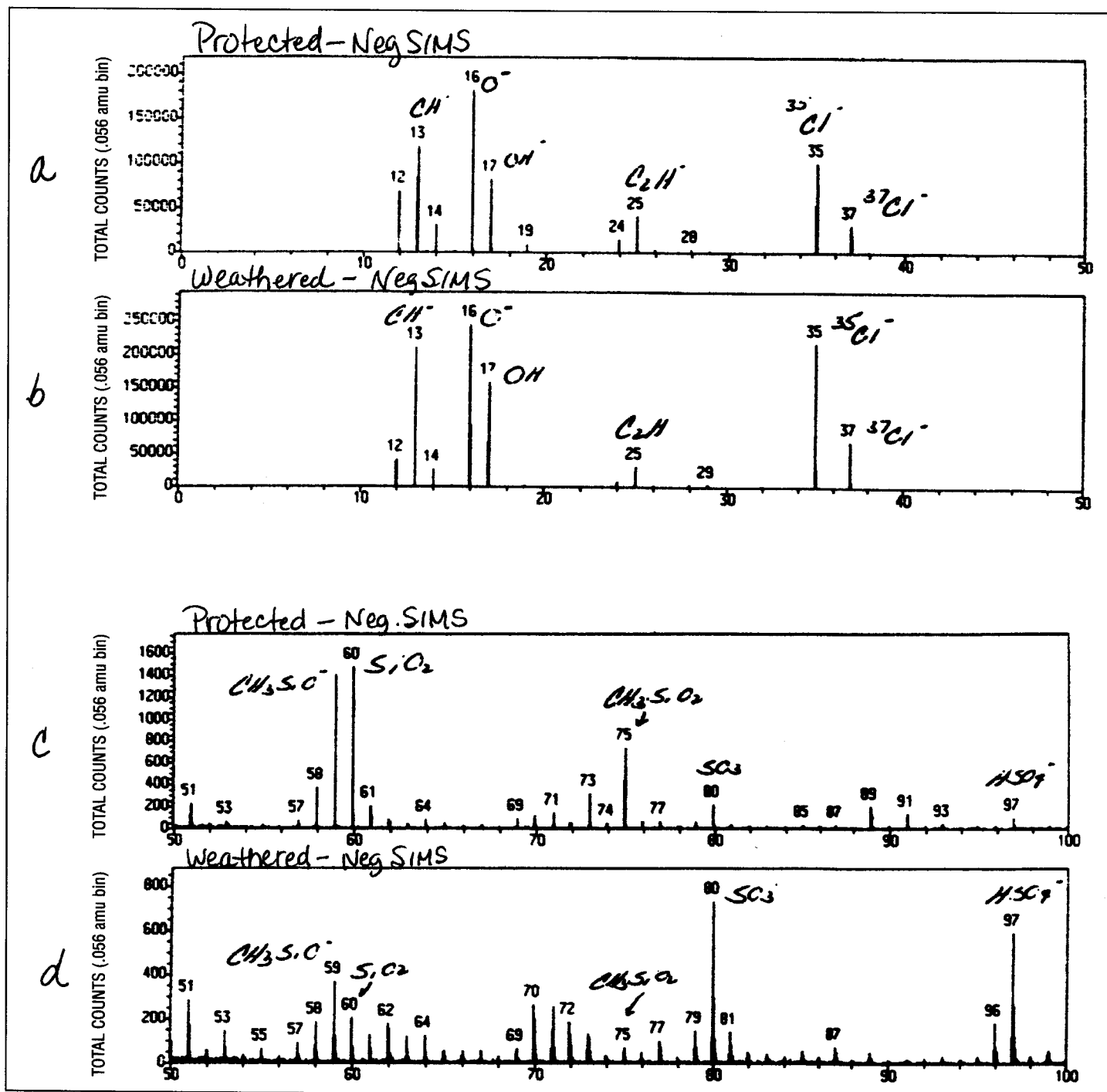
#### *Secondary Ion Mass Spectrometry*

Both positive and negative ion SIMS spectra were collected from the protected and weathered surfaces and their cross-sections. Figures 3 and 4 contain negative SIMS spectra collected from the surfaces of the samples. The Cl from the CSPE polymer is evident on all samples and is more intense in the cross-sectional areas than in the protected and weathered surfaces. Ions emanating from dimethylsiloxane (DMS) dominate the surface and are observed at mass 59(CH<sub>3</sub>SiO),

60( $\text{SiO}_2^-$ ), 75( $\text{CH}_3\text{SiO}_2^-$ ), 89( $\text{CH}_3\text{CH}_2\text{SiO}_2^-$ ), 119( $\text{CH}_3\text{Si}_2\text{O}_5^-$ ), 149[ $(\text{CH}_3)_3\text{Si}_2\text{O}_5^-$ ], 163[ $(\text{CH}_3)_3\text{CH}_2\text{Si}_2\text{O}_5^-$ ], and 223[ $(\text{CH}_3)_5\text{Si}_3\text{O}_8^-$ ]. The ions from DMS on the protected surface and cross-section areas are of equal intensity and greater than those observed emanating from the weathered surface. This DMS may be due to a processing aid. The ions at mass 80( $\text{SO}_3^-$ ) and 97( $\text{HSO}_4^-$ ) possibly emanate from the chlorosulfonate groups in the CSPE or from the surfactant/initiator package used in the manufacturing of the material (Figures 3C and 3D). Fatty acid ions at mass 283 ( $\text{C}_{17}\text{H}_{35}\text{CO}_2^-$ ; stearic)

and 255 ( $\text{C}_{15}\text{H}_{31}\text{CO}_2^-$ ; palmitic) are observed on all of the samples but are more intense on the surface of the protected sample (Figures 4C and 4D) and in its cross section. These fatty acids may be due to processing aids used during compounding and calendaring.

