Studies on Akroflex CD Antioxidant Loss from Neoprene Rubber.   I.   The Determination of Antioxidant Content and the Loss Mechanism During Aging

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Synopsis

An analytical procedure for determining the antioxidant (i.e., Akroflex CD) content in neoprene rubber has been developed.   The method is based on the infrared absorption analyses of chloroform extractables from the cured rubber at 1600 cm^{-1} and 1300 cm^{-1}. Good agreement is found between these two independent sets of measurements.   In an attempt to elucidate the antioxidant loss mechanism found with neoprene, thermal aging studies were carried out over the temperature range of 80°–200°C.   Using the infrared analytical procedure, antioxidant loss rates at the different temperatures were established. The activation energy value (5.1 kcal/mole) for the loss rate as well as other aging data suggest that the antioxidant is lost by a diffusion mechanism.

INTRODUCTION

Neoprene elastomers have found widespread usage in recent years, particularly in areas where a high degree of resiliency has to be combined with oil, solvent, heat, and weather-resistant properties, e.g., for lining tanks and chemical equipment.   It is common practice in the cure of neoprene formulations to add a small amount of an antioxidant (usually about 1.0%) to prevent oxidative degradation of the polymer and subsequent deterioration of the elastomers' engineering properties.   Most of these antioxidants are fugitive in nature, and significant loss can be found under normal service conditions.

In the absence of other available criteria, it has been suggested that the serviceable lifetime of an elastomer such as neoprene can be predicted by determining the rate of consumption of the antioxidant used in any particular formulation.   This is based on the premise that, after all the antioxidant has been consumed, the rubber becomes vulnerable to rapid oxidative degradation and its useful service life is reduced significantly.

Consequently, there is a real need for simple analytical techniques for determining the antioxidant contents of rubbers such as neoprene during service and storage conditions so that the effective lifetime of the elastomer can be determined.   Sometimes, a further stipulation on these analytical

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techniques is that only small plug samples should be removed from "in service" elastomers so that loss of function can be prevented.

This paper describes an analytical method based on absorption infrared spectroscopy which has been developed to monitor the antioxidant content in a standard neoprene rubber formulation referred to as MINS-132.

The antioxidant in question (Akroflex CD from du Pont[1]) has a composition consisting of 65% phenyl-beta-naphthylamine and 35% N,N'-diphenyl-p-phenylenediamine and is present in the neoprene formulation at a level of ~1.0% (by weight).

As an aid to elucidate the mechanism responsible for the loss of antioxidant from the neoprene, accelerated aging studies have also been carried out over the temperature range of 80°–200°C both on the neat Akroflex CD antioxidant and on fully compounded neoprene elastomer samples containing the antioxidant. The infrared analytical method was used to determine the antioxidant loss from the cured neoprene compound at each temperature.

EXPERIMENTAL

Solvents

Several solvents were initially screened as a selective extraction medium for the antioxidant. Chloroform was finally selected for this analytical work for the following reasons: (1) It is anhydrous and will not fog the NaCl plates used in infrared work. (2) It has a clear "window" area in the infrared part of the spectrum of most direct interest to this work (i.e., 2500 cm^{-1} to 1250 cm^{-1}). (3) It is an excellent solvent for Akroflex CD. (4) Because it is volatile, the extracts from the neoprene rubber can be easily concentrated by solvent evaporation.

Although chloroform also dissolved some of the other organic components used in the neoprene formulation, these materials did not appear to interfere with the infrared analyses.

Infrared Spectral Analyses

A Perkin-Elmer-6700 spectrophotometer was used for this study. Demountable, NaCl-window, liquid cells with 1-mm spacers were found to be useful for this work. Fisher C-298 chloroform was used for both the extraction media and the reference cell.

