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EXPOSURE OF A NITRILE RUBBER TO FUELS OF VARYING AROMATICS LEVEL

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ABSTRACT

A nitrile rubber was incubated in fuels to which model aromatic compounds had been added at several levels. Changes in the rubber were determined by standard elastic property determinations after various periods of incubation. The main determinant of attack by the fuel was its aromatics level. Naphthalene was particularly effective in promoting swell and softening, but had about the same effect on elastic properties as mononuclear aromatics at the same level. Cycling of the nitrile rubber between two fuels of considerably different aromatics level degraded tensile properties to a greater extent than did exposure to either fuel alone for the same total period of time.

RÉSUMÉ

Un caoutchouc nitrile a été incubé dans des carburants additionnés de quantités connues de composés aromatiques modèles. Les changements subis ont été mesurés par les caractéristiques élastiques habituelles après diverses périodes d'incubation. Le principal déterminant de l'attaque était la concentration des aromatiques. Le naphatalène était le composé occasionnant le gonflement et le ramollissement les plus marqués mais, à la même concentration, il avait à peu près les mêmes effets sur les caractéristiques élastiques que les aromatiques monocycliques. Le fait de placer le caoutchouc alternativement dans deux carburants contenant des concentrations d'aromatiques très différentes nuisait beaucoup plus aux propriétés élastiques que l'exposition à l'un ou à l'autre des carburants pendant la même durée.

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INTRODUCTION

In recent years, changes in petroleum price and supply have resulted in progressive changes in the properties of aircraft gas turbine fuels. These have in the main been higher aromatics levels and boiling point range, reflecting the decreased availability of light crudes. Some relaxation of specification requirements has been necessary in order to ensure adequate supplies, and it is generally agreed that further changes in this direction will be required in the future. In addition, efforts to develop liquid fuels from alternative sources - tar sands, oil shale and coal - will probably result in products of significantly different chemical nature. The effects, on several aspects of aircraft engine performance, of these changes have become the object of extensive investigation. As an illustration, the maximum permissible aromatics level in Jet A was at one time 20% by volume, and could be readily met. This has been relaxed, by waivers which it appears will now be permanent, to 22% or 25%, and a number of investigations are underway to determine how engine performance will be affected by using fuels of aromatics level in excess of 40%.

One aspect of the problem is the effect of these changes on the elastomers or rubber-like components in fuel storage and delivery systems. These were designed to be compatible with fuels meeting the earlier specifications. A study conducted under NASA sponsorship (1) examined the effects of aromatic variations in jet fuels on the properties of several materials, one of them a nitrile rubber. This is a copolymer of butadiene and acrylonitrile, competitive with natural rubber but superior to it in oil resistance, and extensively used in O-rings, gaskets, and the laminated structures from which flexible fuel tanks are constructed. Fuel aromatics content was adjusted by addition of tetralin, a partly hydrogenated naphthalene, to a base JP-4. Tetralin was chosen as being representative of fuel aromatic constituents in molecular weight and boiling point. The investigators examined in a fundamental way degradation mechanisms and changes in basic physical properties of the elastomers, effected by incubation in the fuels. One object of this work was to develop an approach to failure prediction, failure being defined as an arbitrary extent of degradation in some elastic property.

In a second study, conducted by the University of Dayton for the U.S. Air Force Materials Laboratory (2), a wide variety of elastomers employed in aircraft fuel systems was treated with JP-4 containing additions to produce several final levels of aromatics, mercaptan sulfur and total sulfur. The direction of this work was practical, and the post-immersion physical testing was intended to show how contact with these fuels might affect component service.

The main factor in determining the rate of elastomer degradation was the aromatic level of the fuel; the greater this was, the greater the susceptibility of the elastomer to attack. This was evident particularly with the nitrile rubbers studied in the NASA-sponsored work.

With the increase in aromatics levels in aircraft fuels, and the growing interest in alternative fuel sources, the method of fuel analysis long in use (3), a rough chromatographic separation into aliphatic, aromatic and olefinic constitutents, has been found in some respects inadequate. It has in recent years been supplemented, especially in research programs by more detailed analysis based on gas chromatography, alone or in conjunction with mass spectrometry. It is felt that changing the distribution of hydrocarbon types within the aliphatic and aromatic categories may influence engine performance with the fuel.

It was decided to examine the effect on rubbers of varying fuel composition by preparing blends, i.e. by adding significant amounts (approximately 20-40%) of several markedly different aromatic compounds to a base fuel, and comparing changes in rubber properties after immersion in these blends. If the effect is found to be primarily dependent on total aromatics level, the identity of the model compounds being of secondary importance, one can conclude that there is no reason to anticipate detrimental chemical effects with new fuel types as long as the total aromatics level is controlled.

Another subject of interest is the effect of cycling on elastomers i.e. the effect of passing them between two fuels of markedly differing (low and high) aromatics level, to determine whether degradation is any greater than when incubated the same total time in either fuel alone. This could be of interest if, on a regional basis, fuels developed of differing composition based on origin, so that planes repeatedly loaded fuels of varying aromatics content.

The work reported here was conducted with a nitrile rubber available from the DREO laboratory, and designated SA463. Designed for a more exacting use than engine seals and gaskets, its initial physical properties exceeded specification requirements by a considerable margin. After preliminary work to secure some idea of the magnitude of the changes to be expected, a brief examination of cycling effects was carried out, using a baseline Jet A-1 fuel with two additives. An investigation of specific chemical effects was then made, using three additives at three concentrations each; but it became apparent that, although certain trends in behaviour could be detected, this rubber was not sufficiently sensitive to aromatic variations in the range that can reasonably be anticipated with future jet fuels. In a continuation of the work, commercial nitrile O-rings produced to the appropriate specifications are also being used, to see whether the trends in behaviour observed with SA463 are paralleled, using materials whose properties approximate those called for in the specification.

EXPERIMENTAL

Rubber

The nitrile rubber SA463 is prepared as follows.

Formulation

Polysar Krynac 801	100.00
Zinc Oxide	5.00
Stearic Acid	1.00
Sterling SO(N-550)	50.00
Dibutyl Sebacate	10.00
Flectol H	2.00
Sunproof Improved	1.50
Monex	0.40
MBTS	1.50
Sulfur	1.50
	172.90

Cure
15 minutes at 300 F.

