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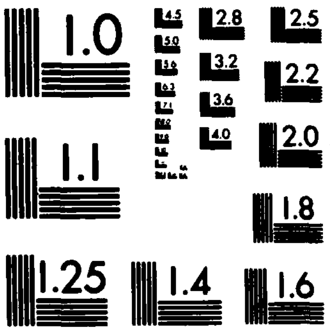

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ABSTRACT

The effects were studied of contacting nitrile O-rings with a variety of fuels and fuel blends. Properties (tensile strength, elongation, swelling) depended markedly on the aromatic content. When O-rings were cycled between fuels of low and high aromatic content, these properties took up values characteristic of the fuel in which the sample was currently immersed.

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Rubber samples were exposed to a commercial fuel (gas oil side stream) of high (>40%) aromatics level and to a Jet A-1 fuel, initially meeting aromatics specifications, whose aromatics content had been artificially increased by addition of reagent chemicals to the same final level as the gas oil side stream. Effects on physical properties (tensile strength, swell, 200% modulus) were considerably greater for the Jet A-1 with added aromatics than for the gas oil side stream.

RÉSUMÉ

On a étudié les effets d'une exposition à divers carburants et mélanges de carburants, de garnitures d'étanchéité en caoutchouc au nitrile. Les propriétés (résistance à la traction, l'allongement et le gonflement) dépendaient beaucoup de la teneur en aromatiques. Lorsque les garnitures étaient exposées alternativement à des carburants pauvres et riches en aromatiques, ces propriétés présentaient des valeurs caractéristiques du carburant dans lequel l'éprouvette avait été couramment plongée.

Des éprouvettes de caoutchouc ont été exposées à un carburant commercial (gas-oil prélevé en cours de raffinage) riche en aromatiques (>40%) et à un carburéacteur A-1 initialiment conforme aux normes relatives à la teneur en aromatques, mais additionné par la suite de produits chimiques appropriés pour rendre la teneur en aromatiques égale à celle du carburant commercial. Le carburéacteur A-1 additionné d'aromatiques modifiait beaucoup plus les propriétés physiques (résistance à la traction, gonflement, module 200%) que le carburant commercial.

TABLE OF CONTENTS

PAGE

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS (CONTINUED)

1.0 INTRODUCTION

In a previous note (1), certain properties of a nitrile rubber were studied, as affected by immersion in liquid fuels intended primarily for aircraft gas turbine engines, and effects on the rubber were noted when the fuel composition was modified by the addition of aromatic compounds. It is expected that in future years turbine fuels will become increasingly aromatic, and the intention was to see whether these changes would affect adversely the behaviour of elastomeric components in fuel supply systems. The rubber used for this purpose was nitrile compounded by the rubber laboratory at DREO and designated by them SA463. It considerably exceeded the requirements of the military specification covering nitrile packing materials. Also, because of inherent limitations in the curing procedure, it was not possible to procure a large number of test pieces from a single batch. O-rings produced from specification rubber in very large lots offered the possibility of doing many experiments with a uniform material; and as these O-rings were designed closer to the specification limit, they should give a better idea of the possible behaviour of actual components exposed to non-specification fuels.

We re-examined an effect studied earlier with the SA463 nitrile. It had been found that when this rubber was transferred back and forth between two fuels, one of high and one of low aromatics content, certain elastic properties appeared to degrade more rapidly than when exposed to either fuel alone for the same total time. However, with the experimental conditions chosen, degradation was extensive, and it was felt necessary to repeat the work under milder conditions, and with a more representative rubber.

In the present work we also look at some phenomena resulting from the exposure of O-rings to two specification fuels, JP4 and Jet A-1, and two Suncor products derived from tar sands. One is kerocut, resembling in some ways JP-5, the kerosene designed for shipboard use; the other is gas oil side stream, a highly aromatic material (40% by volume) used as a railway locomotive diesel fuel. Several synthetic aromatic liquids were blended with the Jet A-1 so as to raise its aromatic level to that of the gas oil side stream, and the comparative effects on the rubber of these blends and the side stream observed. This is of some interest because, in past work on fuel-elastomer compatability, additives such as tetraline have been blended with base fuels to enhance the aromatic level.

2.0 EXPERIMENTAL

2.1 Materials

The JP-4 and Jet A-1 used here had aromatics levels of 13.3% and 18.3% respectively, and the Suncor kerocut, 22%. It was difficult to get an accurate determination of this component in the gas oil side stream, as methods are unreliable for non-petroleum-based fuels; the average of determinations from several sources was 43%; in any case it was well over the specification limit of 22% or 25% for kerosene and wide-cut (JP-4) fuels.

In certain experiments additives were blended with the Jet A-1 to raise the aromatics level to 41%, close to that of the gas oil side stream. These additives were tetraline; xylene; and a mixture of equal volumes of butylbenzene, ethylbenzene, tetraline, zylene and toluene. This mixture was used in an attempt to minimize the effects of an unbalanced composition, with a large preponderance of one chemical component.

The O-rings were procured from a commercial source, in a lot of one thousand, made from a single batch of latex. The compound conforms to the military specification MIL-P-5315B, covering O-ring material intended to contact jet fuels. The military part number was MS 29513-218; the rings themselves were of nominal 31.25 mm internal diameter and 3.53 mm cross-sectional diameter. Physical property testing of a large sampling of these O-rings as received showed that they were quite uniform, the repeatability in measurements being quite satisfactory.

2.2 Procedures

These were as described in the previous note (1). The general conditions prescribed in ASTM D471-75 "Standard test method for rubber property-effect of liquids" were followed as closely as possible during the incubations. For physical testing, ASTM D1414-78 "Standard methods of testing rubber O-rings" was followed.

In the previous work with SA463 rubber, the most useful results came from tensile testing and volume change; hence in this work we carried out measurement of tensile strength and ultimate elongation (including calculation of the 200% modulus, or stress in psi required to produce a 200% increase in length), and extent of swelling.

3.0 RESULTS

3.1 Preliminary

An initial survey was made, employing Jet A-1 and Jet A-1 with tetralin added to produce a final concentration of 41% aromatics by volume. O-rings were incubated in these fluids at several temperatures for four days, then removed and subjected to testing. Tensile strength and elongation are plotted on Figure 1. The rapid falloff in elastic properties above 100°C suggested 70°C as a suitable working temperature, in which a reasonable proportion of the initial rubber properties would be retained, and the effects of fuel composition changes could be distinguished. Figure 2 shows the corresponding percentage volume increases. The effects of temperature and aromatics content are much as expected, and agree with our previous observations.

3.2 Cycling Experiments

To examine the effects of passing a rubber sample between these two fluids, a set of experiments was devised, similar to these described in the previous note (1). First, O-rings were incubated at 70°C in the two fuels (Jet A-1, or fuel A, and Jet A-1 plus tetraline, fuel B) for periods of one, two, four, eight and sixteen days and their physical properties were