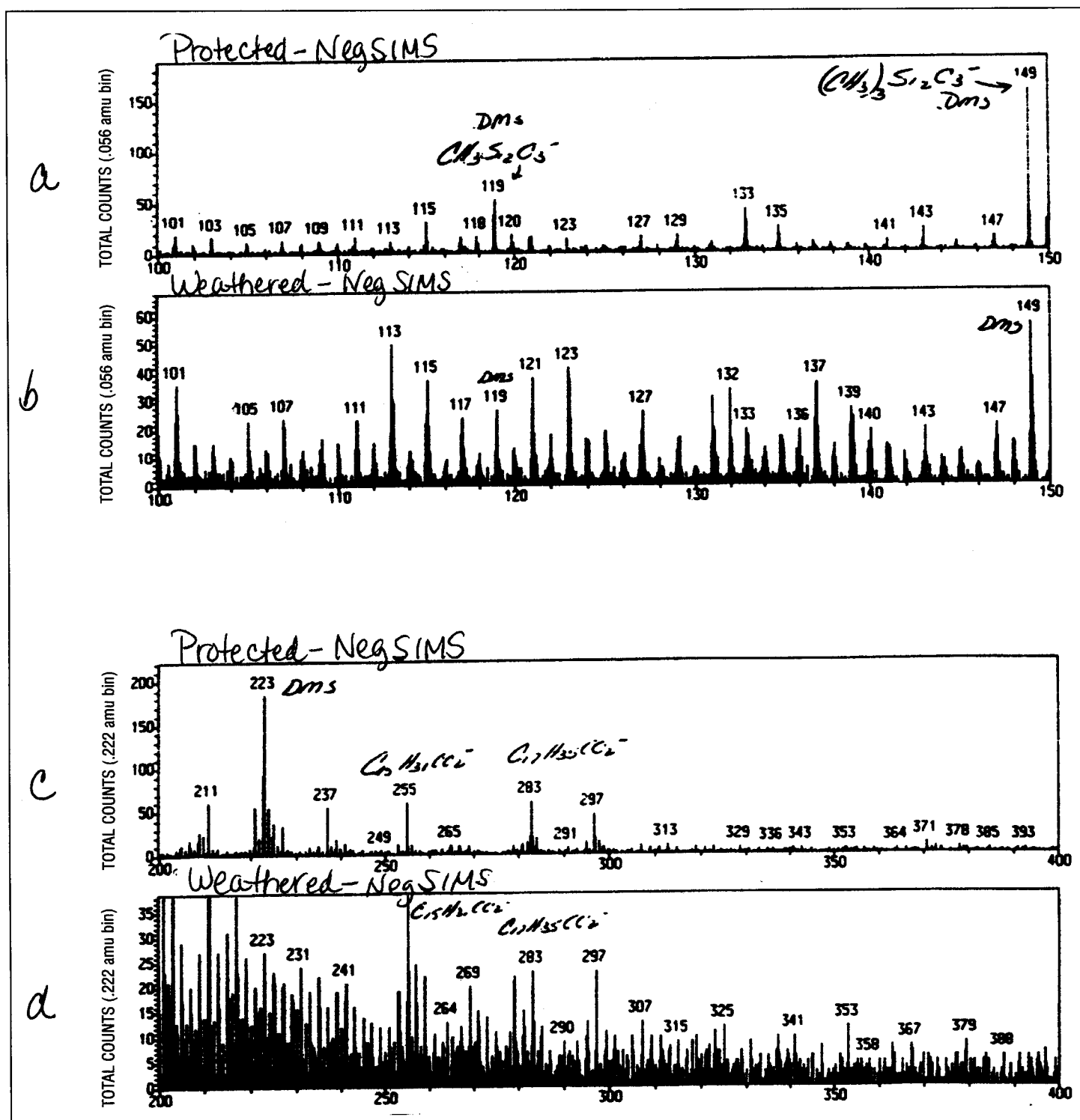
Figures 5 and 6 contain the positive SIMS data collected from the sample surfaces. In general, at the lower mass ranges, data obtained from positive SIMS is very similar for all the samples examined. A typical methyl, ethyl, propyl, butyl-type ion pattern is observed because of polymer back-



Figures 3A, 3B, 3C, and 3D. Negative SIMS spectra showing key ions of interest: 3A) protected surface, mass range 0 to 50; 3B) weathered surface, mass range 0 to 50; 3C) protected surface, mass range 50 to 100; 3D) weathered surface, mass range 50 to 100.

bone fragmentation. The detailed structural information obtainable with negative SIMS is not achieved with the positive ion technique; however, pertinent data is still acquired. Dimethylsiloxane is again observed on all samples as indicated by the ions at mass 73 [ $(\text{CH}_3)_3\text{Si}^+$ ], 147 ( $\text{C}_5\text{H}_{15}\text{OSi}_2^+$ ), and 221 ( $\text{C}_7\text{H}_{21}\text{O}_2\text{Si}_3^+$ ). Also observed are ions centered at mass 207-208, which emanate from the Pb present in the roofing

sheet (Figures 6C and 6D), corroborating the ESCA data. Ions at mass 256 ( $\text{C}_{16}\text{H}_{32}\text{ONH}_2^+$ ) and 284 ( $\text{C}_{18}\text{H}_{36}\text{ONH}_2^+$ ) are also found on the surface of the protected area (Figure 6C) but not on the weathered (Figure 6D) or cross-sectional areas. These ions, which are present at a significant intensity on the protected surface, are due to a fatty acid amide (e.g., stearamide). Centered at mass 177 ( $\text{C}_5\text{H}_7\text{SO}_2\text{C}_2^+$ ) and mass



Figures 4A, 4B, 4C, and 4D. Negative SIMS spectra showing key ions of interest: 4A) protected surface, mass range 100 to 150; 4B) weathered surface, mass range 100 to 150; 4C) protected surface, mass range 200 to 400; 4D) weathered surface, mass range 200 to 400.

	WEATHERED		PROTECTED	
	Average	Std. Dev.	Average	Std. Dev.
Cl	3.10	0.62	10.25	1.09
N	0.39	0.10	1.64	0.24
C	31.41	2.35	45.84	3.66
O	30.46	2.12	18.76	2.90
S	0	0	0.67	0.29
Ti	3.52	0.49	0	0
Mg	4.09	0.68	0	0
Si*	13.85	1.78	0	0
Si**	0	0	2.99	1.53
Ca	3.59	1.30	1.73	0.53
Na	0.61	0.28	0.79	0.76
Al	6.93	0.97	0	0
Pb	0.88	0.13	0.82	0.11
N: Neutral organic (amine, amide, imine, etc.) Cl: Organic S: Sulfate Si*: Silicate Si**: Siloxane				
Weight percents are calculated neglecting hydrogen, which is not detectable via ESCA, and are forced to 100 percent.				

Table 1. Surface elemental composition (weight percent).