This was supplied either as slabs (6" x 6" x .075") from which dumbbells could be cut with a die for tensile measurements, and pieces approximately 1" x 2" for volume change; or occasionally as discs (1.125" diameter approximately .500" thick) for compression set tests. In the table below some of the initial physical properties are listed, and for comparison the requirements of MIL-P-5315B, which governs the procurement of fuel-resistant packing materials for aviation use.

TABLE I

	SA463	MIL-P-5315B
Tensile strength, psi	3000-3500	100
Ultimate elongation, %	400-450	200
Hardness Shore A	65	60-70
Compression set, %	6	0-50
Volume increase after fluid aging, %		
Type I fluid	-	0-10
Type II fluid	-	0-50

It is apparent that SA463 is in these respects considerably better than it need be for this application. Volume increase in the two fluids listed in MIL-P-5315B was not determined, but from their properties and the swelling observed with SA463 in a number of fuels, it is evident that in this respect also, SA463 would exceed requirements by a good margin.

Test pieces of SA463 were supplied in several lots over a period of months. Check on initial properties showed reasonable constancy from lot to lot; but in the experiments to be described comparisons are made among test pieces cut from the same lot, using as reference the rubber in its initial state (air sample).

Test Methods

For each determination three test pieces, separated by glass spacers, were inserted in test tubes of such a size that the samples were completely immersed when the recommended volume of fuel (150 ml) was used. After storage for the desired period at the chosen temperature, the test pieces were removed to a beaker containing the same fuel at room temperature, and allowed to cool. Subsequent testing, wherever possible, was conducted in accordance with ASTM D471 "Standard Test Method for Rubber Property - Effect of Liquids", (4). D471, in addition to describing procedures developed specifically for immersion effects, references other test methods, with any modifications necessary [illegible] this application.

Tensile properties were determined as in D471, paragraph 14.2, "Immediate Deteriorated Properties" with this variation, that 15-20 minutes elapsed between removal of the sample from the fuel and measurement of the tensile properties, to facilitate other concurrent testing. A series of experiments conducted with elapsed times of 2-3 minutes, as called for in the test, and 30 minutes, showed no significant difference in results.

Volume change was measured as in paragraph 10 of D471. Hardness was determined as in D471, paragraph 14, and D2240 (5). Compression set, not a part of D471, was determined by D395 (6), using the buttons described above.

The incubation periods suggested in D471 were, except for one set of experiments, adopted in this work. These periods - 22, 70, 166, 334 and 670 hours - are equivalent to 1, 3, 7, 14 and 28 days, less two hours in each case.

In the tables, averaged experimental results are recorded as they come out of the calculations. There is considerable inherent uncertainty in some of these measurements in particular those made at the break point, and this is reflected in the magnitude of the standard deviations quoted with the data. In the figures, values are plotted as point data, despite the variability, which should be kept in mind. The same is true of hardness values, which are in part subjective and dependent on the operator. They are in fact reliable to ±1 or 2 hardness units only. In inspecting these plots, trends in the data are the most significant observation, and data points on the graphs are linked by straight lines, to assist the eye in following trends.

Fuels and Blending Agents

A kerosene type aviation fuel, Jet A-1, of aromatic level 18.6%, was employed as base line fuel. It was desired to simulate an entirely parafinic reference fuel, so that by adding model compounds blends, of completely known aromatic content would be available. For this purpose a commercially available light paraffin oil from Fisher chemicals (0-119) was chosen. It became apparent, however, during the work that the high viscosity and molecular weight of the material were probably affecting its ability to penetrate the rubber and extract soluble constituents, and a limited amount of testing was conducted with the base fuel decane, whose properties more nearly approximate those of a jet fuel.

The blending agents were:

Xylene (a mixture of isomeric xylenes boiling at 137-140°C)
- a mononuclear aromatic with two side chains.

Tetralin (tetrahydronaphthalene, boiling point 207°C)
- containing two fused rings, one saturated and one aliphatic; and for comparison with tetralin

Decalin (decahydronaphthalene, boiling point 187°C)
- the completely saturated reduction production of naphthalene, with two fused cyclohexane rings

Naphthalene (m.p. 80°C, boiling point 217°C)
- a condensed binuclear aromatic

Blends were made by volume, and final aromatics concentrations are expressed as per cent or added per cent. Thus a mixture of 100 ml paraffin oil and 45 ml tetralin is described as 45% added tetralin, and the final aromatics concentration in volume percent is 45/145 x 100, or 31%, neglecting volume changes in mixing, which are at most about one per cent and can be ignored.

Preliminary Experiments

Figure 1 depicts the effect on the physical properties of SA463, of storage in Jet A-1 at room temperature for 7 and 28 days. Under these benign conditions, a very modest decline in tensile properties and increase in hardness are observed, associated probably with the leaching out of soluble constituents from the rubber, while swelling and compression set even after 28 days are well within the limits of MIL-P-5315B for starting material.

In order to find suitable experimental conditions, samples of SA463 were incubated in Jet A-1 at temperatures ranging from 70 to 150°C. Conveniently measurable degradation in tensile properties was observed after storage periods of from several days to several weeks, at temperatures of 100-120°C; and this temperature range was used in examining the effects of aromatic additives.

Effect of Fuel Variation

A set of incubation experiments was performed at 100°C, employing Jet A-1 with 40% added volume of tetralin as decalin and 36% added volume of xylene. As the Jet A-1 contains 18.6% aromatics by volume, the final aromatics content in the three blends can be calculated as:

Jet A-1 + tetralin	42%
Jet A-1 + decalin	13%
Jet A-1 + xylene	40%

Thus there are two fuels of low and two of high aromatics level, and as Figures 2-5 show, this is the main factor determining the response of SA463. The experimental results, except for elongation (Figure 5) fall into two groups, decalin behaving like an aliphatic diluent for Jet A-1. Its general resemblance to tetralin in molecular weight and size are of no significance; aromaticity is the only factor.