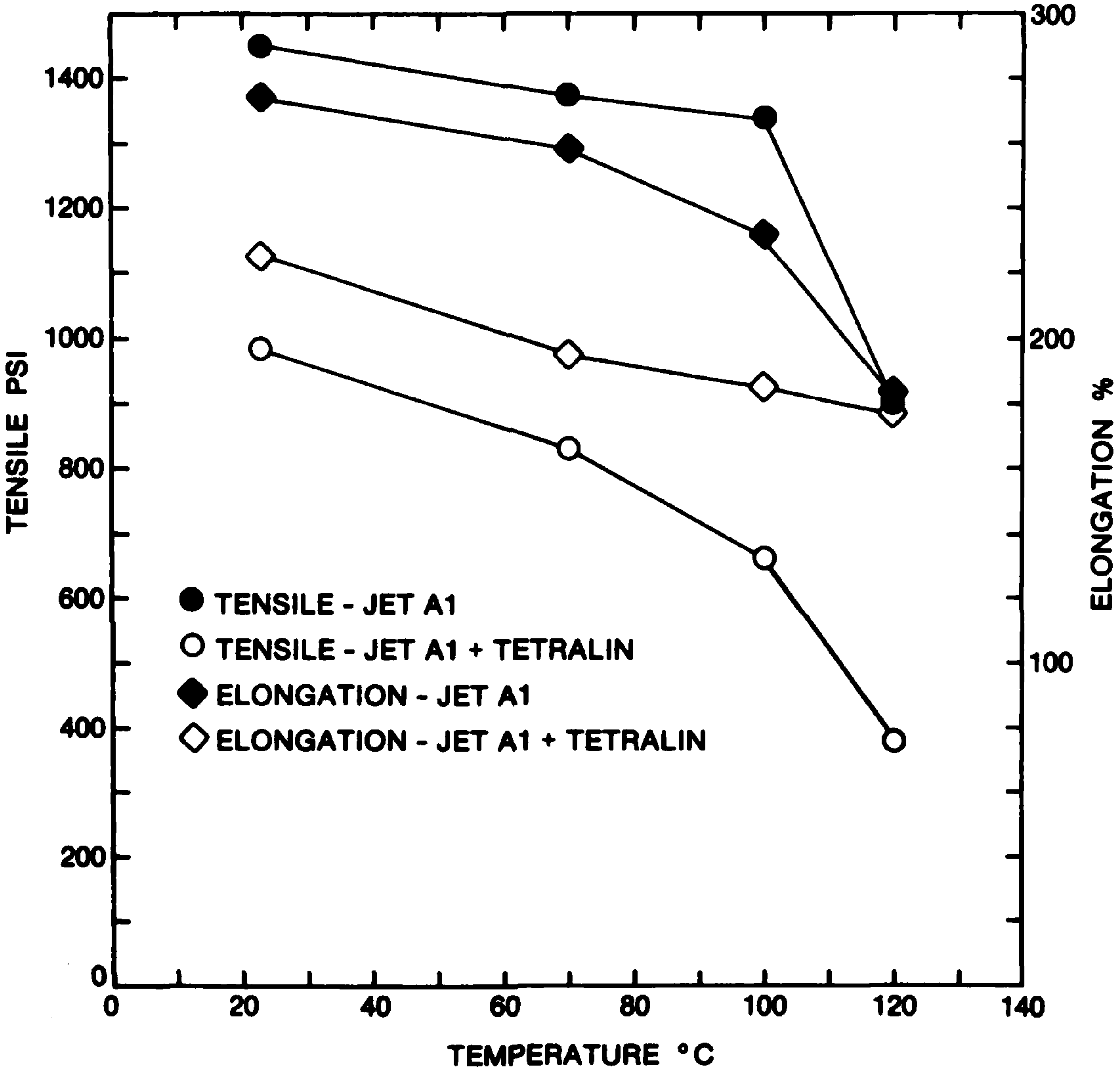

FIGURE 1 - TENSILE STRENGTH AND ULTIMATE ELONGATION OF O-RINGS AFTER FOUR DAYS' IMMERSION, AT SEVERAL TEMPERATURES, IN JET A-1 AND JET A-1 PLUS ADDED TETRALIN.

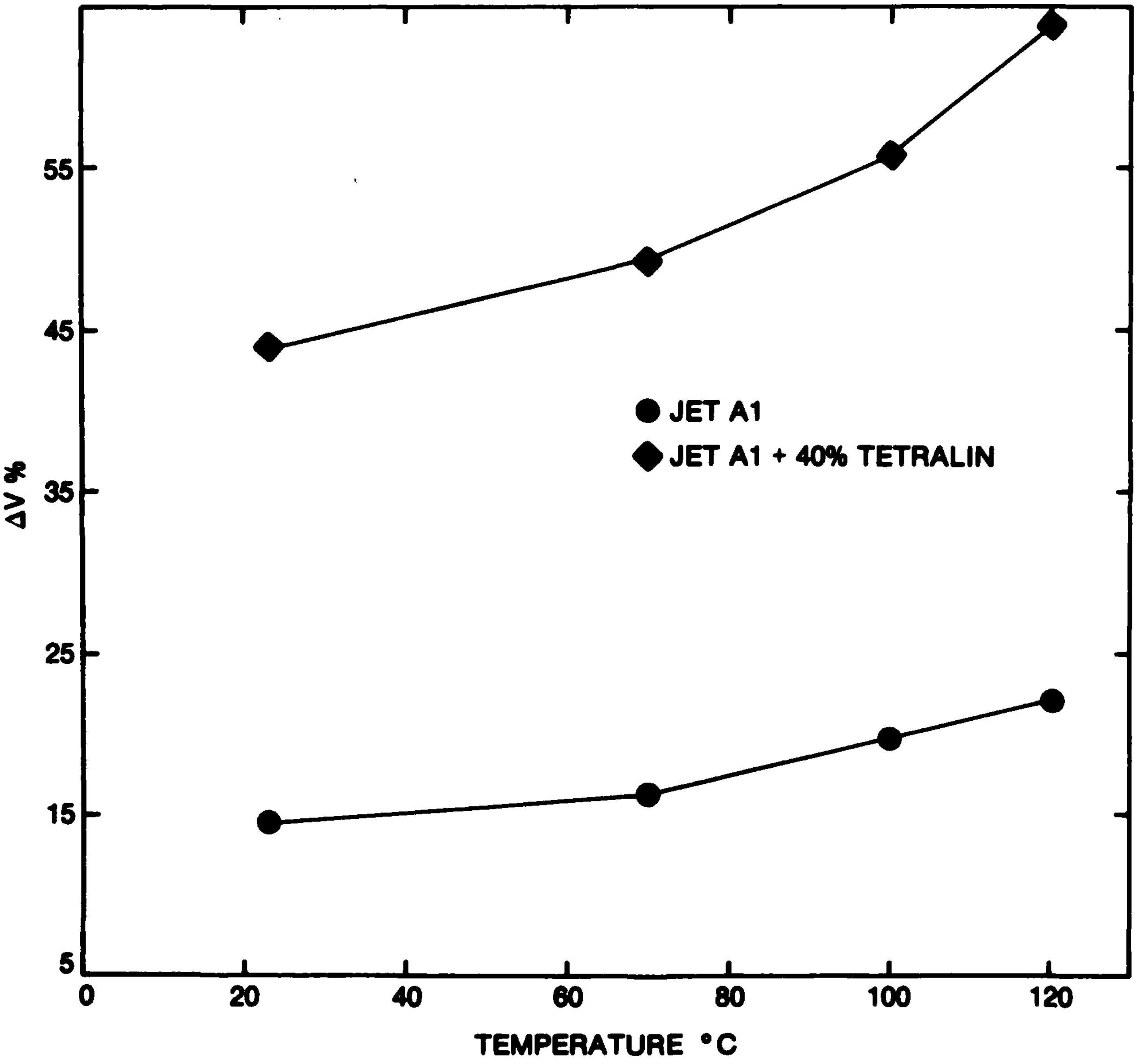

FIGURE 2 - PERCENTAGE VOLUME INCREASE OF O-RINGS AFTER
EXPOSURE TO FUELS UNDER CONDITIONS AS IN FIGURE 1

determined on removal after each period. Next, O-rings were incubated for various periods of time up to twelve days, with one or more changes between fuels A and B, at either one-day or two day intervals; and as before they were removed and tested at the end of each period.

To illustrate the notation adopted to describe these changes, 2A + 2B means two days immersion in fuel A, followed by transfer to fuel B and two days more immersion, then removal and testing; 2(B + A) means four days immersion in total, with daily transfers between B and A, B being the initial and A the final medium.

In Figures 3 and 4 the solid circles show changes in tensile strength and elongation, respectively, after one, two, four, eight and sixteen days immersion in fuel A, (no changes) and the shaded areas show the standard deviation of the experimental values. In Figures 5 and 6 the same data are depicted in the same way for O-ring immersion in fuel B. Focussing attention first only on this data, one sees an initial rapid decline in these properties from their initial values (in air), followed by a levelling-off during the balance of the sixteen day period.