191(C<sub>4</sub>H<sub>9</sub>SO<sub>3</sub>Cl<sub>2</sub><sup>+</sup>) are ions emanating from CSPE polymer because of fragmentation along the polyethylene backbone. The intensity of these ions is greatest in the protected surface and cross-sectional areas. The intensity of these ions on the weathered surface is decreased by at least a factor of three, indicating that polymer degradation is occurring upon weathering. Polymer degradation can also be observed by monitoring the Mg and Ti levels in the formulation. The ions at mass 48(Ti<sup>+</sup>) and 24(Mg<sup>+</sup>) can be observed on the weathered surface but not on the protected surface, indicating that the polymer is wearing away and exposing the inorganic species (Figures 5A and 5B). This data directly corroborates that obtained in the ESCA analyses.

The degradation of the CSPE polymer upon exposure can be observed further by examining the ion at mass 27. There are generally two species—Al<sup>+</sup> and C<sub>2</sub>H<sub>5</sub><sup>+</sup>—that give rise to this ion, which is due to organic species. Figure 7 contains the positive SIMS spectra centered at mass 27 for the weathered and protected surfaces. On the protected surface, mass 27 is almost exclusively organic in nature (C<sub>2</sub>H<sub>5</sub><sup>+</sup>) with little Al<sup>+</sup> observed. Upon exposure however, the ratio of organic species (C<sub>2</sub>H<sub>5</sub><sup>+</sup>) to Al<sup>+</sup> changes dramatically with the surface now dominated by the Al<sup>+</sup> ion, indicative of polymer breakdown.

#### Solvent Extraction and Bulk Compositional Analysis

FTIR analyses of the THF extract of the membrane show a substantial amount of carboxylic acid (1712 cm<sup>-1</sup>), along with an increase in C-O functionality, in the weathered sample (Figure 8). Lack of appreciable C-Cl absorption at 664 cm<sup>-1</sup> in the IR spectra suggests incomplete solubilization of the base polymer in both samples. This is not surprising considering CSPE roof membranes are typically crosslinked after applica-

tion for increased durability. Also a decrease in aromatic functionality at 1509 cm<sup>-1</sup> in the weathered sample vs. the protected is likely due to the consumption of Epon 828 epoxy-based curing agent on aging.<sup>5,7</sup> Surface infrared analyses (Figure 9) show a loss of hydrocarbon functionality (2849 cm<sup>-1</sup> and 2919 cm<sup>-1</sup>) on the weathered surface as compared to the protected surface.

A 25-mm by 25-mm (1-inch by 1-inch) piece of weathered membrane weighs 80 percent as much as a piece of the protected membrane of the same size. Thermogravimetric analysis shows the ratio of pigment to binder remains unchanged on weathering of the membrane, indicating both pigment and binder are lost on a constant ratio basis. The weight percent of THF extractables is approximately equal for the weathered and protected membranes, 36.5 percent and 35.7 percent (w/w basis), respectively.

#### Rheological Properties of the Membrane

Using dynamic mechanical thermal analysis (DMTA), the weathered sample shows a shallower minimum in the tan delta curve than the protected sample; this suggests lower molecular weight in the weathered sample (Figure 10). Also, the weathered sample exhibits decreased modulus, and therefore, a decrease in the mechanical strength of the membrane relative to the protected sample (Figure 11). Unfortunately, the presence of the reinforcing scrim complicates the analysis and prevents the authors from obtaining more information about the polymer from the DMTA data.

#### Molecular Weight Characterization

Gel permeation chromatography (GPC) analyses indicate a decrease in molecular weight on weathering. The THF-soluble fraction of the weathered sample shows two major components at 113,000 and 28,000 daltons, while the THF-soluble fraction of the protected sample shows one major component at 133,000 daltons (Figure 12). The GPC analysis only accounts for the part of the sample that is both soluble in THF and filterable. Previous work has shown the polymer is not completely soluble in THF. However, the GPC evidence for molecular weight decrease indicates the same trend towards polymer degradation as is indicated by the rest of the analytical data obtained.

#### Hypothesis for Surface Degradation

Based on the analytical data, it appears the CSPE sheet is degrading by a polymeric decomposition mechanism. This based on the gravimetric analyses showing the bulk ratio of pigment to pigment plus polymer is unchanged, but the total amount of pigment plus polymer decreases with weathering. This can be seen on a macro scale as chalking of the weathered membrane. Micro surface analyses show the loss of polymer as evidenced by correspondingly high pigment to binder levels. The lost binder causes the loose pigment to chalk easily.

Because the polymer (binder) provides the adhesive properties for retaining the pigment in the matrix, its degradation is the most critical factor in understanding and elucidating a mechanism. The following hypothesis is based on the summary findings from each of the analytical techniques previously described. Theoretically, the C-S bond in CSPE is labile enough (approximately 57 kcal/mol) to be broken under UV light conditions, typical of natural sunlight, thus forming radical species.<sup>8</sup> The formation of these radicals leads to poly-