Hardness (Figure 2) shows a drop during the first day, followed by recovery over the remainder of the immersion period. With the two more aromatic fuels the initial decline in hardness is marked, and the original hardness is not recovered during the test; with Jet A-1 and Jet A-1 plus decalin, the final hardness value surpasses the original. These observations are related to volume change (Figure 3), the initial swelling, greater for aromatic fuels, being followed by shrinkage as fuel-soluble constituents of the rubber are leached out.

From Figure 4 it is seen that higher fuel aromatics levels are associated with lower tensile strength. On the other hand the ultimate elongation data depicted in Figure 5 are inadequate to support any conclusions about aromatic effects.

Effect Of Cycling Between Fuels

Jet A-1 of 18.6 % aromatic level was used as a low aromatics fuel (Fuel A); and as high aromatics fuels Jet A-1 plus 40% added tetralin (Fuel B; 42% aromatics level); and Jet A-1 + 36% added xylene (Fuel C; 40% aromatics level).

Samples of SA 463 were exposed to the three fuels at 120°C individually, for periods of five and of ten days (more exactly 118 and 238 hours). Changes in the rubber were followed by determining physical properties after each of these immersion periods. In Figures 6-9 these trends for each single fuel are shown by the points linked by straight lines.

In addition, other rubber samples were exposed to two fuels for a total of ten days, five days in total in A and five days total in either B or C, as in the schedule:

A-5 + B-5
A-2 + B-2 + A-2 + B-2 + A-1 + B-1

A-5 + C-5
A-2 + C-2 + A-2 + C-2 + A-1 + C-1

Two of these entail one fuel change, and two a total of five fuel changes each. The same physical properties were measured after the ten day period, and by comparison with the results of ten day exposure to single fuels, the effect if any of alternating the fuels could be inferred.

Table II summarizes the experimental data. In Figures 6-9 the isolated open symbols at the ten day mark, which represent the properties of fuels subjected to one or more fuel changes, are to be compared with the results of trends occurring with the single fuels and the values at the tenth day (solid points).

Swelling (Figure 6) in all experiments rises to a maximum some time during the first few days, and is in decline by the tenth day, the extent of swelling as before being dependent on aromatic content. With samples passed between two fuels (A and B, or A and C) the per cent swelling observed after ten days is characteristic of the fuel to which it was last exposed, and is practically identical to the swelling observed when the sample was exposed to this fuel for the entire ten day period. In other work, not reported here, it was found that the rubber, once penetrated with fuel, would dilate or contract depending on the aromatic content of the fuel in which it was inserted, approaching equilibrium within a day or two.

In the earlier work (Figures 2 and 3) it was observed that swelling and softening are related. This is not borne out in these cycling experiments however. While the final degree of swelling is that produced by the last fuel (B or C) in which the rubber was immersed before measurement, final hardness values (Figure 7) scatter, but lie generally closer to those assumed after ten days in Fuel A.

Tensile strength effects are shown in Figure 8. The single data points at the tenth day, referring to properties determined after fuel changes, demonstrate that deterioriation is significantly greater than that found after ten days exposure to any single fuel. Also, comparing rubber subjected to one and to five fuel changes, deterioration is clearly greater in the latter case. These findings are borne out, though not so emphatically, by the elongation data shown in Figure 9.

Aromatic Additions To Paraffin Oil Base

Further experiments were carried out in order to determine the effects of systematic variations of type and level of added aromatics. The light paraffin oil of zero aromatic content was used as baseline fluid, with three additives (tetralin, xylene and the condensed binuclear aromatic naphthalene) each at levels of 15, 30 and 45 per cent added volume; these

TABLE II

Effect of Cycling Between Fuels on Physical Properties of SA463

Rubber Exposure[1]	Tensile Strength psi	Ultimate Elongation %	ΔV%	Shore A Hardness
(Air)	3179	444	-	66.8
A5	1842	193	5.27	69.1
A10	1649	153	3.38	71.1
B5	1886	233	20.93	55.5
B10	1623	182	18.30	57.1
C5	2095	228	16.41	58.7
C10	1867	182	13.73	62.3
A5 + B5	943	110	18.03	64.1
(A+B) frequent shift	666	72	17.65	67.1
A5 + C5	977	83	12.93	70.2
(A+C) frequent shift	664	58	13.89	72.2

[1] Symbols explained in text.

resulted in final aromatics levels of 13, 23 and 31 per cent respectively, assuming no volume change on mixing. Immersion periods, at 100°C, were of one, three, seven and fourteen days.

Results of all tests are listed in Table III, including tension or modulus to several intermediate elongations preceding break.

With pure paraffin as immersion fluid, elongation at break (Figure 10) declines smoothly from values near that of the initial (air) sample. Additives at all levels result in a rapid drop in elongation, most of it occurring during a relatively short initial exposure period. Over long times, the only useful observation is the obvious one of a general decline occurring in all fuels. Tensile strength at break is plotted in Figure 11. The immediate effect of aromatic additives, as with elongation, is a sharp fall-off, the values thereafter remaining nearly constant or recovering in part. In paraffin alone, the tensile strength falls off gradually with increasing exposure. No discrimination among these results based on aromatic types appears possible. That additive level is in a very general way associated with tensile strength is suggested by the plots of Figure 12. Here, for each of the four incubation periods, tensile strength is plotted as a fraction of that for rubber incubated in pure paraffin for the same period. Apart from some marked irregularities with naphthalene, to be referred to again, the connection between increasing aromatic content and diminution in tensile strength is evident.

Volume changes (Figure 13) are regular and accurately determinable. In paraffin the rubber shrinks, at first rapidly and then more slowly as soluble constituents dissolve out into the fuel. Addition of aromatics superimposes an initial swelling on this, the extent of swelling being highly dependent on aromatic level and type. At the same volume per cent level, tetralin and xylene are indistinguishable, their v versus time curves being nearly superimposed. Naphthalene is more aggressive, being about twice as effective in swelling this rubber as tetralin or xylene at the same concentration (compare curve A of Figure 13a with curve B of Figure 13b).