Akroflex CD antioxidant (0.11–0.01 g) was dissolved in 25 ml chloroform, and an aliquot was placed in the sample cell with fresh chloroform in the reference cell. The heat-aged antioxidant samples were treated in the same manner. Spectrum 1 in Figure 1 shows a typical infrared spectrum obtained from a 0.114 g/25 ml solution of Akroflex CD in chloroform. The extracts from the neoprene samples were diluted to 25 ml with chloroform and run on the spectrophotometer as described previously. A typical infrared trace thus obtained is shown by spectrum 2 of Figure 1.
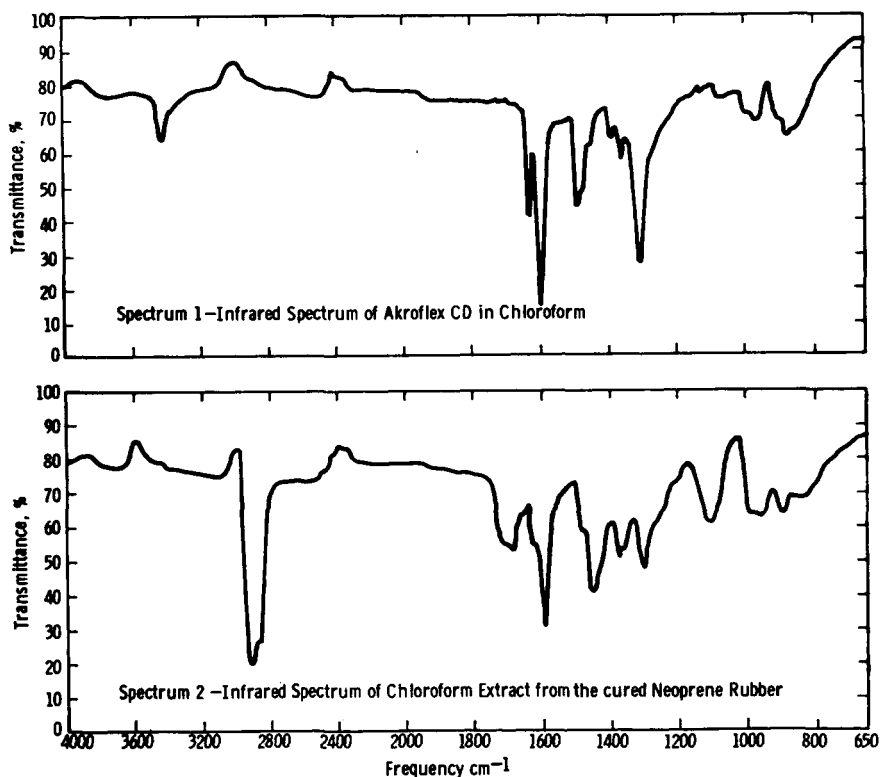
Fig. 1. Chloroform solution infrared spectra.

Accelerated Thermal Aging Tests

Antioxidant. Approximately 2-g samples (weighed to 0.1 mg) of Akro-flex CD were placed in a 50-ml Pyrex beaker, covered with a watch glass, and then aged in a forced-air oven at the desired temperature for the pre-scribed time. The aging temperatures chosen for these studies were 80°C, 110°C, 150°C, 175°C, and 200°C. A total aging time of 192 hr was employed on each sample.

Elastomer. Plugs, $^3/_8$-in. diameter, were cut with a cork borer from the neoprene material and masticated on a two-roll, cold rubber mill. The mill was set to an opening of approximately 0.001 in., and each plug was passed through the rolls ten times. Both cured and uncured samples were pre-pared in the same manner.

Approximately 5.2 g (weighed to 0.1 mg) of the milled material was placed in 3-in. glazed crucibles, with covers, and aged as described above.

Extraction Method

A Soxhlet extraction apparatus was employed consisting of a 300-ml round flask, a Soxhlet extraction tube, and an Allihn-type condenser, all
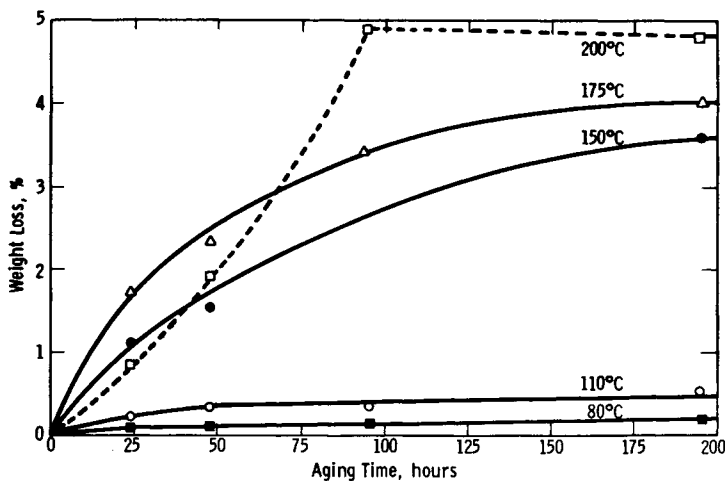
Fig. 2. Thermal aging weight loss data for neat Akroflex CD.