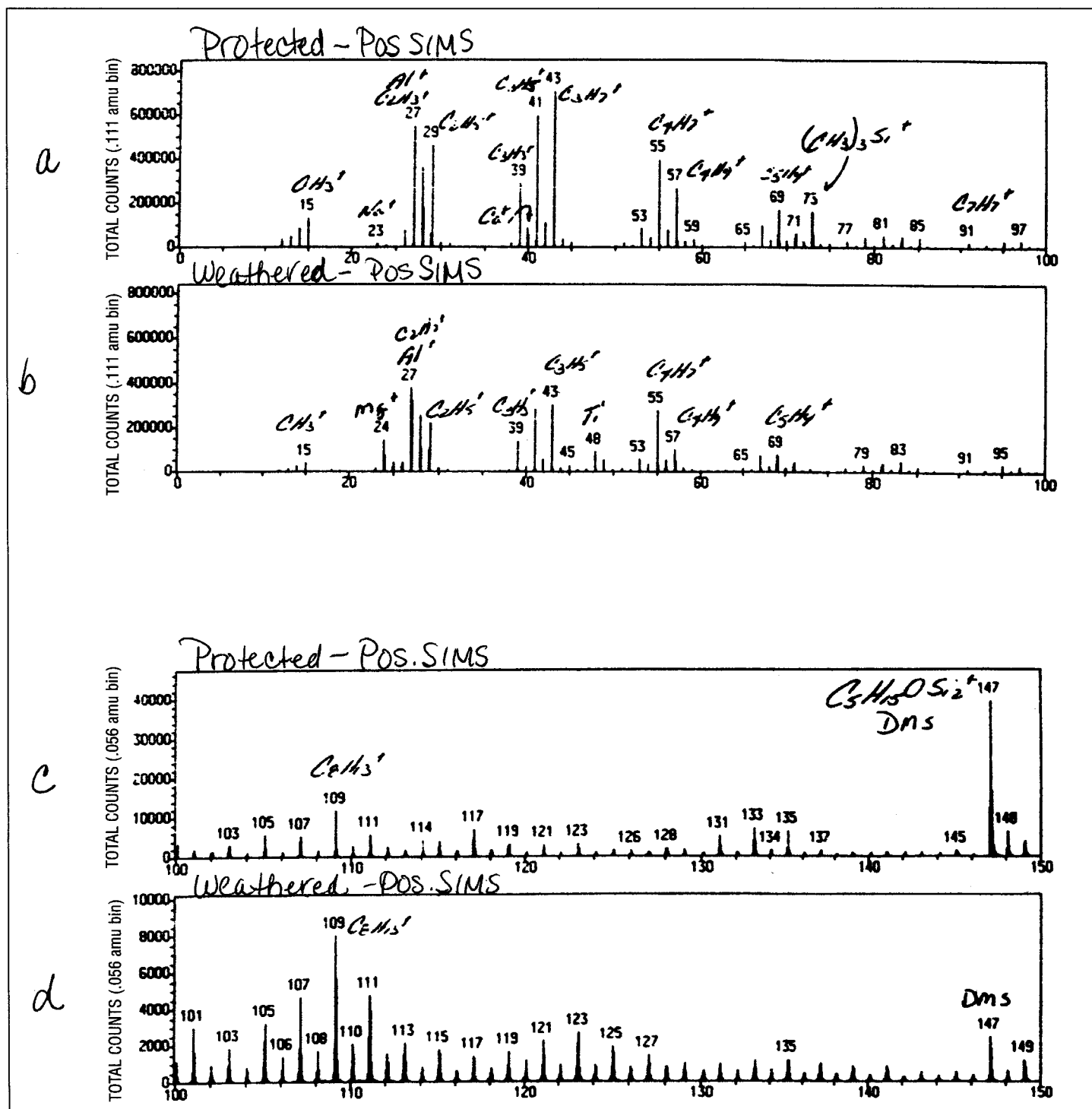
mer chain scission. This was confirmed by molecular weight studies. This chain scission and accompanying polymer degradation results in the gross effects of cracking, chalking, and loss of CSPE adhesion to the reinforcing scrim.

The chlorine level has been shown in this paper to decrease with weathering and may separate from the CSPE backbone by a radical mechanism, sulfonyl chloride species formation, or degradation via a dehydrohalogenation reac-

tion. This latter mechanism is seen in the decomposition of other chlorinated polymeric species, such as PVC.<sup>9</sup>

#### Maintenance Techniques

From the previous sections on chemical and physical degradation studies and from the elucidation mechanism, it is possible to theoretically design maintenance coatings that would prolong the chlorosulfonated polyethylene membrane roof's

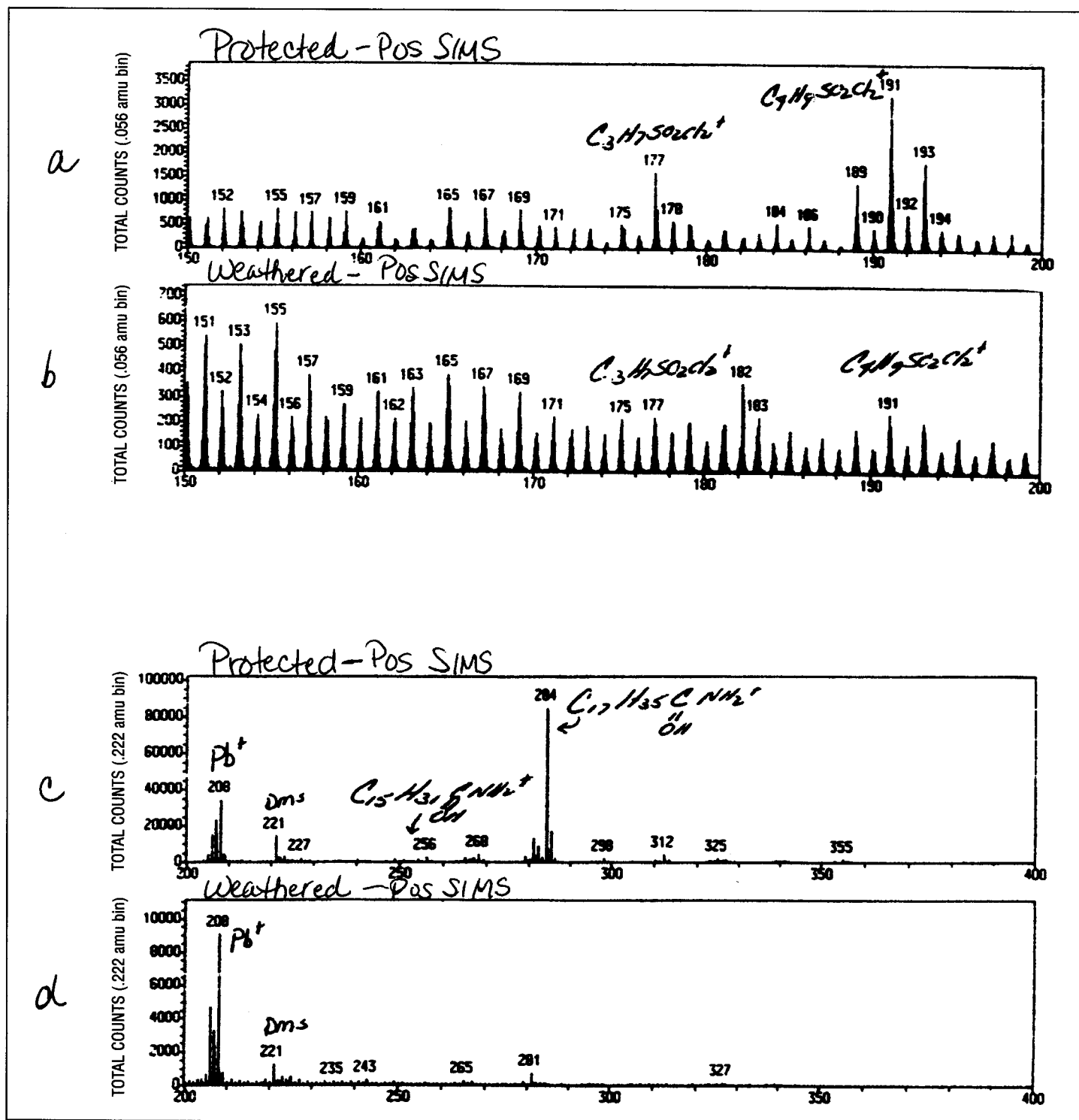


Figures 5A, 5B, 5C, and 5D. Positive SIMS spectra showing key ions of interest: 5A) protected surface, mass range 0 to 100; 5B) weathered surface, mass range 0 to 100; 5C) protected surface, mass range 100 to 150; 5D) weathered surface, mass range 100 to 150.

