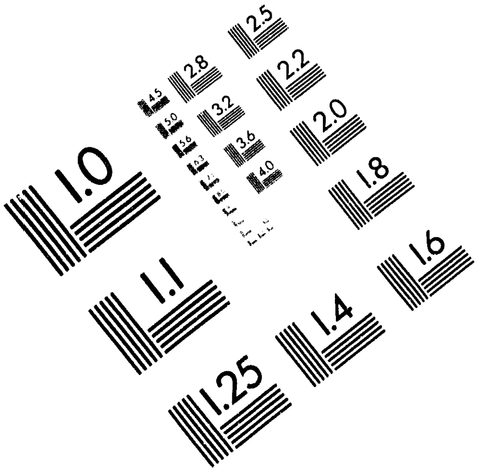

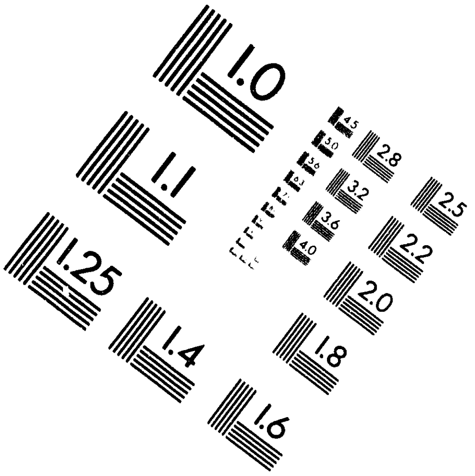

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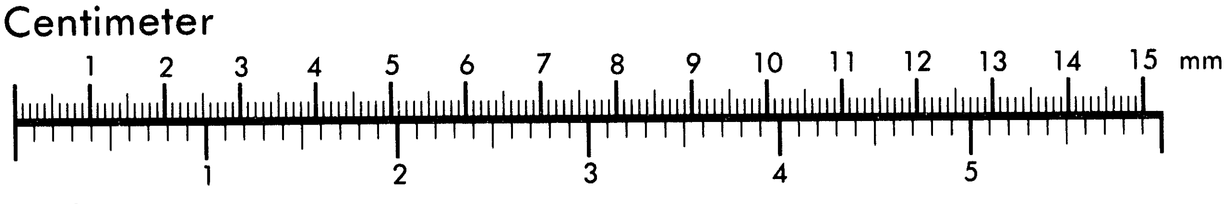