connected by interchangeable ground-glass joints. The extraction thimble (33 mm × 80 mm) used was of the single-thickness cellulose type. Chloroform (125 ml, Fisher C-298) was charged to the flask, and one Boileezer (Fisher B-365) was added to prevent bumping of the solvent upon heating. The weighed sample (~5 g), prepared as described above, was then placed in the extraction thimble and inserted into the extraction tube. The extraction tube with condenser attached was then fitted to the flask. All ground-glass joints were lubricated with a minimum of Dow Corning High-Vacuum Grease (Silicone). Cold water was passed through the condenser continuously throughout the extraction operation. A rate of 15 to 20 passes per hour of fresh solvent through the sample was maintained for 2 hr after the initial charging of the extraction tube. The extract was then removed from the apparatus and the chloroform solution concentrated by gentle heating to a volume of 15–20 ml. After cooling the solution to ambient temperature, the volume was adjusted to give a concentration of 5.2 g sample/25 ml chloroform. The infrared analyses were then carried out on the extracts as described above.

Weight Loss

Weight loss was determined by the differential weighing method. The aged samples were cooled to ambient temperature in a desiccator (containing Drierite to prevent moisture absorption) and then weighed. Weight loss data at 80°C, 110°C, 150°C, 175°C, and 200°C are shown in Figure 2 for neat Akroflex CD and in Figure 3 for the fully cured neoprene formulation.

Infrared Calibration Curve

The relationship between the absorption of a particular wavelength of radiation and the number of molecules absorbing (i.e., molecular concen-
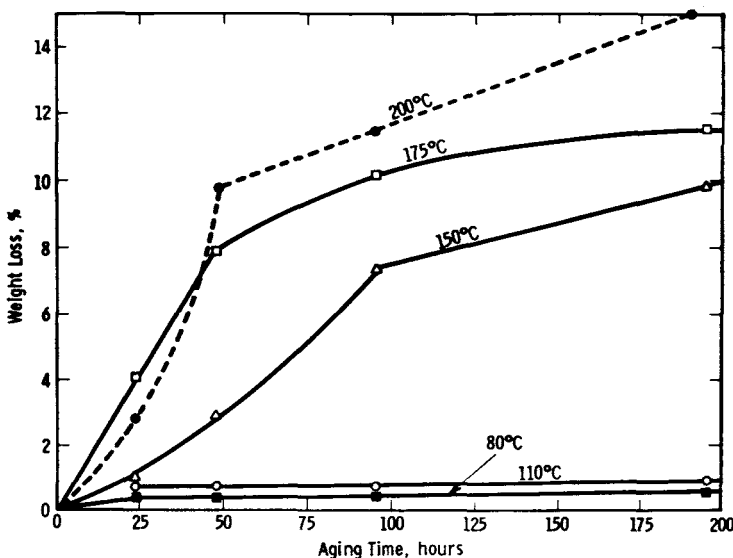
Fig. 3. Thermal aging weight loss data for the cured neoprene rubber.

tration) is referred to as the Beer-Lambert absorption law.[2]   This can be written as

$$I = I_0 e^{-abc}$$

or more normally as

$$A = \log_{10} I_0/I = \log_{10} 1/T = abc$$

where A = absorbance or "optical density," b = cell path, cm, c = material concentration, g/l., a = specific absorptivity of the material, I_0 = intensity of infrared radiation incident on the sample, I = intensity of infrared radiation transmitted by the sample, and $T = I/I_0$ = transmittance = fraction of infrared radiation transmitted.

The infrared spectrum of Akroflex CD in chloroform solution (at a concentration of 4.560 g/l.) in a 1.0-mm cell is shown in spectrum 1.   It can be seen that the spectrum exhibits strong absorption bands at 1600 cm^{-1} and 1300 cm^{-1} (from the $\rangle$C=C$\langle$ and C$_6$H$_5$—N$\langle$ stretching vibrations); both of these were used to construct Beer-Lambert calibration curves for Akroflex CD in chloroform.