life. Ideally, this coating would itself not be susceptible to degradation normally attributable to roofing environments. The ideal coating would have excellent UV resistance and adhesion to the existing weathered membrane and would provide some measure of water resistance. Light (white) color would be preferred as it would compliment the existing roof color and provide similar solar reflectance and high

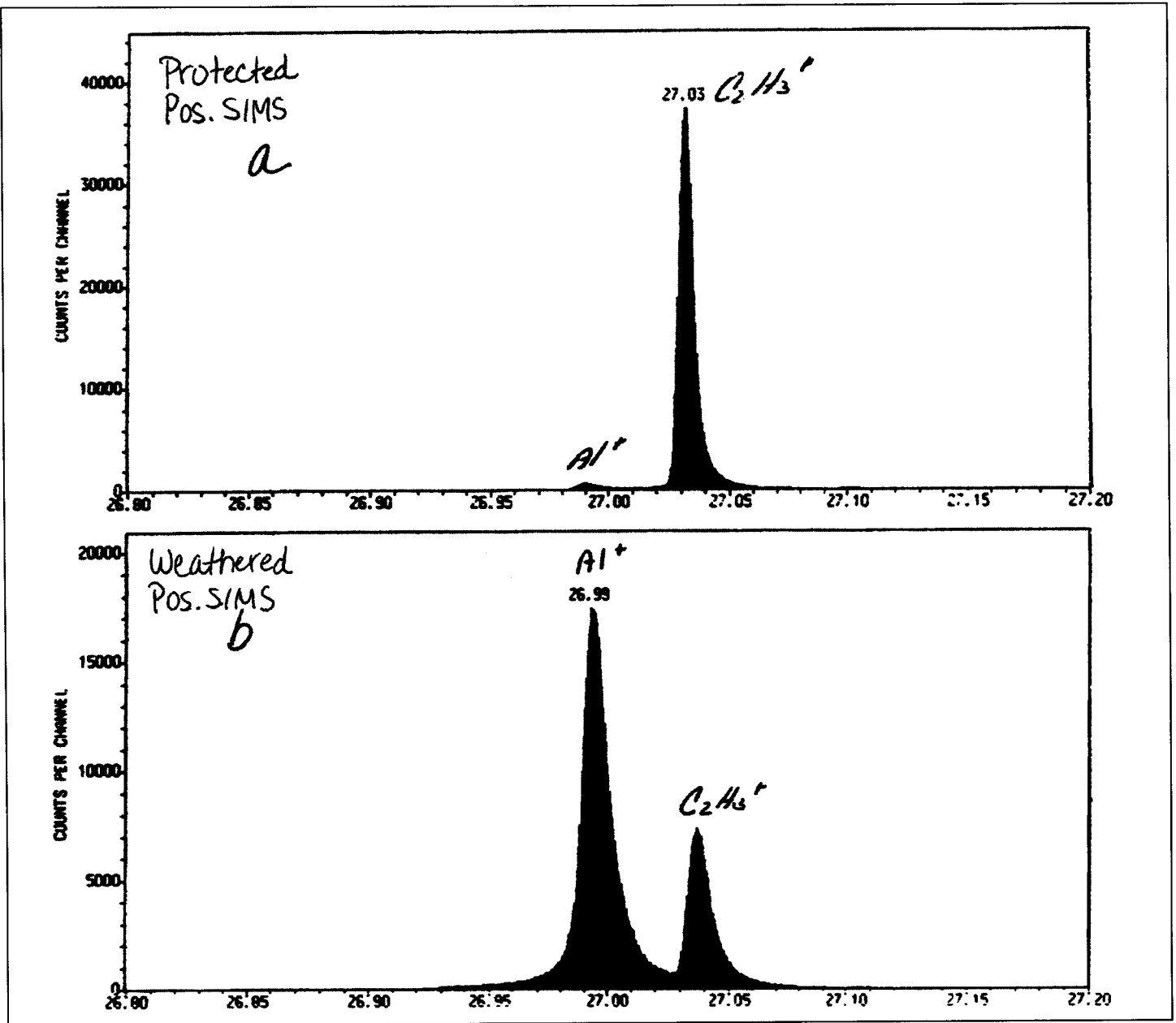
albedo as the original material.

In 1989, the authors began investigating techniques for maintaining chlorosulfonated polyethylene membrane roofs. Months of laboratory testing were conducted on various coating chemistries. Specifically, adhesion mechanisms were studied to optimize the bond between the coating and the aged, weathered membranes. The coating needed excellent low-temperature flexibility and similar tolerance for



Figures 6A, 6B, 6C, and 6D. Positive SIMS spectra showing key ions of interest: 6A) protected surface, mass range 150 to 200; 6B) weathered surface, mass range 150 to 200; 6C) protected surface, mass range 200 to 400; 6D) weathered surface, mass range 200 to 400.





Figures 7A and 7B. Positive SIMS spectra of mass spectral region centered at mass 27, showing change in ratio of organic  $C_2H_3^+$  ions to  $Al^+$  ions on CSPE membrane surface as a result of weathering: 7A) protected surface, 7B) weathered surface.

movement as the original single-ply to cope with the stresses of wind flutter associated with mechanically adhered roof systems. Laboratory studies emerged into accelerated weathering studies using Weather-O-Meters and QUV apparatus. Finally, actual field exposure tests were conducted on existing aged weathered roofs. These coated test roofs have been in place since 1990 and thus far demonstrate excellent durability and have stopped further degradation associated with the original membrane.