The same four figures also show the effect of alternating between fuels on these elastic properties. The various fuel combinations used are listed on the graphs, using the notation explained above. The symbols are open, to distinguish them from the solid circles. Triangles are used for fuel changes at one day intervals, diamonds for two day intervals.

Previous work with SA463 rubber (1) had shown that physical properties were influenced by the final fuel in which samples were immersed before testing. Accordingly it was decided to plot results from all sequences of fuel change in which the last fuel used as A on Figures 3 and 4, which show property trends as a function of immersion time in Fuel A alone; when was the final fuel in cycling experiments, results are plotted on Figures 5 and 6. Again, each recorded property determination has a span to indicate standard deviation. It is evident that the final immersion fluid is the major determinant of physical properties, which adapt themselves in turn to each successive fuel. With two exceptions, 2(B + A) and 2(A + B) the final physical properties of samples after cycling between fuels, lay within the limits of error of the property determined after immersion in the final fuel only for the same period of time.

Stress and elongation, being properties measured at break, are highly suceptible to the presence of flaws in the test sample. Volume changes can be determined with much greater accuracy. Figure 7 shows the percentage volume increases of the rubber in the two single fuels, with their standard deviation, as two narrow hatched bands.

On the same figure are plotted as open bands the final volume changes, with their standard deviations, observed at the end of "cycling" experiments between the fuels. It is evident that when O-rings are transferred from, say, fuel A to fuel B, their volumes rapidly adjust and approach the value characteristic of fuel B, the process being nearly completed after one day.

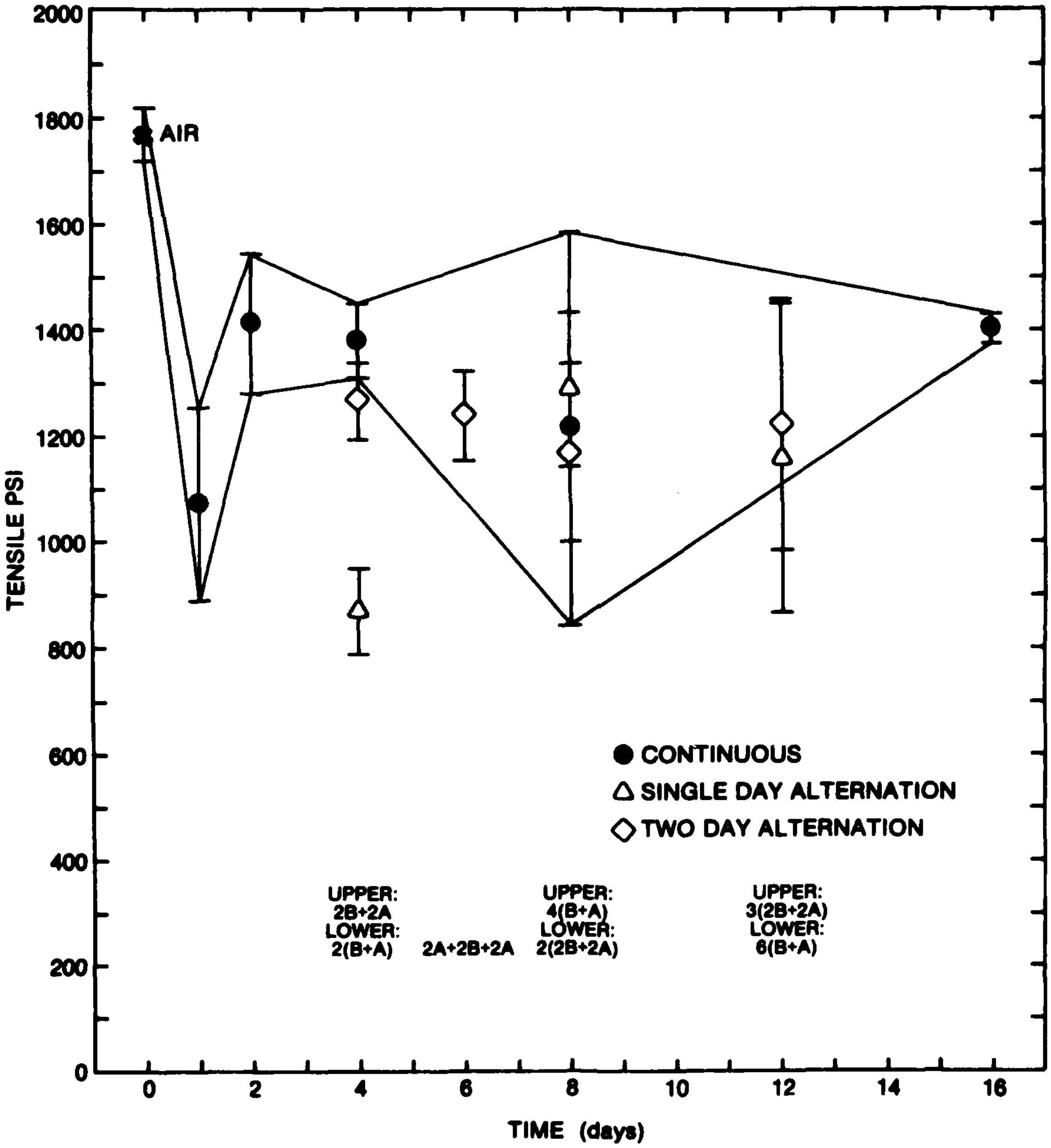

FIGURE 3 - EFFECT OF ALTERNATION BETWEEN FUELS A AND B ON TENSILE STRENGTH OF O-RINGS. SOLID CIRCLES AND ENCLOSED AREA: EFFECT ON TENSILE STRENGTH OF IMMERSION IN FUEL A ALONE, FOR SEVERAL TIME PERIODS. OPEN SYMBOLS: EFFECT ON TENSILE STRENGTH OF CYCLING O-RINGS BETWEEN FUELS A AND B, WITH A THE FINAL IMMERSION MEDIUM. PROGRAM OF FUEL CHANGES INDICATED AT BOTTOM OF FIGURE.