Very much the same is true of the hardness measurements shown in Figure 14. With paraffin, the hardness begins to increase above the initial air value (approximately 66) from the commencement of incubation; with tetralin, xylene, and naphthalene, hardness initially falls and then recovers. Again, tetralin and xylene are very similar in their behaviour at low concentration, while naphthalene produces a noticeably greater softening. As before, these results are correlatable in a negative sense with observations on swelling. However, at 45% added volume naphthalene behaves anomalously and confuses the results. These and other irregular results at the higher (45%) level, may be due to crystallization of naphthalene from these paraffin solutions, which was observed when they were cooled. The solubility of naphthalene in paraffin oil is relatively low at room temperature, and if it deposited within the rubber on cooling it would obviously perturb hardness and tensile measurements in an unpredictable fashion.

TABLE III

Effect on Physical Properties of SA463 of Exposure, At 100°C to Paraffin Alone and Containing Additives, For Several Incubation Periods

P = paraffin   T = tetralin   X = xylene   N = naphthalene

eg. P + 15T = 100 volumes paraffin + 15 volumes tetralin (15 added % tetralin)

Fuel	200% modulus psi	tensile strength psi	ultimate elongation %	shore A hardness	volume change %
(air sample)	1350 ± 84	3179 ± 142	405 ± 42	66 ± 0.6	-
22 HOURS					
P	1605 ± 36	3315 ± 316	379 ± 40	72.4 ± 0.6	-7.14 ± 0.01
P + 15T	1469 ± 19	2766 ± 314	340 ± 41	66.3 ± 0.3	-0.66 ± 0.01
P + 30T	1305 ± 30	2640 ± 92	342 ± 9	62.8 ± 1.0	5.44 ± 0.01
P + 45T	1267 ± 40	2485 ± 87	336 ± 8	60.0 ± 0.3	10.76 ± 0.24
P + 15X	1469 ± 7	2468 ± 132	300 ± 11	67.5 ± 0.3	-0.56 ± 0.02
P + 30X	1387 ± 3	2506 ± 116	315 ± 15	63.8 ± 0.4	5.15 ± 0.04
P + 45X	1382 ± 10	2128 ± 232	274 ± 25	63.7 ± 0.4	9.50 ± 0.04
P + 15N	1444 ± 20	2083 ± 340	273 ± 20	62.5 ± 0.3	7.20 ± 0.06
P + 30N	1223 ± 29	2265 ± 143	311 ± 19	57.7 ± 0.4	18.93 ± 0.04
P + 45N	1336 ± 48	2315 ± 104	306 ± 11	64.3 ± 0.4	27.80 ± 0.10
70 HOURS					
P	1791 ± 23	3301 ± 75	337 ± 13	73.0 ± 0.9	-7.86 ± 0.02
P + 15T	1615 ± 14	2900 ± 272	324 ± 29	67.8 ± 0.4	-1.22 ± 0.06
P + 30T	1601 ± 30	2627 ± 163	301 ± 21	64.2 ± 0.5	5.57 ± 0.23
P + 45T	1437 ± 68	2432 ± 108	295 ± 5	59.4 ± 0.6	10.23 ± 0.75
P + 15X	1606 ± 46	2771 ± 177	307 ± 24	67.2 ± 0.3	-1.08 ± 0.03
P + 30X	1689 ± 12	2371 ± 288	256 ± 25	64.2 ± 0.7	4.54 ± 0.03
P + 45X	1453 ± 53	2206 ± 135	264 ± 7	61.3 ± 0.6	10.37 ± 0.02
P + 15N	1550 ± 44	2423 ± 150	277 ± 13	63.9 ± 0.4	6.58 ± 0.04
P + 30N	1481 ± 58	2322 ± 124	279 ± 8	59.7 ± 0.4	15.22 ± 0.03
P + 45N	1418 ± 21	2378 ± 158	296 ± 16	65.1 ± 0.2	26.67 ± 0.1

TABLE III (Continued)

166 HOURS					
P	2285 ± 39	3145 ± 274	285 ± 32	75.5 ± 0.7	-8.51 ± 0.15
P + 15T	1882 ± 49	2940 ± 71	295 ± 13	69.9 ± 0.5	-1.46 ± 0.04
P + 30T	1581 ± 28	2778 ± 37	304 ± 1	65.6 ± 0.7	4.16 ± 0.03
P + 45T	1520 ± 20	2476 ± 72	322 ± 24	62.3 ± 0.8	9.31 ± 0.01
P + 15X	1884 ± 27	2954 ± 222	291 ± 24	70.3 ± 0.8	-2.18 ± 0.02
P + 30X	1743 ± 17	2348 ± 508	249 ± 41	66.3 ± 0.9	3.43 ± 0.03
P + 45X	1644 ± 59	2142 ± 292	240 ± 20	62.8 ± 0.6	9.99 ± 0.2
P + 15N	1711 ± 20	2165 ± 323	236 ± 24	65.6 ± 0.4	6.17 ± 0.03
P + 30N	1578 ± 8	2286 ± 221	258 ± 18	59.7 ± 0.3	17.80 ± 0.04
P + 45N	1534 ± 20	2360 ± 21	272 ± 1	63.4 ± 0.4	26.80 ± 0.04
334 HOURS					
P	2454 ± 30	2958 ± 231	265 ± 31	78.9 ± 0.5	-8.82 ± 0.02
P + 15T	2114 ± 35	3018 ± 105	276 ± 8	72.5 ± 0.3	-1.99 ± 0.01
P + 30T	1762 ± 27	2639 ± 420	274 ± 38	68.3 ± 0.3	3.74 ± 0.03
P + 45T	1708 ± 15	2641 ± 96	283 ± 8	65.1 ± 0.4	8.52 ± 0.06
P + 15X	2173 ± 26	2877 ± 115	253 ± 9	72.6 ± 0.6	-2.32 ± 0.01
P + 30X	2038 ± 68	2440 ± 187	228 ± 19	67.6 ± 0.7	2.53 ± 0.01
P + 45X	1903 ± 56	2148 ± 106	213 ± 8	66.3 ± 0.4	8.35 ± 0.04
P + 15N	1910 ± 43	2725 ± 206	261 ± 20	66.5 ± 0.4	5.69 ± 0.02
P + 30N	1662 ± 21	2252 ± 440	245 ± 34	59.3 ± 0.7	18.11 ± 0.04
P + 45N	1544 ± 20	2155 ± 527	251 ± 43	62.9 ± 0.5	26.28 ± 0.18