Laboratory and field exposure test results show the original weathered membrane can be maintained with a 100 percent acrylic elastomeric coating, provided the reinforcing scrim is still intact and has not lost its tensile strength. The actual maintenance technique involved making spot repairs where fasteners had backed out or where field seams had

opened. These spot repair techniques have been documented in an article by Robinson.<sup>10</sup> Then, the entire roof was washed with a garden hose and broomed to remove dirt and chalked degradation products. Then, a single coat of 100 percent acrylic elastomeric roof coating was applied using an airless sprayer. Dry film thickness recommendations are for a minimum of 15 mils (385  $\mu m$ ).

Life cycle cost analyses for an approximately 9288-m<sup>2</sup> (100,000-square-foot) roof described in Table 2 clearly show the economic advantage for coating after 10 years rather than reroofing. Detailed in the table are the capital costs and maintenance costs of the options expressed as Present Value. (Individual spreadsheet calculations are also enclosed.) Each alternative should extend the roof life from the original roof life of 10 to 20 years. However, the coating option

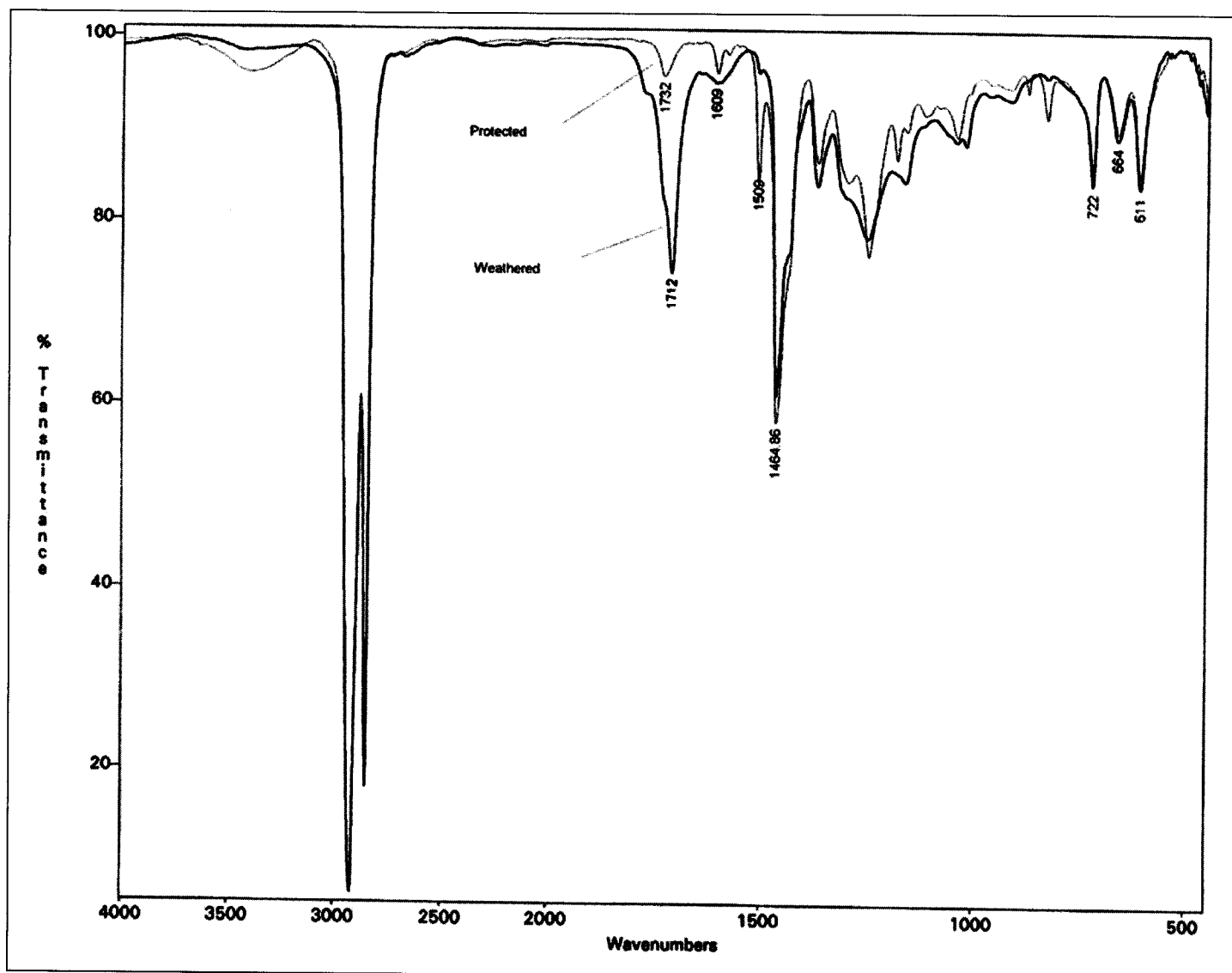


Figure 8. Transmission infrared spectra of the THF-soluble fractions of weathered and protected CSPE membranes. Samples were analyzed as cast films on AgCl plates.

clearly provides the lower life cycle cost. This projection is supported by similar studies using the same coating, over other asphaltic and nonasphaltic roof membranes. These studies demonstrate more than 10 years of successful field performance for the maintenance coating, but the total life for this maintenance coating is not known with certainty.

In this manner, the CSPE roof can be routinely maintained using coatings. This will eliminate the need for costly replacement and the associated inconvenience of tear off and disposal. This roof system is truly maintainable.

## CONCLUSIONS

This paper has elucidated a mechanism for the surface degradation of this chlorosulfonated polyethylene-based single-ply roof membrane. Summarily, the CSPE polymer, which provides the waterproofing, adheres the pigments together and provides adhesion to the reinforcing scrim, degrades as a result of UV (sunlight) exposure.

It has also demonstrated that this membrane is maintainable using 100 percent acrylic elastomeric coatings. Thus, the original roof can be maintained in a more cost-efficient man-

ner than the traditional technique of reroofing severely deteriorated CSPE membranes.

## RECOMMENDATIONS

- Conduct further mechanistic studies to elucidate the degradation of other single-ply thermoplastic and thermoset roof membranes.
- Conduct fundamental laboratory investigation into the applicability of 100 percent acrylic elastomeric coatings as a technique to maintain other single-ply roof membranes. Initiate field exposure studies based on laboratory findings.
- Determine the compositional changes in an acrylic-coated weathered CSPE membrane and compare to the data obtained at the time of coating the weathered CSPE membrane.