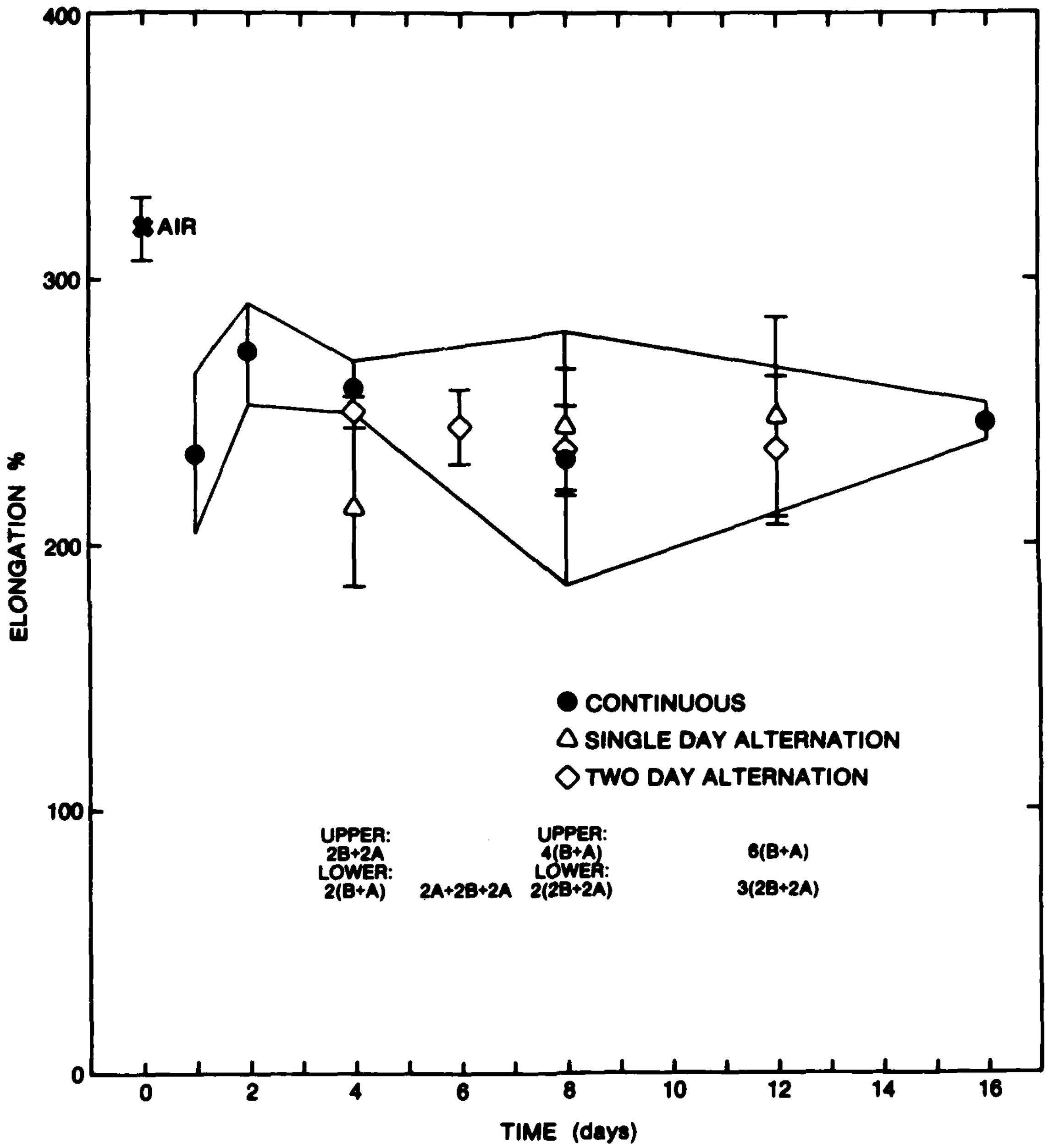

FIGURE 4 - AS FIGURE 3, BUT ELONGATION THE MEASURED PROPERTY.

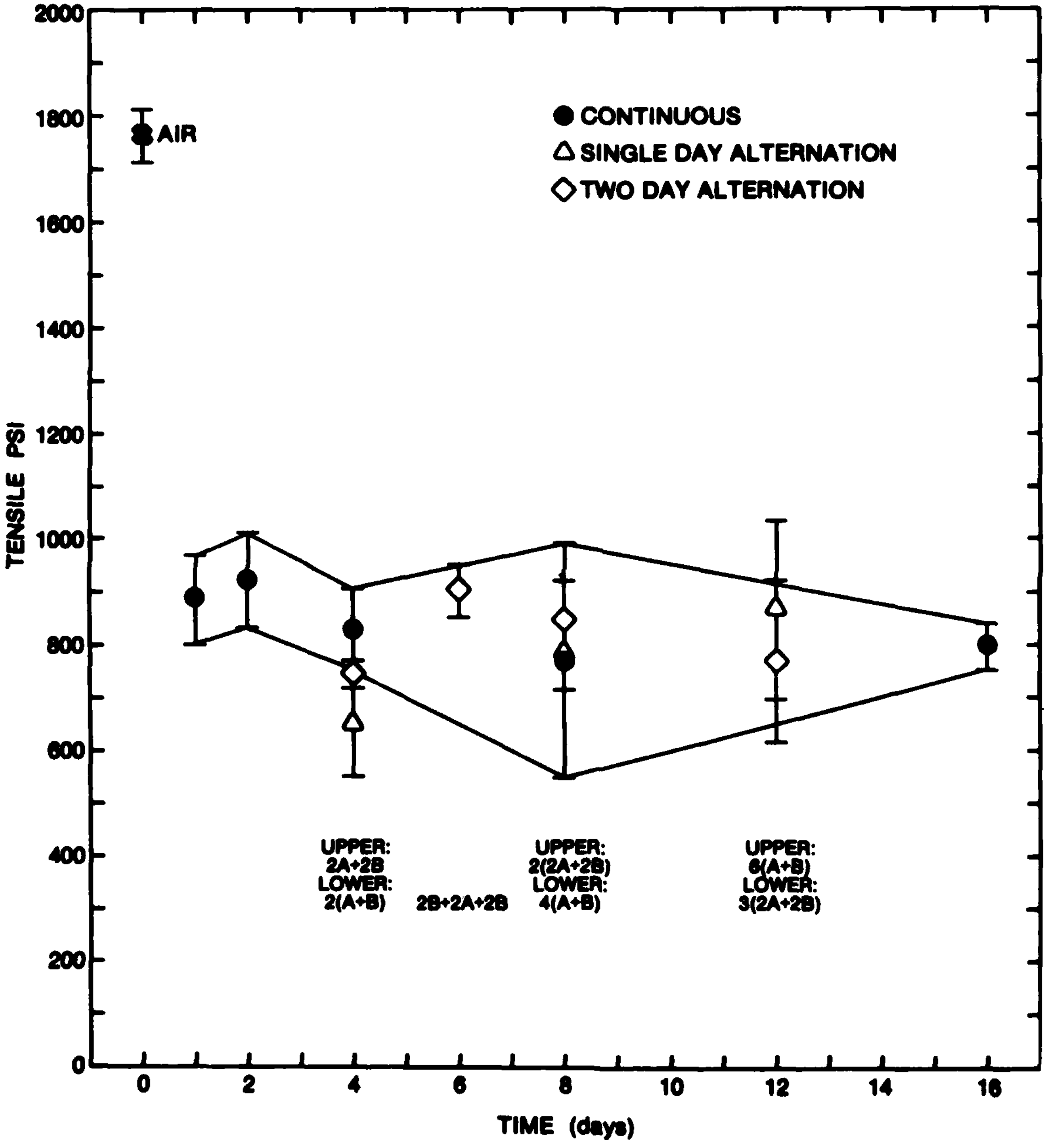

FIGURE 5 - EFFECT ON O-RING TENSILE STRENGTH OF ALTERNATION BETWEEN FUELS A AND B. SOLID CIRCLES AND ENCLOSED AREA: EFFECT ON TENSILE STRENGTH OF IMMERSION IN FUEL B ALONE, FOR SEVERAL TIME PERIODS. OPEN SYMBOLS: AS IN FIGURE 3, CYCLING BUT WITH B THE FINAL IMMERSION MEDIUM. PROGRAM OF FUEL CHANGES INDICATED AT BOTTOM OF FIGURE.