Another disadvantage of paraffin oil, not appreciated when it was chosen as base fluid, is its relatively high viscosity and molecular weight. It has been observed already that when on the one hand paraffin alone, and on the other hand paraffin plus any additive in any concentration are used as immersion fluid, there is a notable difference in the course of elastic property change in the rubber; in the former case values fall smoothly from the initial (air) value, in the latter they had already experienced a sizeable drop by the time of the first measurement. The difference could be due either to the swelling action of the additives, or to their smaller molecular size which allows rapid penetration of the rubber structure. Additional experiments were accordingly set up, employing as base fluid decane, again a pure paraffinic compound, but of molecular weight and physical properties more characteristic of jet fuel materials. Figures 15 to 18 illustrate the affect on SA463 properties of immersion in decane with and without 30 per cent added xylene, the corresponding data for paraffin oil with and without xylene being plotted for comparison.

One striking difference is seen in volume change (Figure 15). SA463 immersed in paraffin oil undergoes an immediate rapid contraction, followed by a slower contraction presumably due to leaching out of soluble rubber components; with decane there is an initial swelling, the decane molecule from its size being able to penetrate the rubber rapidly. In both cases the addition of xylene displaces the v versus time curves positively.

Immersion in both paraffinic fluids leads to an increase in hardness (Figure 16). The most significant results, however, are shown in Figures 17 and 18, relating to elastic properties; the low molecular weight decane produced the same initial rapid fall in tensile and elongation observed everywhere in this work except with paraffin oil itself, whose anomalous position is again apparent from these figures. It became evident, in fact, as the tests progressed that it would have been more realistic to employ as a paraffinic baseline fluid a material whose physical and chemical properties lay in the jet fuel range. Decane or dodecane are ideal for this purpose, but in the amounts required to repeat the full range of experiments would be prohibitively expensive. As a compromise, Jet A-1 with additions made as in Table III would produce fuels of varied aromatic level and so heavily weighted toward one of the three types: mononuclear aromatic (xylene), bicyclic aliphatic-aromatic (tetralin) and condensed binuclear aromatic (naphthalene) that if any specific chemical effects exist they should be detectable by such experiments. Variations in hydrocarbon composition to be anticipated in future alternative fuels will certainly be less drastic than those produced by addition to Jet A-1 of single aromatic hydrocarbons in the amounts employed here. It is planned to carry out such studies, to a limited extent with SA463, but with particular emphasis on the use of O-rings.

SUMMARY AND OBSERVATIONS

The work described here confirms generally the fact of a decline in the value of rubber elastic measurements with increased aromatic content of the incubating medium, and suggests that two of the model compounds employed, xylene and tetralin, have within experimental error the same effect at the same concentration level. Naphthalene was effective out of proportion to its concentration in promoting softening and swell, and at higher concentrations led to erratic results in elastic property measurements. However it should be noted that naphthalene, because of its exceedingly detrimental affects on combustion will not in actual fact be present at nearly the levels used here; and also that the use of paraffin oil as a base fluid in some of the work perturbed the results.

SA463, a relatively resistant high quality nitrile, was not very sensitive to amount or type of aromatic additions in the 15 - 45% range of greatest practical interest for fuels. It is hoped that repetition, using O-rings as experimental material may bring out distinctions more clearly.

Cycling between two fuels, even with SA463, have effects on elastic properties significantly greater than those shown with either fuel singly. This work will also be repeated, employing O-rings.

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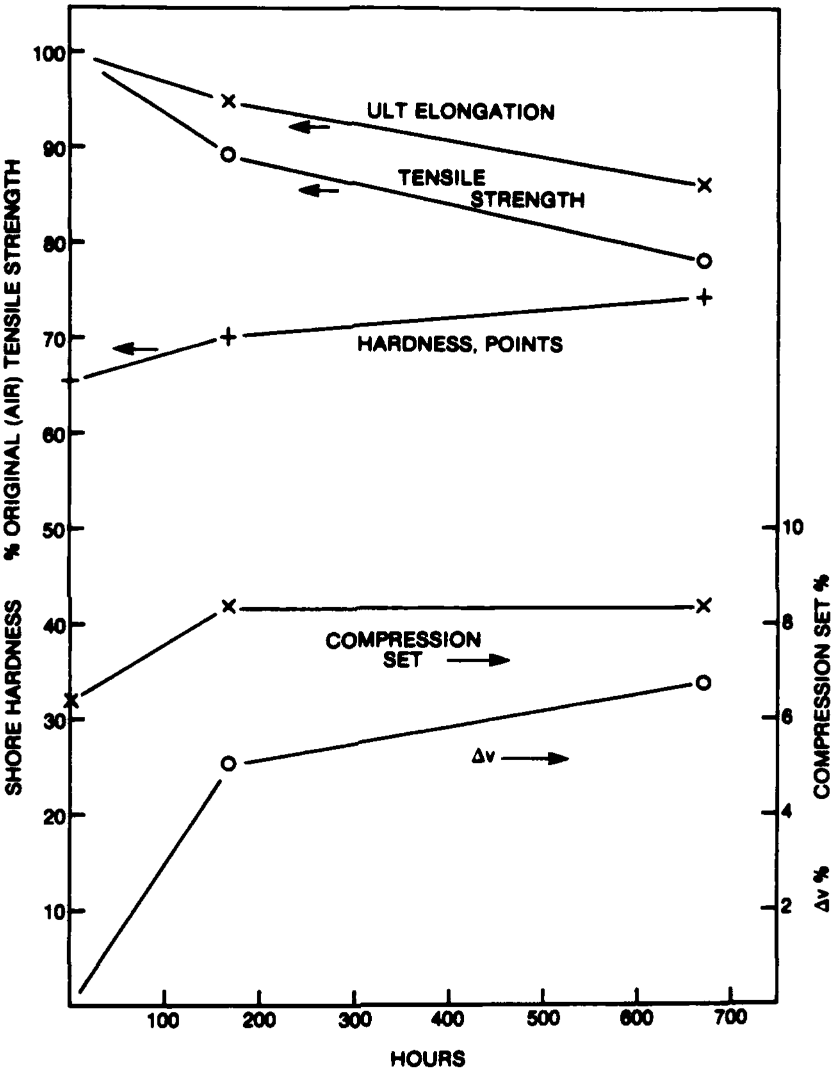

Fig. 1 Effect on rubber (SA 463) properties of room temperature storage in Jet A-1.