In this calibration curve, six different concentrations of Akroflex CD in chloroform were made up (ranging from 4.560 g/l. to 0.285 g/l.) and the infrared spectra were recorded in 1-mm liquid cells.   The % transmittance (T_s) was determined for each sample at 1600 cm^{-1} and 1300 cm^{-1}; and, after correcting for the "baseline" absorbance (T_0), a plot of $\log_{10} (1/T_c)$ versus absorbance (A/b) was made, as shown in Figure 4.   In this computation,
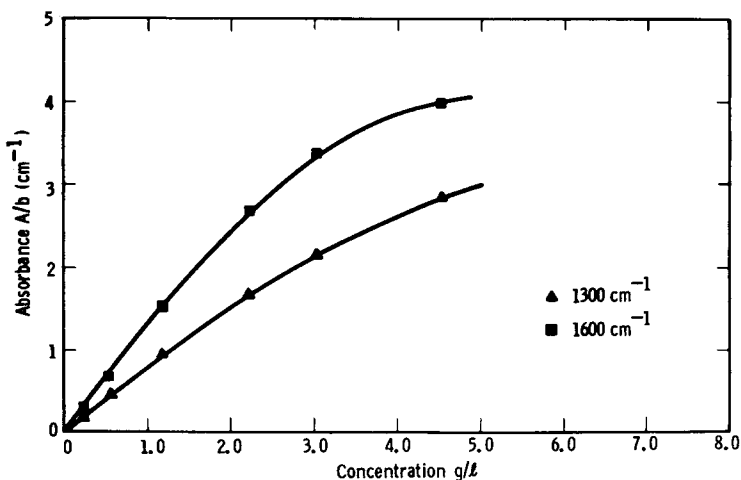
$$T_c = T_0 + T_s$$

Fig. 4. Akroflex CD calibration curve (infrared absorption) in chloroform using bands at
1300 cm^{-1} and 1600 cm^{-1}.

where T_0 = baseline transmittance, T_s = sample transmittance, and b = cell thickness (0.1 cm).

It can be seen from Figure 4 that neither 1600 cm^{-1} nor the 1300 cm^{-1} absorption bands give linear dependence of absorbance on Akroflex CD concentration, thereby showing that deviations from the Beer-Lambert law are occurring.   (However, below a concentration of 2.5 g/l., linearity does seem to be observed by both absorption bands.)   The deviations in the absorption law in no way render this analytical procedure invalid since the concentration values can be read directly from the calibration curves. (If the Beer-Lambert law is obeyed, the values can normally be calculated algebraically.)

Thus, this analytical method can be used to measure Akroflex CD contents in the neoprene rubber.   The statistical treatment of several determinations on the Perkin-Elmer 700 spectrophotometer showed that the experimental accuracy of these measurements was ±4%.   A greater degree of accuracy would be anticipated on a higher resolution infrared spectrophotometer.

Sources of Contamination

Early spectra gave rise to some unexplained peaks for the known samples in solution as compared to similar samples in KBr pellets.   It was found that contamination from some or all of the following items led to erroneous spectra: (1) contaminated solvent, (2) dirty NaCl windows, (3) plasticizer from washing bottle, (4) Fisher Cello-Seal lubricant (used for glass joints), (5) moisture from the atmosphere, and (6) leaking sample cells.   However, with due care and attention, these sources of contamination can be eliminated.

RESULTS

Weight Loss Data

As might be expected, greater weight losses are shown by the higher temperature samples with the neoprene rubber (Fig. 3) showing considerably more than the neat Akroflex CD (Fig. 2). This suggests that oxidative degradation or volatilization of some of the organic components in MINS-132, in addition to Akroflex CD loss, is occurring. Below 110°C, the data suggest that for both the neat Akroflex CD and the neoprene samples, the oxidative degradation is proceeding at a very low rate (after a more rapid initial rate). Above 110°C, the degradation proceeds at appreciably higher rates.

