The Reaction of a Coolant Solution on its Bladder Made from a Specific Fluorocarbon Elastomer

INTRODUCTION

Aqueous coolant solutions used in space applications such as the Skylab program typically contain corrosion inhibitors which can adversely affect the chemical, structural, and mechanical properties of materials used in the coolant system. This note reports an incident in which the mechanical and chemical properties of a bladder manufactured from an elastomeric compound based on a copolymer of hexafluoropropylene and vinylidine fluoride were adversely affected by such a solution after long-term exposure simulating the operational time of the bladder in space vehicles.

RESULTS AND DISCUSSION

The bladder used for storage of the coolant solution consisted of a diaphragm-type compound based upon a fluorocarbon elastomer (Viton A). The cured bladder compound was supplied by Coastcraft with their designation of 77-6. The material had a hardness of 75 Shore A and $a + 3^{\circ}F$ glass transition temperature. This elastomeric compound was immersed in a coolant solution containing 2% (by weight) dipotassium hydrogen phosphate, 0.2% (by weight) sodium borate dissolved in deionized water with 500 parts per million (vol/vol) of a bactericide consisting of a mixture of alkyl dimethylbenzylammonium chlorides (the alkyl groups ranging from 5 to 17 carbons). After 70 days at 158°F, the volume swell reached an asymptotic 36% (by wt). At 75°F after 70 days, the elastomer had swollen 6%-8%. The corresponding value at 158°F immersion in deionized water only reached an asymptotic 10% after 41 days. Actual bladders were intermittently exposed for 49 and 80 weeks at 75°F to the coolant solution. After this exposure, the elastomeric compound exhibited cracks, tears, and surface pits. This degradation was reflected in the mechanical properties of the compound which were measured before and after both the 49 and 80 week exposure to one side of the bladder material. The data are presented in Table I. After containing the coolant solution for 49 and 80 weeks, the hardness, tensile modulus, tear strength, and compression set increased substantially, with a corresponding decrease in specific gravity, ultimate tensile strength, and elongation.

An infrared spectral analysis of the dry elastomer compound indicated that fundamental chemical changes had occurred during exposure (Fig. 1). The absorption at 1720 cm⁻¹ indicated that some type of acid carbonyl (C=O) group had formed¹ or, less probably, C=CF₂ olefinic unsaturation.² The absorption at 1225 cm⁻¹ is indicative of a C-O vibration associated with an acid carbonyl group, and the absorption at 885 cm⁻¹ is associated with the normal -CF₃ bending vibration of the hexafluoropropylene monomer in the copolymer.^{2,3} No hydrogen-bonded acid hydroxyl groups were seen in the spectrum due to the intense scattering of the infrared radiation by carbon in the formulation obscuring this absorption band. Examination of the surface of the elastomer using x-ray

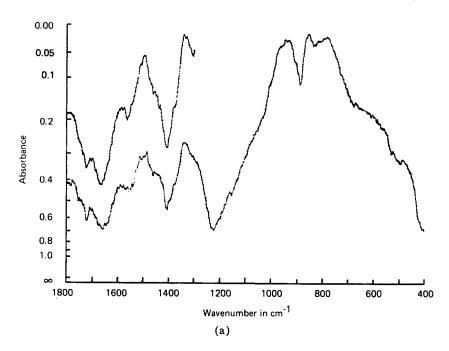
	Percentage change	
Measurement	49-Week exposure	80-Week exposure
Specific gravity	-4	
Hardness	+22	+25
Tensile strength	-41	-36
50% Modulus	+253	
100% Modulus	<u> </u>	+136
Elongation	-55	-49
Tear strength	+58	
Compression set	+98	+118

TABLE I

Properties of Exposed and Degraded Viton A Compound Compared to the Same Compound in
the Unexposed Condition (Expressed as a Percentage Change Relative to the Unexposed
Materials)

Journal of Applied Polymer Science, Vol. 22, 841–845 (1978) © 1978 John Wiley & Sons, Inc.