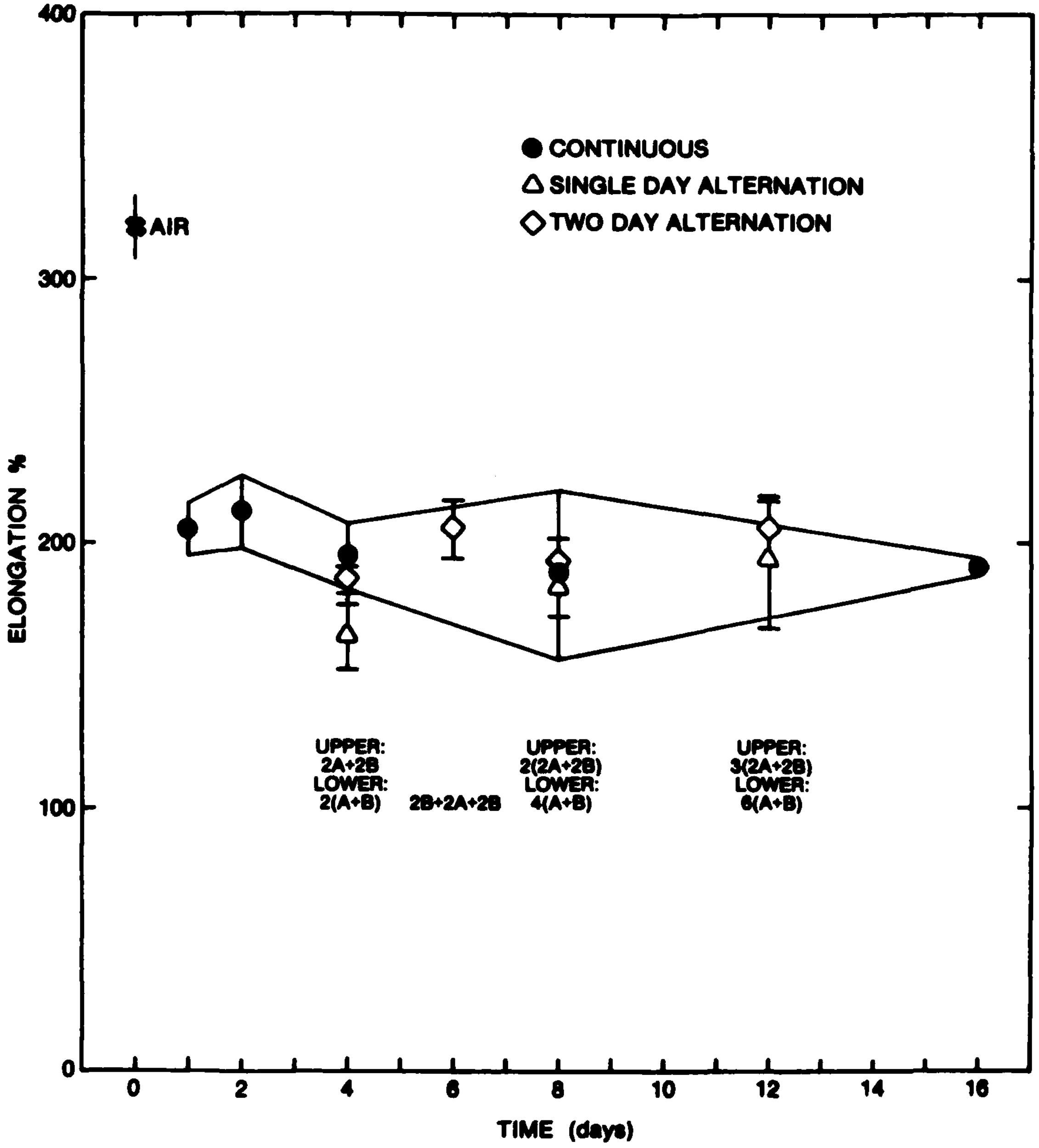

FIGURE 6 - AS IN FIGURE 5, BUT ELONGATION THE MEASURED PROPERTY.

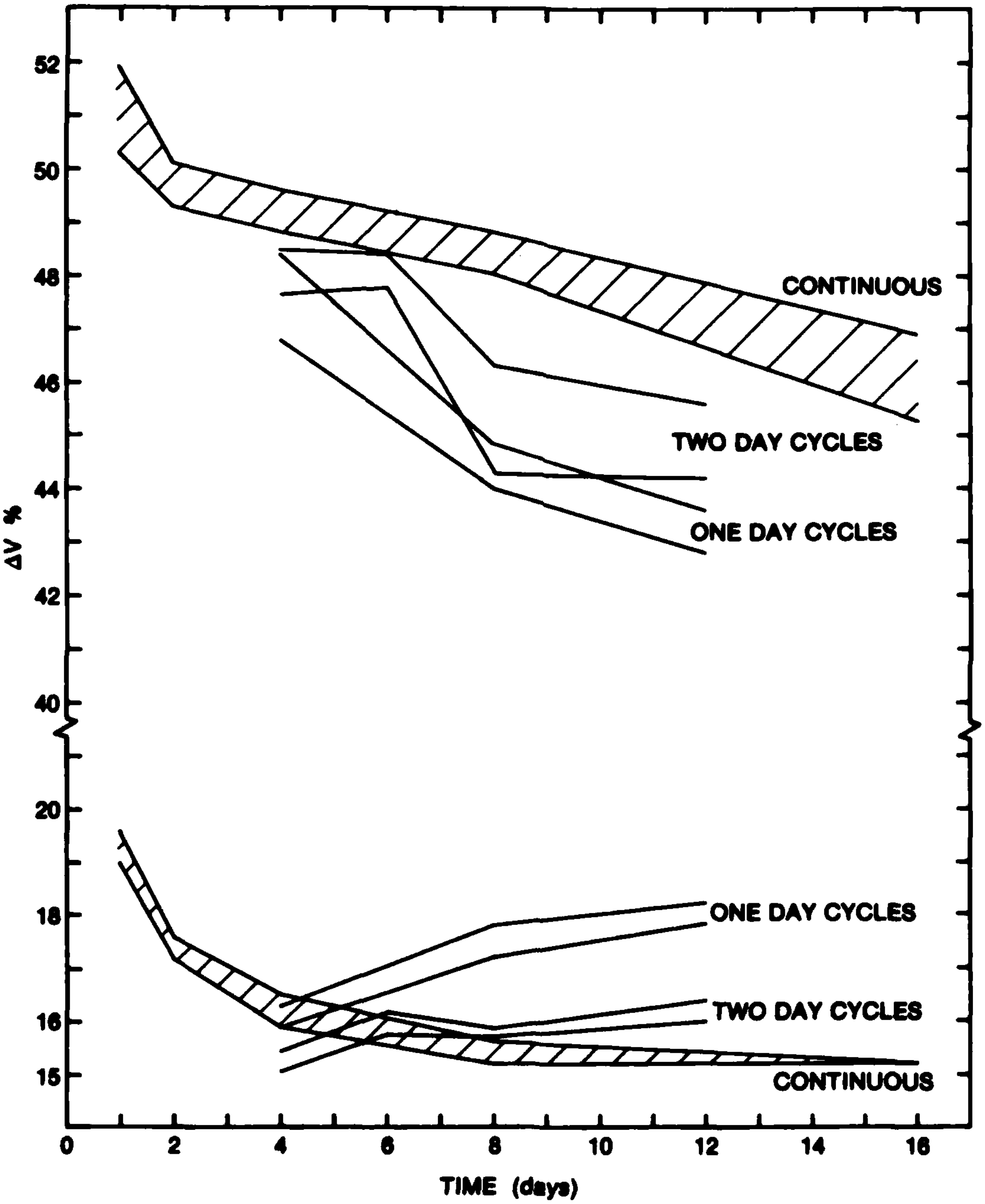

FIGURE 7 - HATCHED BANDS INDICATE FINAL EXTENT OF SWELLING AND ITS STANDARD DEVIATION FOR O-RINGS IMMERSED IN FUEL A (LOWER AREA) AND FUEL B (UPPER AREA) FOR SEVERAL PERIODS OF TIME. OPEN BANDS ADJACENT TO LOWER AND UPPER HATCHED BANDS SHOW EXTENT OF SWELLING OF O-RINGS SUBJECTED TO CYCLING BETWEEN FUELS A AND B. SWELLING IS DETERMINED BY FUEL LAST CONTACTED BEFORE REMOVAL FOR TEST.

This work suggests that when a rubber is placed in a succession of fuels the changes occurring are largely reversible, and that there is no sign of what might be called a synergistic effect leading to accelerated degradation. One cannot of course, extrapolate with any assurance from these artificial conditions to an actual sitituation.

3.3 Aromatic Additions to Jet A-1

Figure 8 shows the volume changes resulting when O-rings are incubated, using the same procedure as before, in a variety of fuels and blends at 70°C. The maximum in swelling was reached before the first measurement at one day, and volumes declined thereafter to a nearly constant value which depended on the aromatic level, the values at sixteen days for JP4, Jet A-1, kerocut and gas oil side stream increasing in order of their aromatic content.