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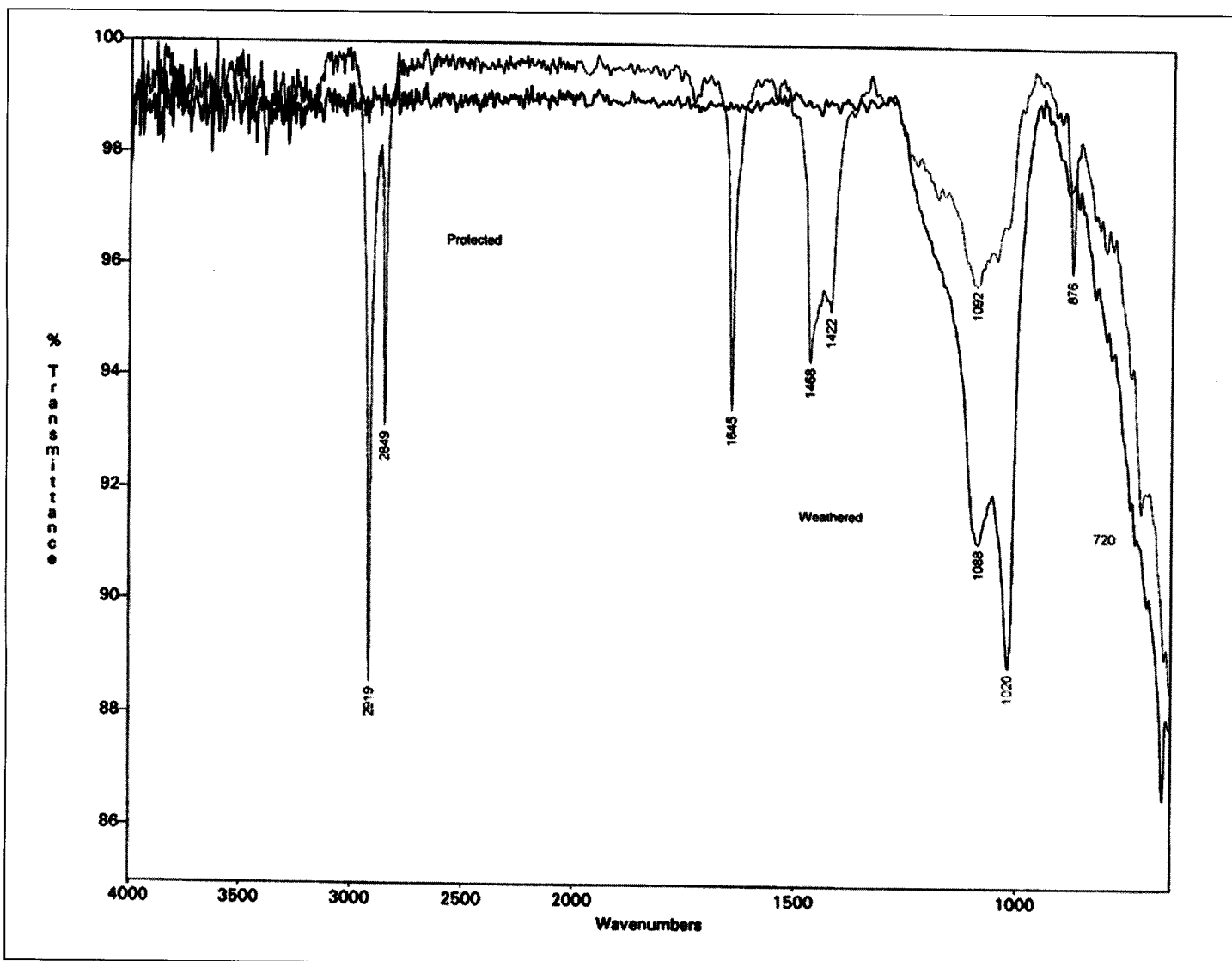


Figure 9. Surface infrared spectra of the weathered and protected CSPE membrane surfaces. Note the loss of long-chain hydrocarbon (2919  $\text{cm}^{-1}$  and 2849  $\text{cm}^{-1}$ ) and  $\text{CaCO}_3$  (1422  $\text{cm}^{-1}$  and 876  $\text{cm}^{-1}$ ) on weathering.

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Capital Costs (PV)	Approach #1	Approach #2
(Present Value)		
	(Reroof)	(Coat)
Initial Investment	\$300,000	\$300,000
Roof Recover	\$105,000	
Roof Coating		\$26,250
<b>Maintenance Costs (PV)</b>		
Repair Leaks	\$7,142	\$7,142
Interior Damage	\$928	\$928
Wasted Energy	\$1,489	\$1,486
PV of 20 Year Expenditure	\$414,558	\$335,808
Equivalent Annual Value	\$48,711	\$39,457
(cost) UCR		
i=10% 20 Years (.1175)		
Depreciated Annual Value (Cost)	\$42,403	\$34,348
Straight Line 39 Years 40% Tax		
Rate PV		
Cost Savings over Approach #1	\$0.09	\$/ft <sup>2</sup> /year

Table 2. Life cycle cost summary.

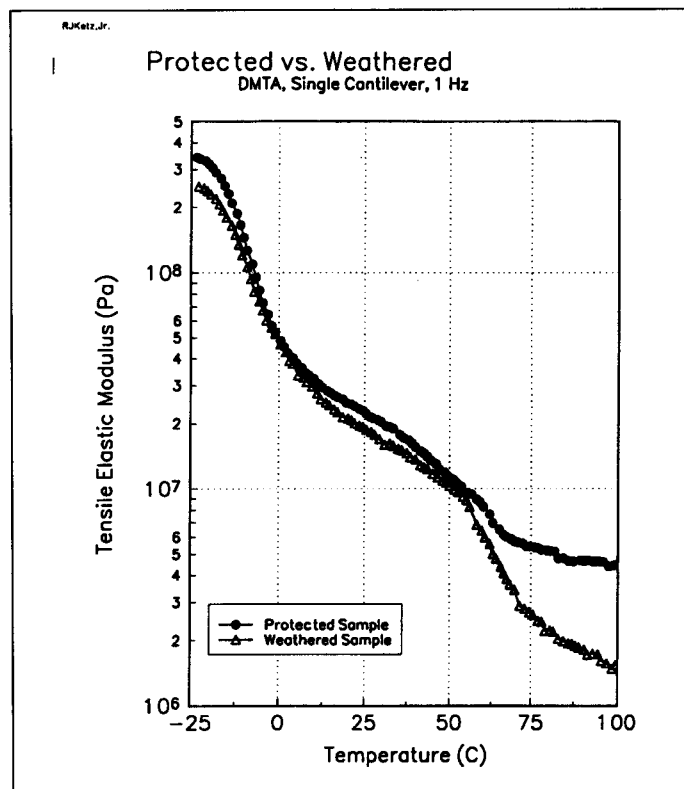


Figure 11. Tensile elastic modulus curves for the protected and weathered CSPE membrane.