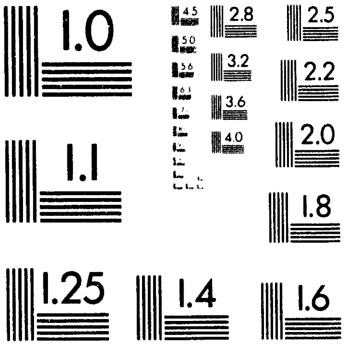

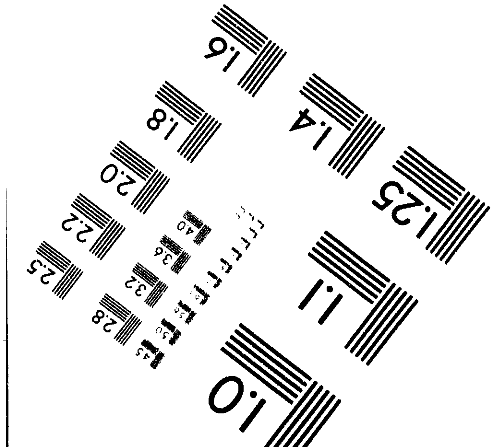

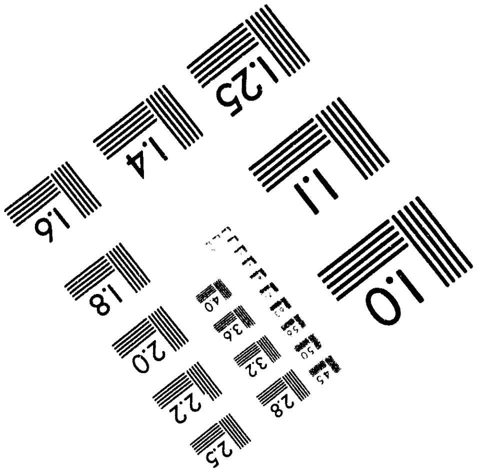

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COMPLEX OXIDATION EFFECTS IN POLYMER DEGRADATION

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We are working to understand why predictions of degradation behaviors and rates, based on accelerated thermal aging experiments, often fail to match with aging of polymers under service conditions. A main goal of our studies is to develop more reliable lifetime prediction methodologies [1].

Difficulties in accelerated aging experiments are often the result of complex oxidation phenomena. An illustration of this is seen in thermal aging studies that we have carried out on nitrile rubber [2]. Aging experiments performed at a series of temperatures (over the range of 65°C - 125°C) give the result that one set of macroscopic mechanical property changes (elongation at break) correlates well over the entire temperature range using the Arrhenius time-temperature superposition methodology. In contrast, attempted correlation of a related type of mechanical property measurement obtained on this same material (tensile strength at break), fails entirely.

Our studies show that strongly heterogeneous degradation commonly occurs in the thermal aging of elastomers, due to diffusion limited oxidation [3]. This phenomenon often exhibits a complicated dependency on time and temperature, typically becoming much more pronounced in the later stages of aging due to dramatic decreases in oxygen permeability coefficient as the material degrades.

Diffusion-limited oxidation is indeed present for thermally-aged, 2.1 mm-thick nitrile rubber samples, throughout the temperature range investigated, as shown by the technique [4] of modulus profiling. The extent of oxidation in the interior of the nitrile rubber samples aged at different temperatures and for different lengths of time is very different. As a result, aging-induced changes in the tensile strength (which is defined as the integrated force throughout the sample thickness) are quite diverse at different temperatures. However, elongation-at-break results are found to correlate with aging-induced changes in the surface modulus of the material. This can be understood in terms of failure via a crack that forms at the surface (the most oxidized, and hence most embrittled region of the sample). Once formed, the crack then rapidly propagates through the material. Since oxidation of the surface is independent of diffusion effects, the elongation results are not affected by temperature-dependent heterogeneous oxidation.

Even in cases where consistent Arrhenius correlations are obtained in laboratory aging experiments over a range of elevated temperatures, the prediction of aging rates under low-level, long-term service conditions involves a major assumption. The assumption is that a straight-line extrapolation will apply throughout the range between the lowest temperature used in the laboratory aging study, and the temperature of the application. Often, complications in the degradation mechanism cause a breakdown in this assumption, with the result that lifetime predictions frequently go awry. We are working to develop sensitive techniques that will allow direct measurement of degradation rates under accelerated laboratory conditions and under low level application conditions. If successful, such an approach would allow direct correlation of accelerated aging experiments with the application being modeled. For a given set of aging experiments, this capability would yield either 1) verification of a "straight line" extrapolation of aging rate, or 2) an indication of the direction and magnitude of a correction factor that may apply over the temperature range of interest.

A viable analytical technique for correlating accelerated aging with real-world conditions must meet several criteria. 1) The technique must be extremely sensitive, to obtain data under very low level aging conditions during reasonable time periods. 2) The technique must measure something that correlates with macroscopic property changes of interest. 3) Aging-related changes measured in the early stages of degradation (obtained under service conditions) must be correlatable with changes at a more advanced stage of aging.

Since oxidation is pivotal to the aging process of organic materials in typical air environments, we are evaluating two oxidation-sensitive analytical techniques for potential incorporation into an accelerated aging methodology. These are 1) oxygen consumption (and closely related CO_2 production) by gas chromatographic analysis using closed containers, and 2) microcalorimetry.