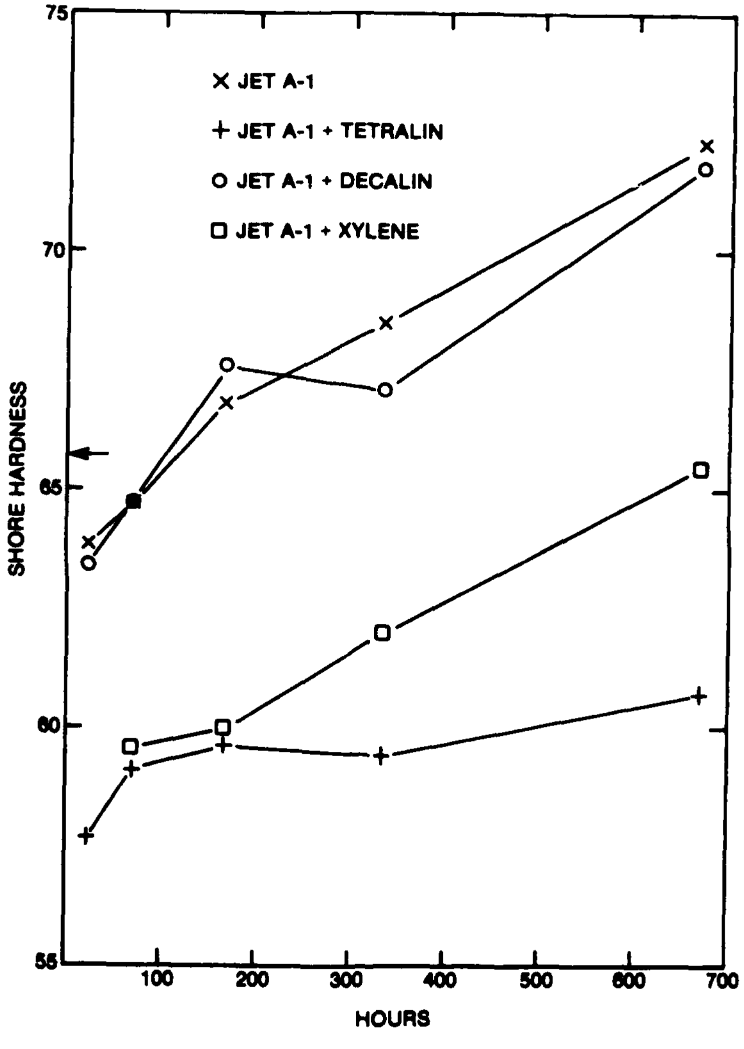

Fig. 2 Effect on hardness of storage at 100°C in several fuels. Arrow indicates initial (air) value.

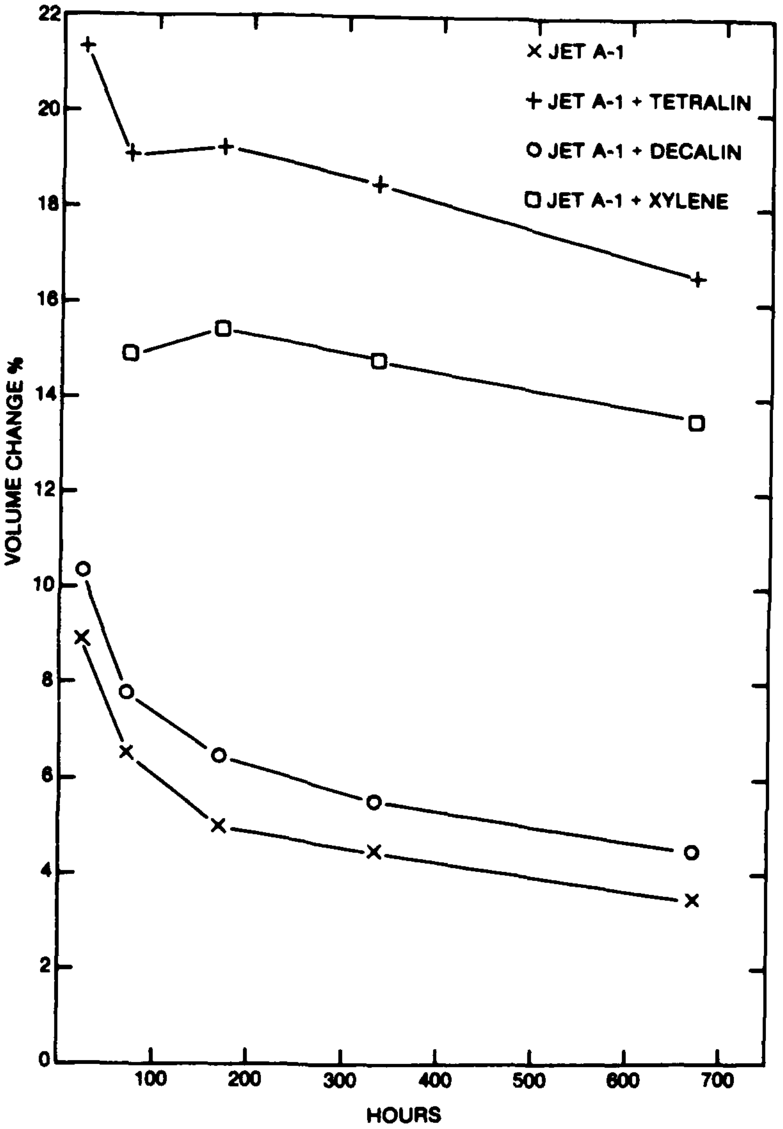

Fig. 3 Effect on swelling of storage at 100°C in several fuels.