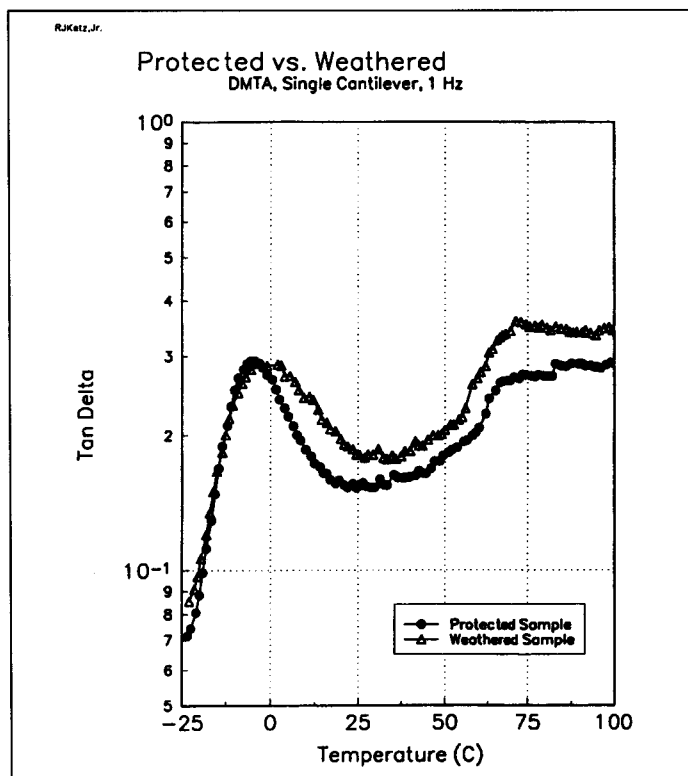


Figure 10. Tan delta curves for the protected and weathered CSPE membrane.

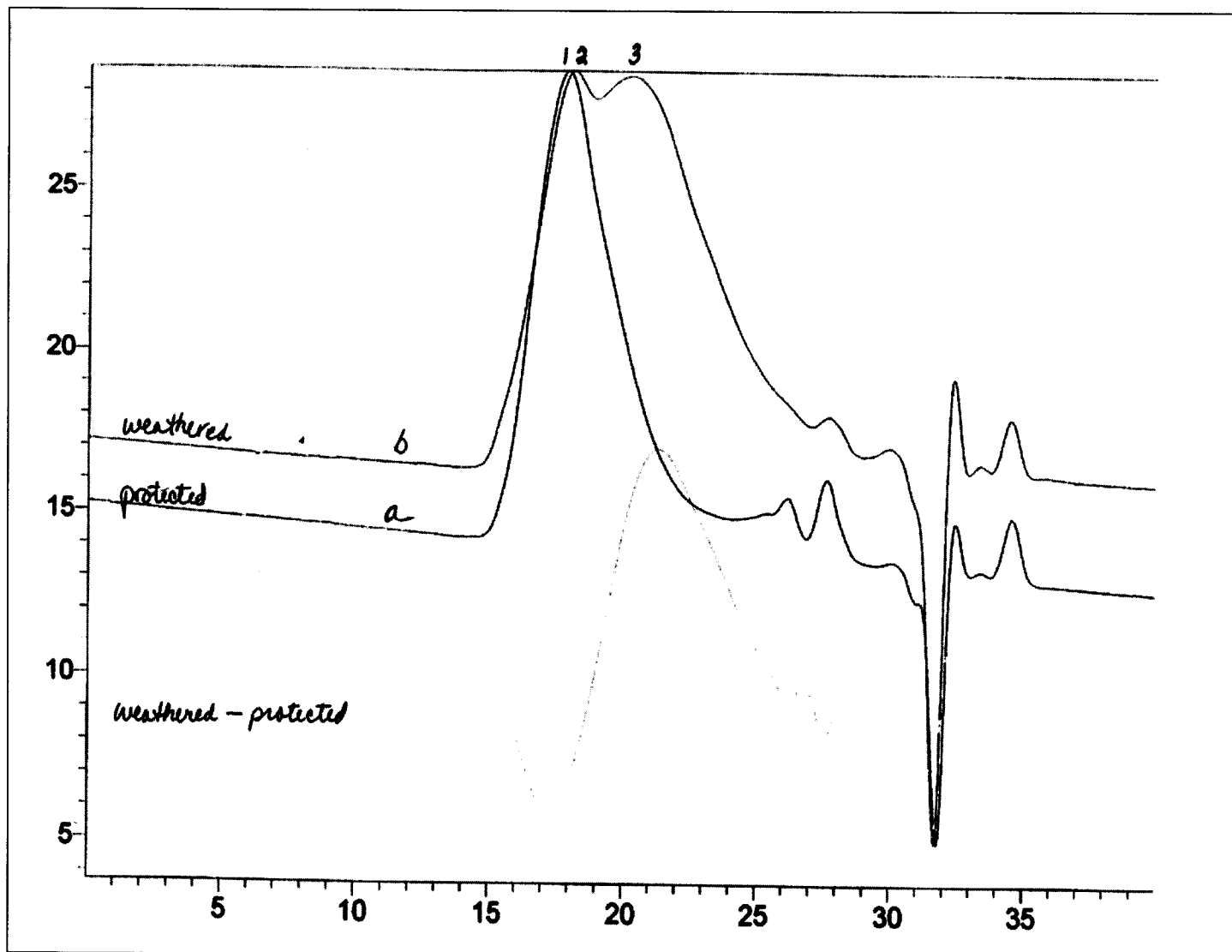


Figure 12. Gel permeation chromatograms for THF-soluble fractions of protected (a) and weathered (b) CSPE membrane. Approximate molecular weights: Peak 1—133,000 daltons; Peak 2—113,000 daltons; Peak 3—27,900 daltons. Molecular weights are based on a polystyrene calibration.