Infrared Spectral Studies

The studies on the neat Akroflex CD samples showed that after aging at elevated temperatures for periods more than 24 hr, some minor changes in the spectra were detectable. This is shown in Figure 5, where a comparison of the thermally aged material (200°C for 192 hr) is made with the original. (These samples were recorded as pressed KBr pellets.)
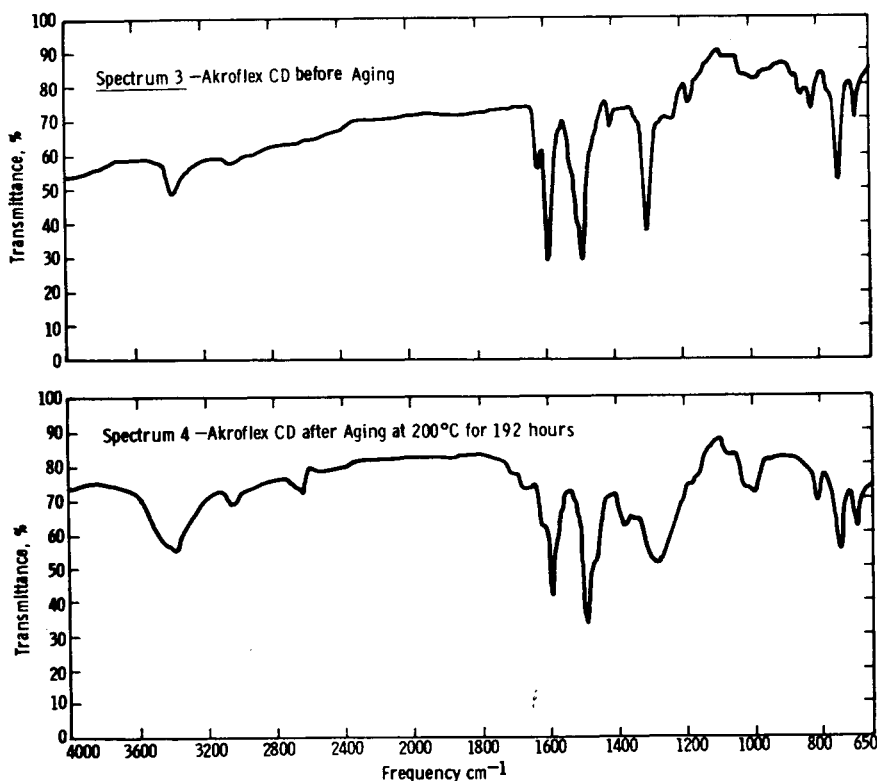

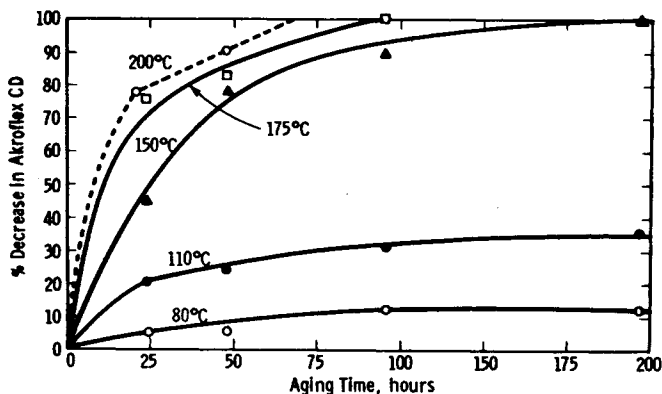Fig. 5. Infrared spectra of neat Akroflex CD before and after aging.

Fig. 6. Loss rate of Akroflex CD from cured neoprene with aging at different tempera-
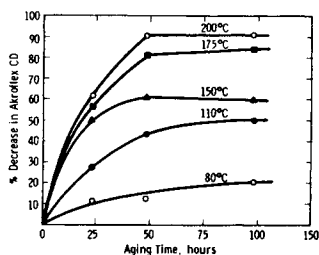tures (using 1600 cm^{-1} infrared band).

Fig. 7. Loss of rate of Akroflex CD from cured neoprene with aging at different tempera-
tures (using 1300 cm^{-1} infrared band).

It is observed that this aged sample does exhibit noticeable changes in its spectrum. The sharp absorption band at 1300 cm^{-1} (from the C$_6$H$_5$—N$\diagdown$ stretching vibration) shows a reduction in intensity compared to the other bands (e.g., at 1500 cm^{-1}). The absorption band at 1300 cm^{-1} also becomes broader, and a shoulder peak develops at 1380 cm^{-1}.