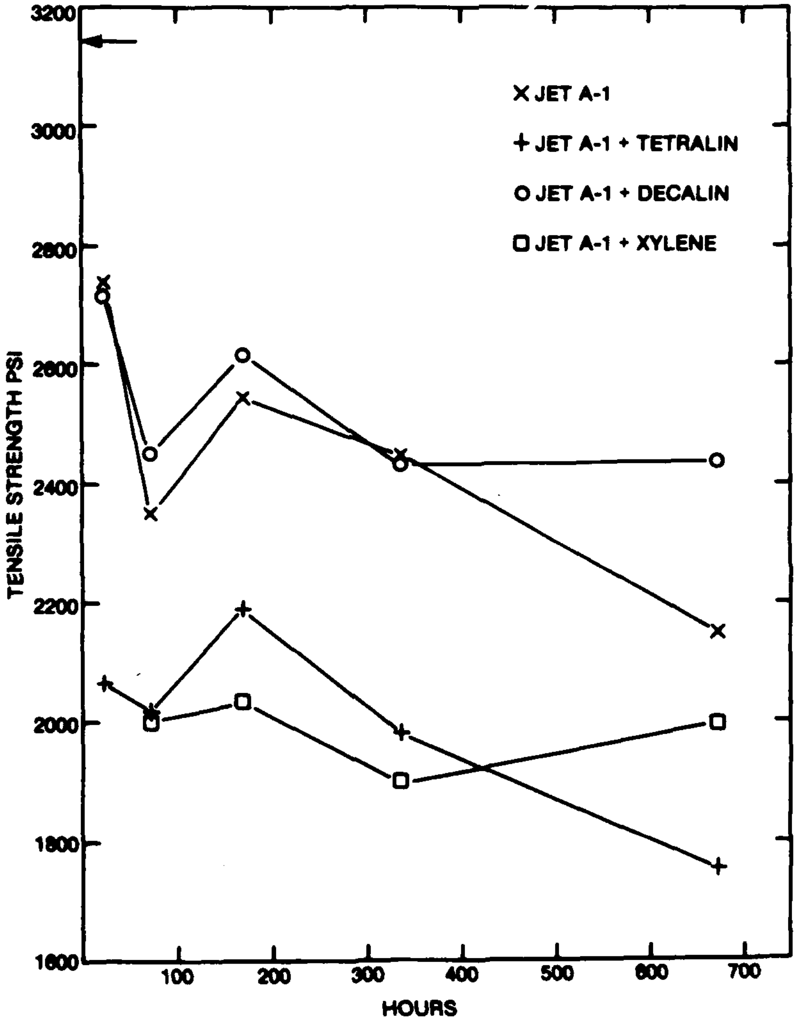

Fig. 4 Effect on tensile strength of storage at 100°C in several fuels. Arrow indicates initial (air) value.

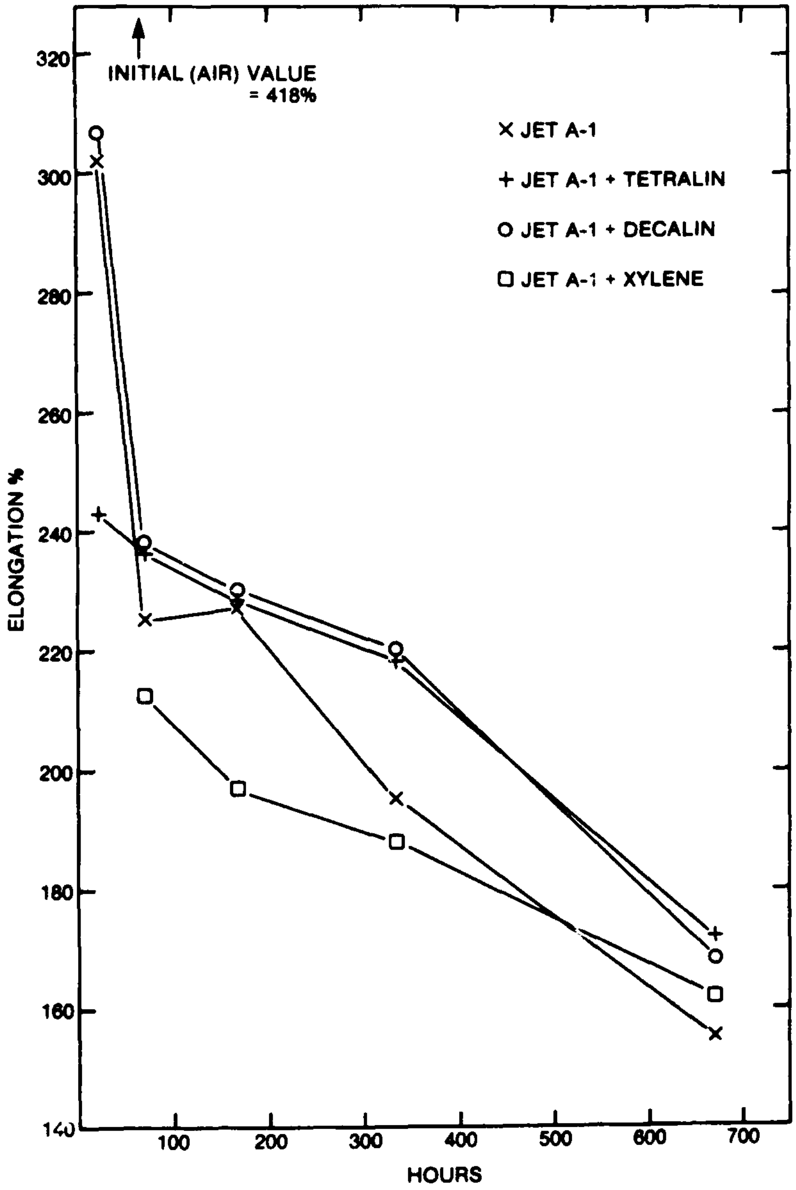

Fig. 5 Effect on ultimate elongation of storage at 100°C in several fuels.