0021-8995/78/0022-0841\$01.00



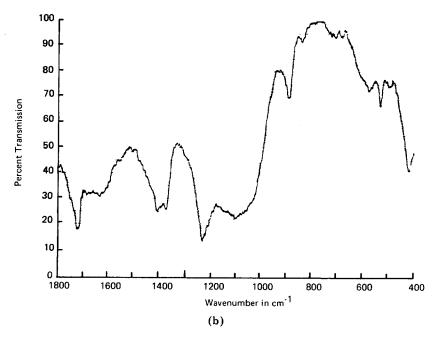


Fig. 1(a). Infrared spectrum of unexposed Viton A compound. (b) Infrared spectrum of 49-week water coolant-exposed Viton A compound. (c) Infrared spectrum of 80-week water coolant-exposed Viton A compound.

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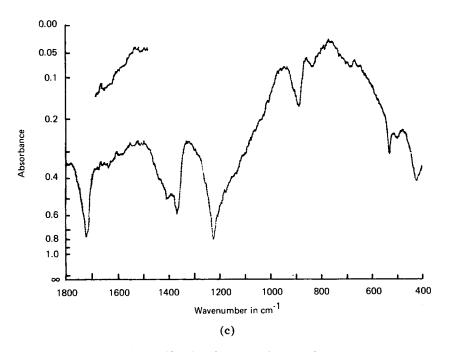


Fig. 1. (Continued from previous page.)

fluorescence analysis showed that phosphorus and hence phosphate was present on the surface in contact with the coolant solution. Although this phosphate is not strongly basic, this could indicate basic attack of the elastomer resulting in the chemical changes seen in the infrared spectrum.

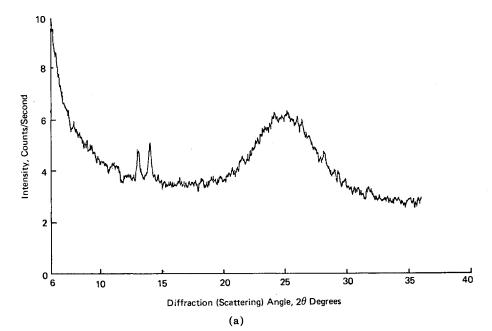


Fig. 2(a). X-Ray diffraction spectrum of an unexposed Viton A compound. (b) X-Ray diffraction spectrum of an 80-week water coolant-exposed Viton A compound.

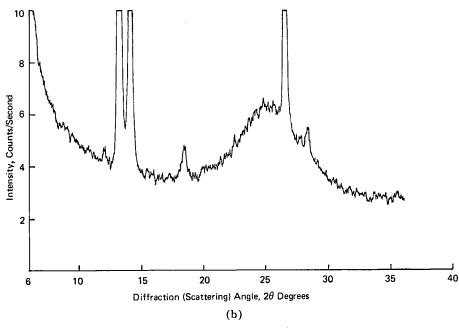


Fig. 2(b). (Continued from previous page.)

The elastomer was examined before and after coolant exposure by x-ray diffraction (Fig. 2). The unexposed sample exhibited a broad amorphous peak between the scattering angles (θ) of 20°-30°. After exposure, however, crystalline regions were detected, one peak appearing for example at a scattering angle of 26¹/₂ degrees [Fig. 2(b)]. The coolant solution appeared to be attacking the elastomer through base hydrolysis, oxidation, or a combination of both so as to induce regions of crystallinity² and thereby cause localized stiffening of the bladder producing cracks and tears.

CONCLUSIONS

The chemical, structural, and mechanical changes observed in bladders after 49 and 80 weeks of exposure to a coolant solution may have been the result of base-catalyzed hydrolysis, oxidation, or a combination of both. This conclusion was determined from data provided by ASTM mechanical tests coupled with infrared and x-ray spectroscopic analyses on the elastomeric compound before and after coolant solution exposure.

Much more work needs to be done in this area to identify the actual aging mechanism and to determine whether or not the effect is general for other fluorocarbon elastomeric compounds. Even so, this note demonstrates the need to evaluate material compatibility between materials such as a fluorocarbon polymeric compound and an aqueous salt solution which intuitively would appear problem free. Expensive mistakes may thus be avoided.

References

1. E. G. Brame, Jr., E. I. du Pont de Nemours & Company, private communication.

2. A. J. Tobolsky and H. F. Mark, *Polymer Science and Materials*, Wiley-Interscience, New York, 1964, pp. 11–18.

3. L. J. Bellamy, The Infrared Spectra of Complex Molecules, 2nd Ed., Wiley, New York, 1954, pp. 328–330.

NOTES

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