On the same figure are shown results (open symbols) for Jet A-1 blended with three combinations of aromatic compounds to a final aromatics level of 41%, close to that of the gas oil side stream. These are tetraline; xylene; and a mixture of equal volumes of butylbenzene, ethylbenzene, tetralin, xylene and toluene. All show abnormally large volume increases, out of line with the aromatic content. This irregularity was observed first with tetralin, and it was thought this might be due to peroxide formation in tetralin; but the results with the other two blends, in particular xylene which has no tendency to peroxidation, indicate that it is connected with the presence of aromatic additives generally.

Measurements of tensile strength, elongation and 200% modulus were also made, employing the same fuels and blends and the results are shown in Figures 9-11. With the four original fuels (no additives) the course of tensile strength and elongation changes are nearly the same (Figures 9 and 10); but again, Jet A-1 with the three aromatic additives causes rapid deterioration in these rubber properties to a significantly lower level, which then remains nearly constant for the remainder of the sixteen day period.

Modulus at 200% extension is an elastic property but, not depending of break, it is not like the others susceptible to the presence of weak points in the test sample. The data depicted in Figure 11 for this property indicate a gradation primarily dependent on aromatics content. This observation prompted some further treatment of the modulus data. Modulus is the actual tension in units of pressure per square inch, at some stated extension before break, and is calculated with reference to the original undistorted dimensions of the test piece. With some of the fuels and blends used here, it is known that there is considerable swelling, so that the modulus would be smaller if calculated on the basis of tension per unit of actual cross-sectional area of the sample under the conditions of measurement. In Figure 12 a rough account is taken of this by dividing the moduli shown in Figure 11 by the factor $(1 + \frac{\Delta V\%}{100})$.

Comparing Figures 12 and 11, it is seen that this correction leads to a spreading out of the modulus values, in inverse order of aromatic content,

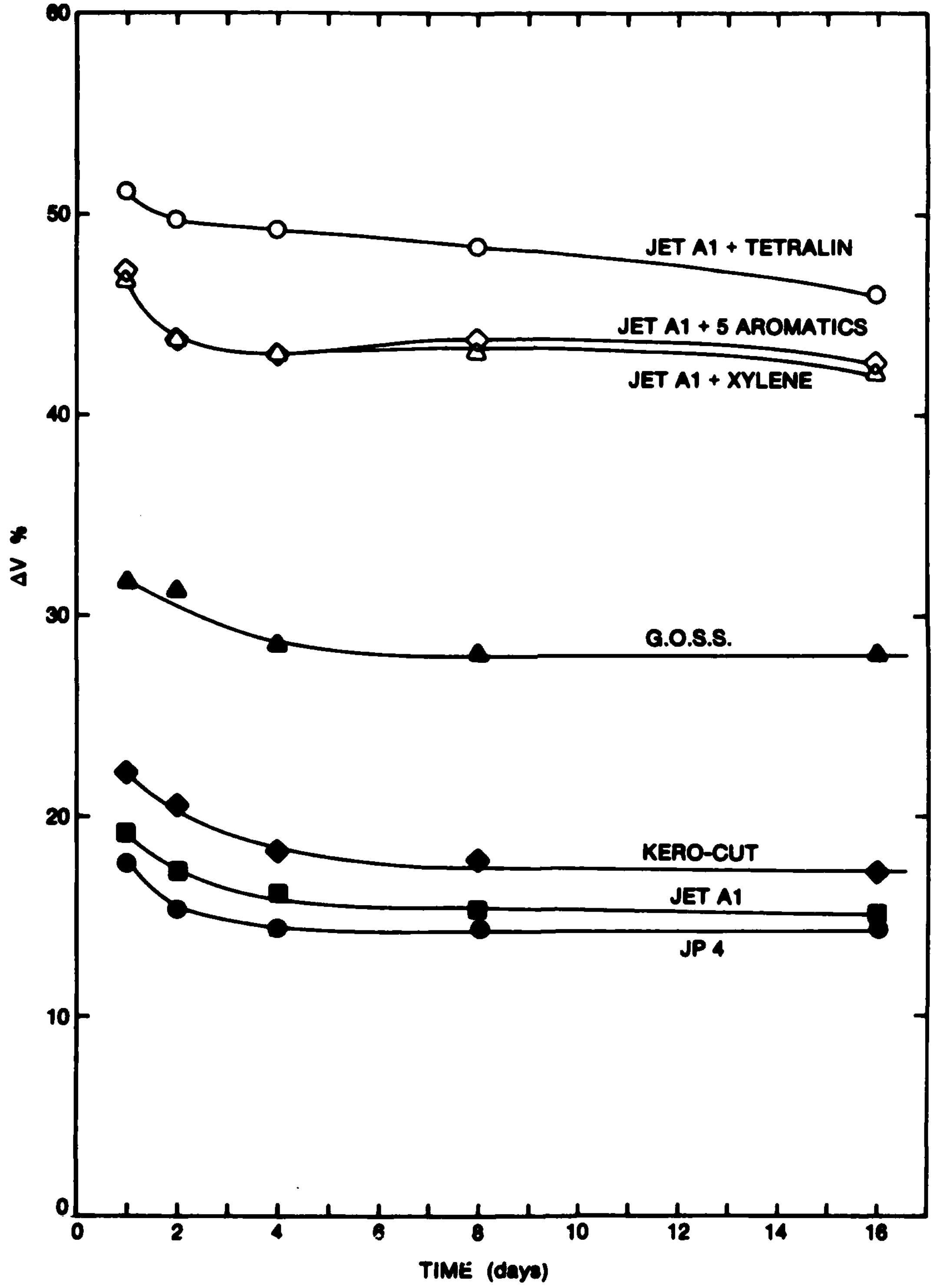

FIGURE 8 - VOLUME CHANGE IN O-RINGS AFTER IMMERSION IN SEVERAL FUELS, AND IN JET A-1 CONTAINING SEVERAL AROMATIC ADDITIVES.