Using the same nitrile rubber material discussed earlier, we have now obtained oxygen consumption data over a broad temperature range, as shown in Fig. 1. The technique appears very promising for aging-prediction purposes. The measurements are sufficiently sensitive to yield reproducible oxygen consumption data at ambient temperatures (23°C). Furthermore, over the temperature range used in the accelerated aging experiments discussed at the beginning of this report, the oxygen consumption data can be time-temperature superposed using the <u>same</u> activation energy that resulted in superposition of the elongation-at-break and edge-modulus data, indicating a probable correlation with these physical property changes. Finally, for this material (which is a typical commercial formulation containing stabilizer additives), the oxygen consumption rate remains fairly constant over a wide extent of aging. For example, at 80°C, the consumption rate varies little (Fig. 1) over a timescale during which the elongation-at-break of the samples ranges from its unaged value to about 10% of the initial value.

Microcalorimetry results are much more preliminary, but this technique may also hold promise. We have obtained heat evolution measurements on nitrile rubber samples in air at 80°C. Furthermore, using thermochemical calculations for known oxidation chemistry (involving production of aldehydes, alcohols, CO_2, etc.), we have been able to obtain reasonable correlations between heat production and our measured oxygen consumption rates at this temperature.

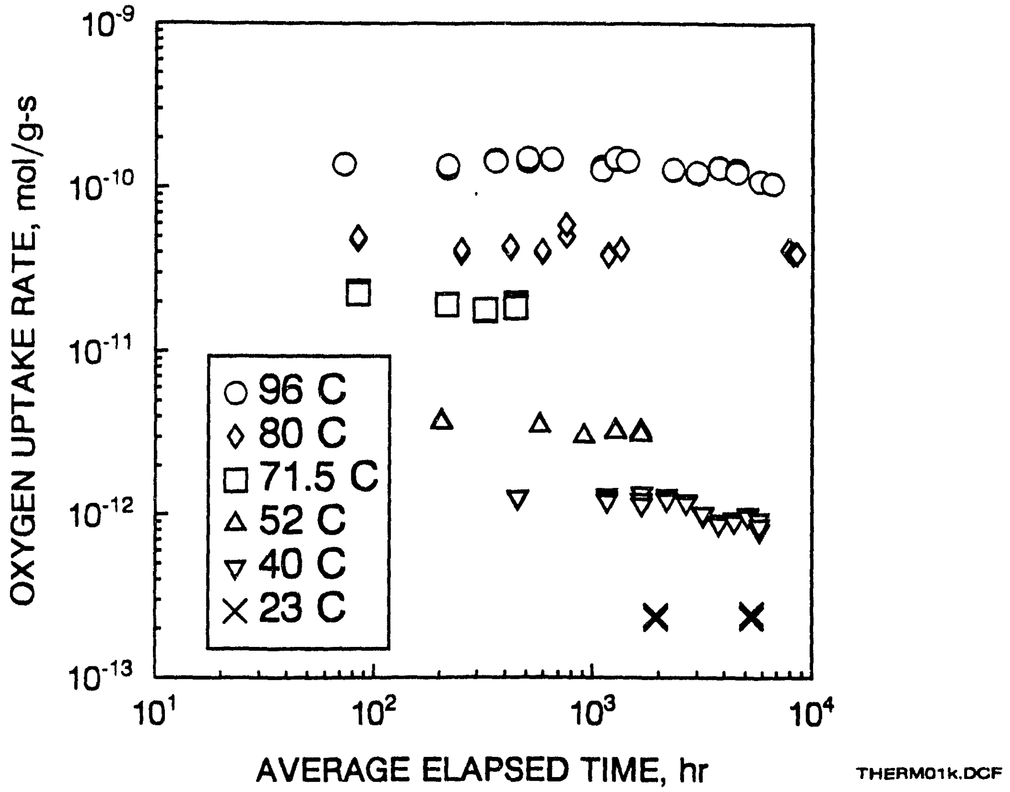

Figure 1 Oxygen Consumption rates for nitrile rubber samples at various temperatures.

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1. This work was performed at Sandia National Laboratories, supported by the U. S. Dept. of Energy under Contract DE-AC04-94AL85000.

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