The spectrum of the aged material also exhibits enhanced absorptions at 3400 cm^{-1} and 1000 cm^{-1} compared to the original sample. These spectral changes would appear to be associated with oxidative modification of the amine groups in the antioxidant.[3] These spectral modifications were also shown by the samples that were aged at the lower temperatures, but the changes were somewhat less marked than those found with the 200°C samples.

The neoprene samples that had been subjected to thermal aging were analyzed for Akroflex CD content using the chloroform extraction pro-cedure described previously. From the calibration curves, the rate of disappearance of the antioxidant at the different temperatures could be estimated. Two separate and independent sets of curves could be con-structed, i.e., for the infrared absorption measurements at 1600 cm^{-1} and 1300 cm^{-1}, as shown in Figures 6 and 7, respectively.
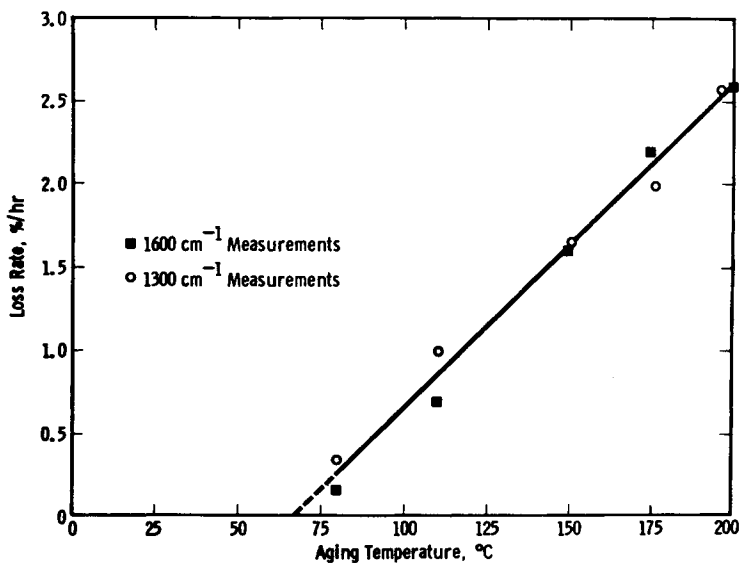
Fig. 8. Dependence of Akroflex CD loss rate (initial) on aging temperature of cured neoprene.

In the case of the 1300 cm^{-1} data, the Akroflex CD rate of disappearance was only followed up to 96 hr as shown in Figure 7. Interference of an oxidized by-product from the neoprene in the infrared measurements at that wavelength gave rise to erratic results. However, the similarities between the rate data obtained at 1600 cm^{-1} and 1300 cm^{-1} are very striking (i.e., a very rapid initial loss rate followed by a slower one).

This is shown more clearly by making a plot of the initial loss rate (i.e., the *average* % rate of decrease in Akroflex CD content over the first 50 hr of aging) against the aging temperature. This is shown in Figure 8, where it can be seen that very good agreement is obtained by the Akroflex CD initial loss rate values for the two methods of measurement.

Extrapolation of these data to "zero % loss rate" suggests that below 68°C, no decrease in the Akroflex CD content will occur during aging (at least not under *static* aging conditions). This then suggests that below ~68°C the decrease of Akroflex CD content due to diffusion will be extremely slow. However, losses that occur below 68°C will most likely be due to the interaction of the antioxidant with oxygen from air diffusing into the rubber. This type of antioxidant consumption is not defined by the present mechanism.