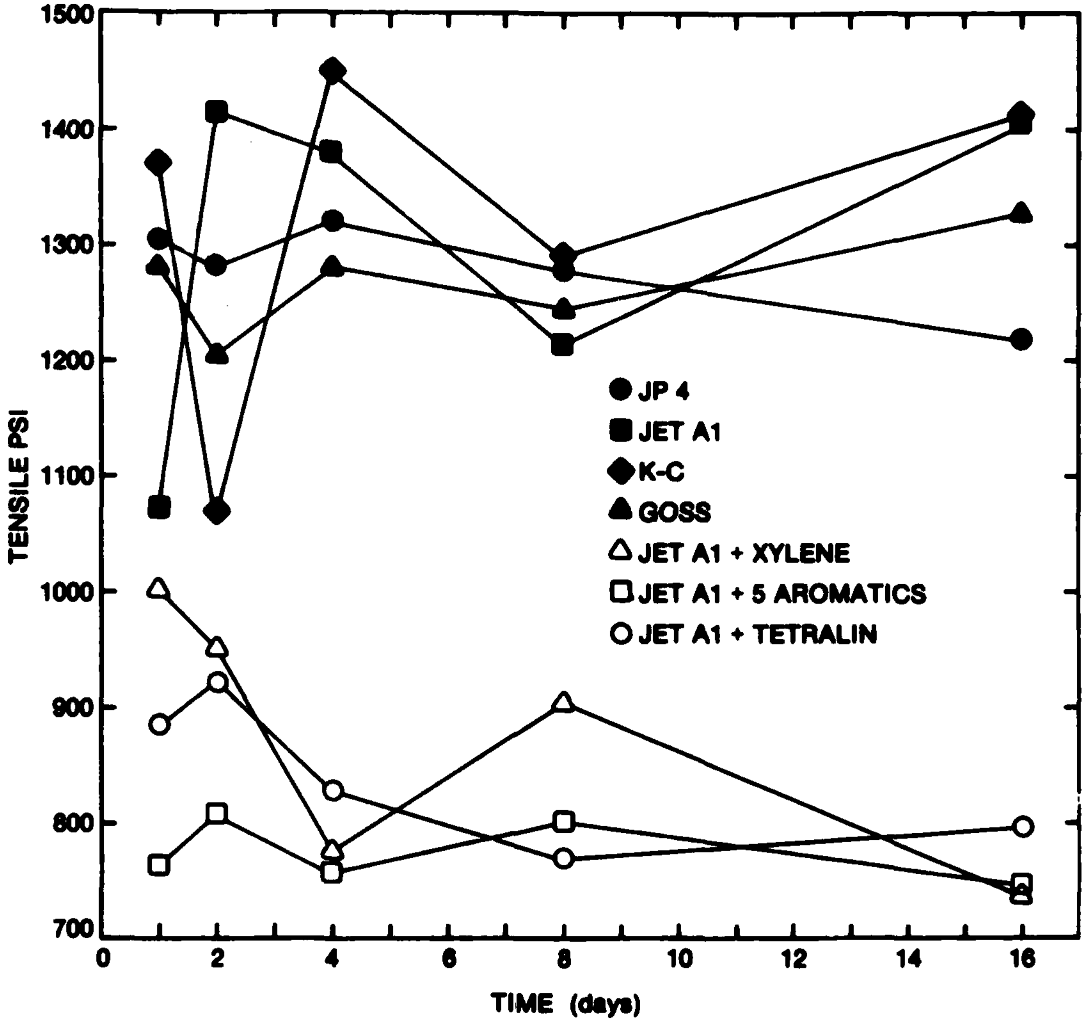

FIGURE 9 - TENSILE STRENGTH CHANGES IN O-RINGS AFTER IMMERSION IN SEVERAL FUELS, AND IN JET A-1 CONTAINING SEVERAL AROMATIC ADDITIVES.

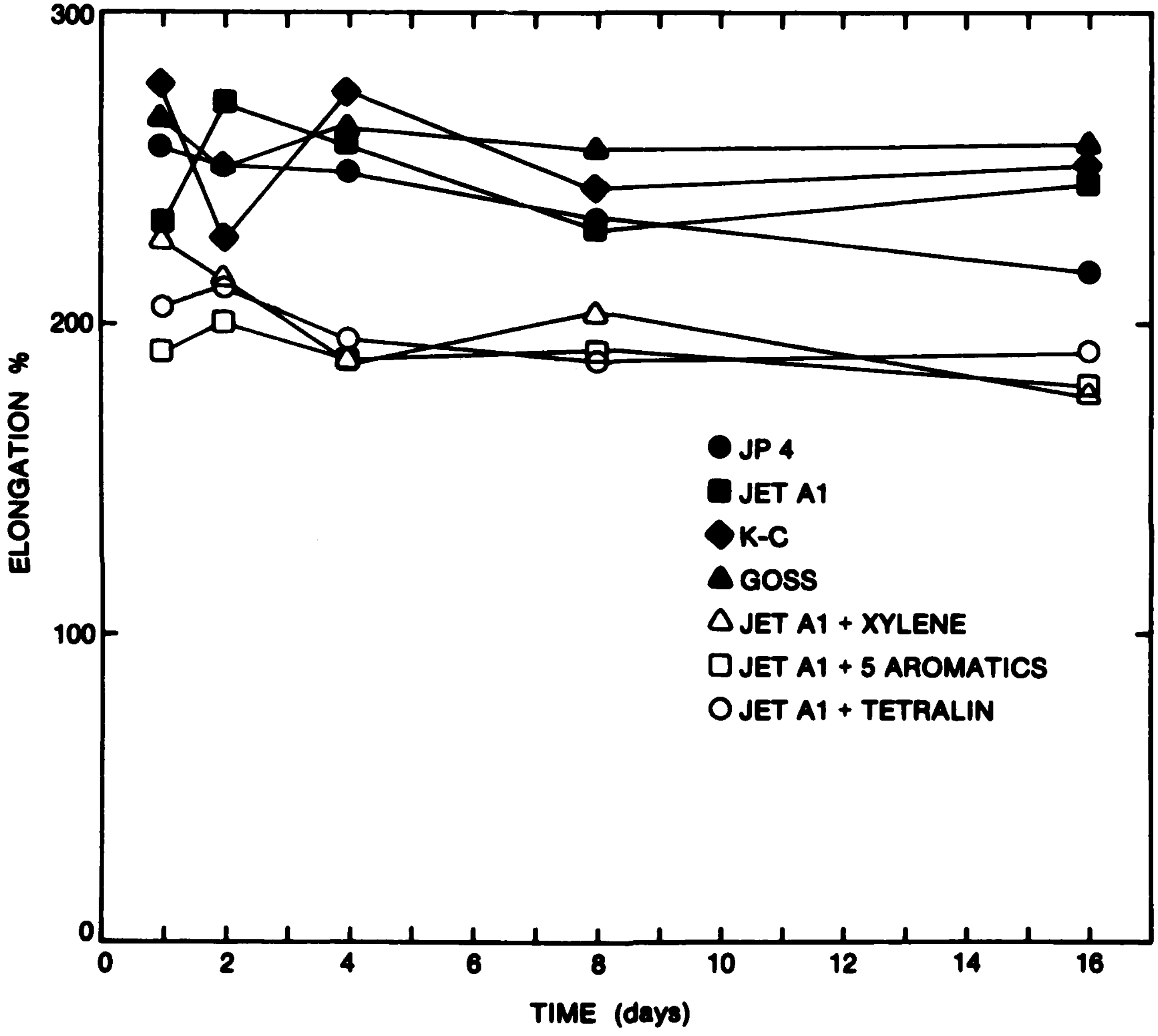

FIGURE 10 - CHANGES IN ULTIMATE ELONGATION IN O-RINGS AFTER IMMERSION IN SEVERAL FUELS, AND IN JET A-1 CONTAINING SEVERAL AROMATIC ADDITIVES.

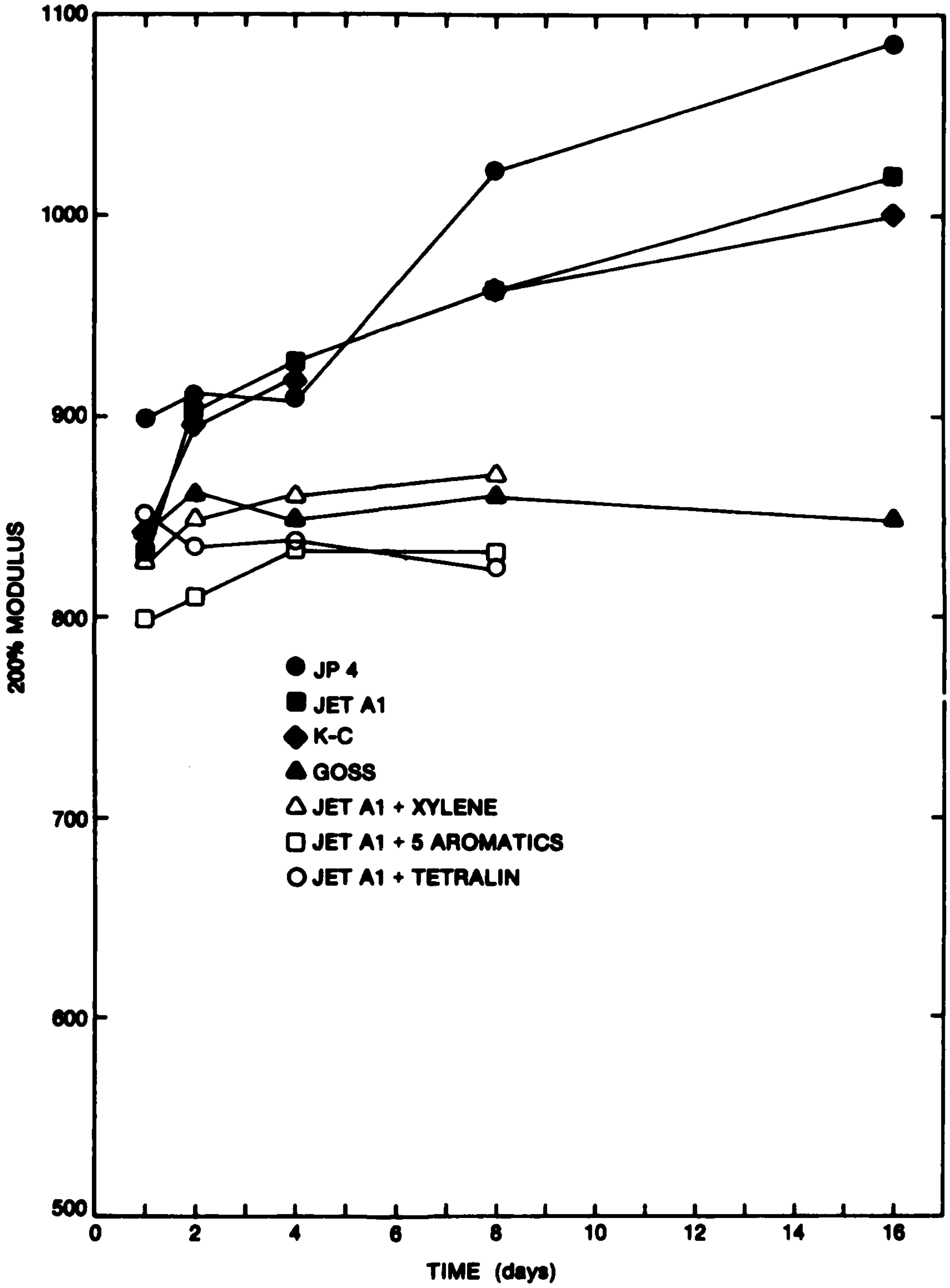

FIGURE 11 - CHANGES IN 200% MODULUS IN O-RINGS AFTER IMMERSION IN SEVERAL FUELS, AND IN JET A-1 CONTAINING SEVERAL AROMATIC ADDITIVES.

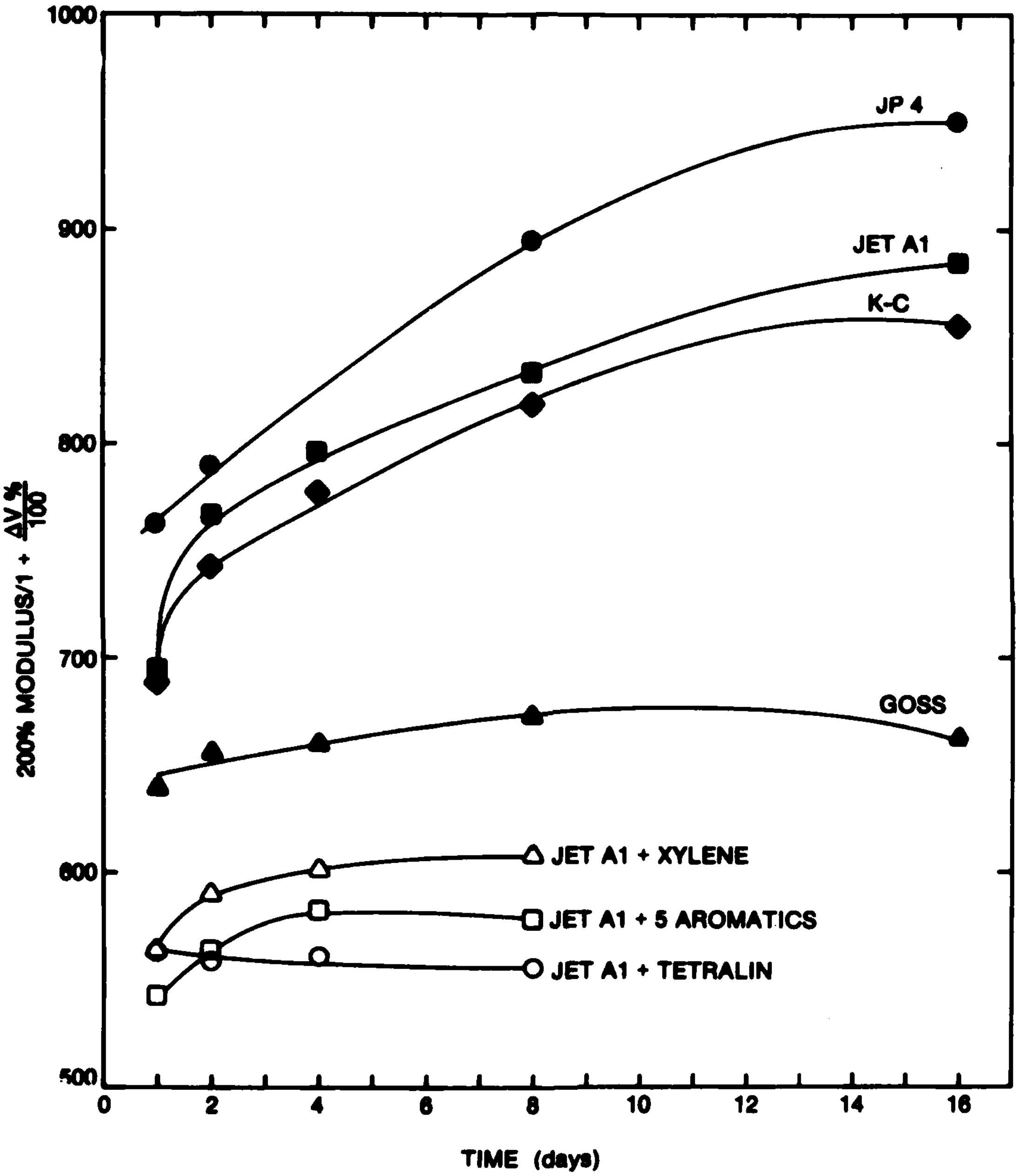

FIGURE 12 - AS IN FIGURE 11, BUT 200% MODULUS CORRECTED FOR VOLUME CHANGE OCCURRING IN O-RINGS DURING IMMERSION.

JP4 with 13.3% having the highest modulus and gas oil side stream the lowest. Again, however, results with the three Jet A-1 blends show that the added aromatics have the same disproportionately large effect for their concentration.

4.0 DISCUSSION

The conditions chosen for the fuel alternation experiments maintain a constant temperature and expose the rubber samples to abrupt shifts between two strikingly dissimilar fluids, a specification fuel and one with nearly twice the allowable concentration of aromatics. Within the accuracy of the experiment one can say that no deterioration of rubber properties resulted from this cycling. The actual situation, however, would be better approximated with much longer cycling periods, perhaps of several months, and lower incubation temperatures. Again the test itself may be too severe to be realistic. It measures dynamic properties under stress-extension to break - of the rubber after immersion in the fluid, whereas most O-rings function in a passive mode; they are seated in place and then expand to fill the available cavity and prevent fuel leakage. From this point of view, the additional expansion resulting from higher aromatics levels could be within limits an advantage. However, these short-term experiments that measure properties under stress do imply that the problems with high aromatics fuels are not as serious as was once thought. The increase in aromatics is anticipated to be a gradual process, with percentages creeping up over a period of years; and it is probable that progressive adjustement of compounding formulas in the direction of greater fluid resistance will resolve any problems that may arise.

The effect on swelling and on elastic properties of blending aromatic hydrocarbon cannot be explained. The viscosity of the Jet A-1 blends will be lower than that of the gas oil side stream, and rubber penetration somewhat faster, but this could hardly have an effect persisting after sixteen days at 70°C. Again, one must have reservations about the conclusions drawn from such findings as these. It appears however, that one cannot be certain of simulating all the effects of a high aromatic fuel of natural origin by using, as here, aromatic additions to a specification fuel.

5.0 REFERENCES

1. Coleman, J.R. and Gallop, L.D., DREO Technical Note 82/26.

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