DISCUSSION

Using the data of Figure 8, an Arrhenius plot, i.e., $\log_{10}$ rate versus $1/T(°K)$, can be made for the neoprene samples. This is shown in Figure 9. In this plot, the 80°C rate data have been omitted because of the temperature spread.
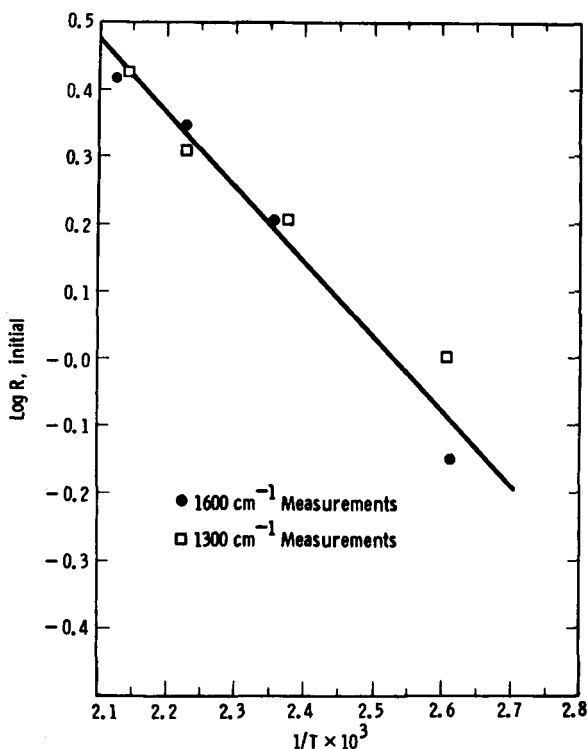
Fig. 9. Arrhenius plot for Akroflex CD loss rate from cured neoprene.

It is noted that a fairly good linear plot is obtained with the eight rate values. From this gradient, the activation energy (ΔE) was calculated to be 5.1 kcal/mole.

This value is somewhat low for a normal free-radical oxidative-type reaction where values four to five times higher are usually obtained. This is predictable on the basis of the oxidative aging studies on the neat Akroflex CD samples where it was found that only minor changes in the structure of the antioxidant will occur even after prolonged heating at 200°C. It has long been suspected that the Akroflex CD is fugitive in neoprene rubber formulations and that loss occurs by migration to the surface during aging. This would be consistent with the low activation energy value obtained in this work. The migration of Akroflex CD through this neoprene rubber can be interpreted as a diffusion phenomenon. Low activation energies are usually found in such reactions. Barrer[4] has determined the activation energies of diffusion for a series of gases (including water vapor) through neoprene rubber and found that the values lie in the range of 6.0–11.1 kcal/mole.

Corman et al.[5,6] have studied the activation energies of diffusion for hydrocarbon oils through a series of rubbers using ^{14}C-labeled compounds. The activation energies found ranged from 3.1 to 9.9 kcal/mole. They

concluded that the similarities of the activation energies for the various hydrocarbon oils provided evidence that the diffusion of large organic molecules in rubber is much more dependent upon the nature of the polymer than on the nature of the diffusing species.

On this basis, it would seem that the antioxidant loss in this particular neoprene formulation is almost completely a thermally induced diffusion effect. The contribution from oxidative degradations to this loss would be very minor.

Although the effects of ozone were not evaluated in this work (the aging tests were run in forced-air ovens), it would be expected that exposure to the more severe ozone environment would result in more rapid oxidation of the residual unsaturation of the neoprene rubber. However, it is unlikely that the loss rate values for the Akroflex CD at the different temperatures would deviate greatly under these conditions from the values found in this work.

It should also be pointed out that the neoprene accelerated aging tests in this work were carried out under essentially *static* conditions (i.e., the rubber samples were not subjected to any stress or strain during aging). It would be anticipated that under more *dynamic* conditions of testing, e.g., continuous flipping, higher diffusion rates would be encountered.

Thus, the diffusion rate values found in this series of experiments are only valid for neoprene rubber under static conditions of aging in the temperature range of 80° to 200°C. Below 80°C, the thermal diffusion of antioxidant becomes less important and other loss mechanisms may predominate.

The effect of dynamic aging on antioxidant loss and the influence of these losses on the physical properties of neoprene will be the subjects of future publications in this area.

References

1. du Pont Elastomer Chemicals Dept., Technical Bulletin No. 23, Nov. 1963.

2. Infrared Spectroscopy Committee of the Chicago Society for Paint Technology, *Infrared Spectroscopy; Its Use in the Coatings Industry*, 1969, Chap. IV, p. 52.

3. C. Walling, *Advan. Chem. Ser.*, **75**, 166 (1968).

4. R. M. Barrer, *Trans. Faraday Soc.*, **35**, 628 (1939).

5. J. E. Lewis, M. L. Deviney, Jr., and B. G. Corman, *Rubber Chem. Technol.*, **42**, 474 (1969).

6. B. G. Corman, M. L. Deviney, Jr., and L. E. Whittington, *Rubber Chem. Technol.*, **43**, 1349 (1970).