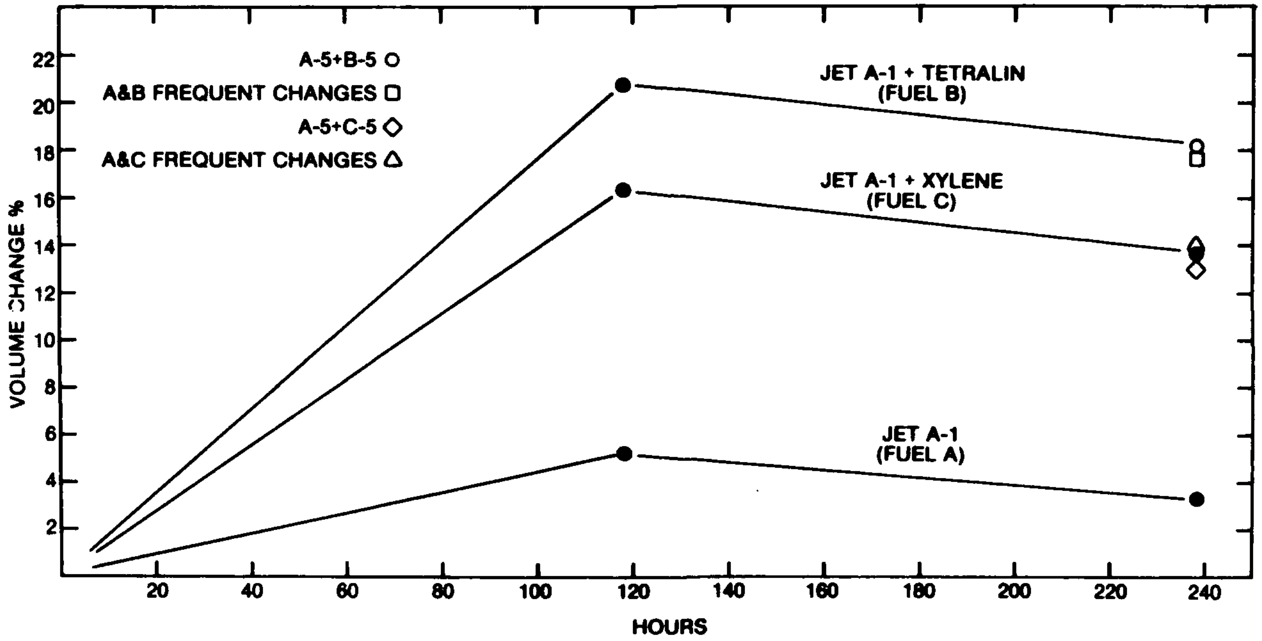

Fig. 6. Effect on swelling of cycling at 120°C between two fuels.

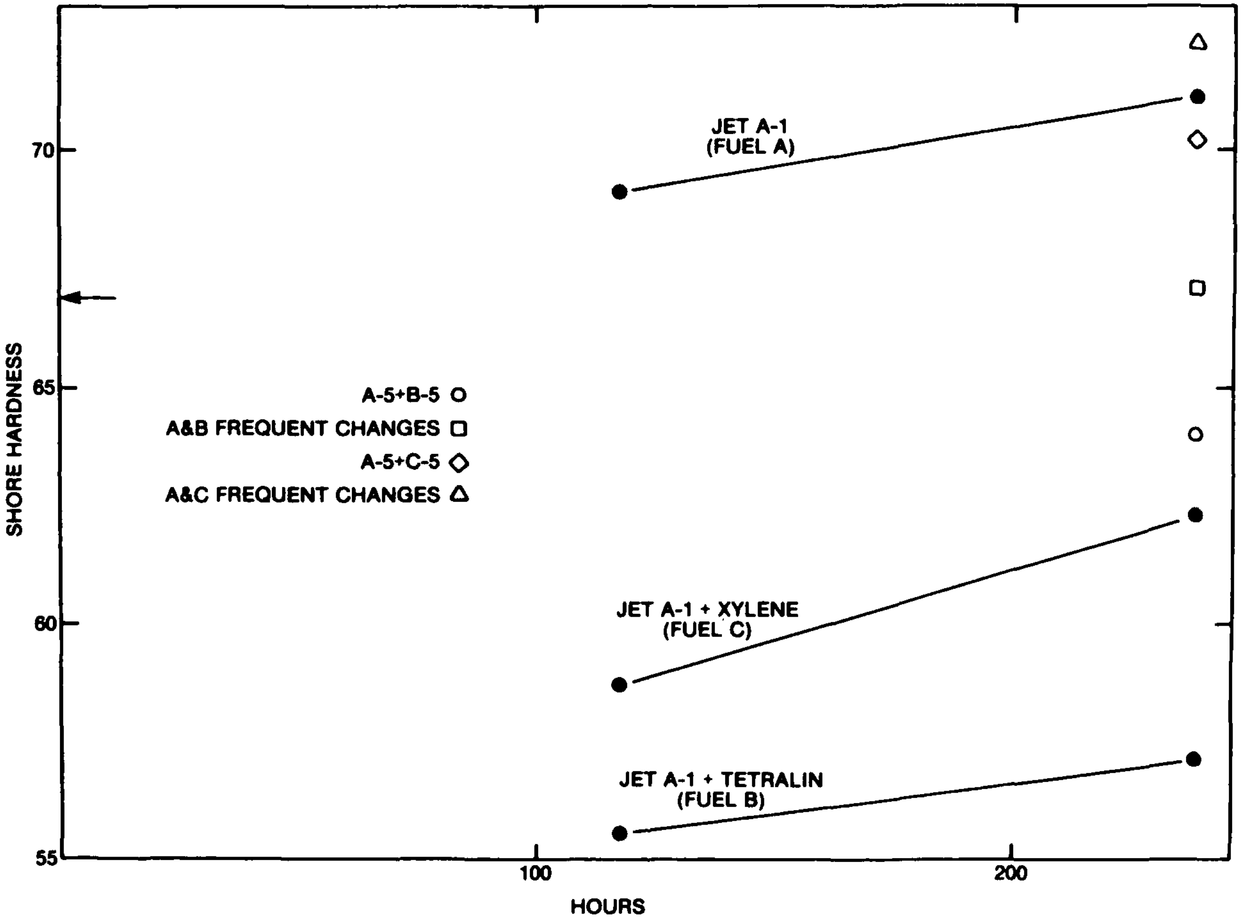

Fig. 7 Effect on hardness of cycling at 120°C between two fuels.

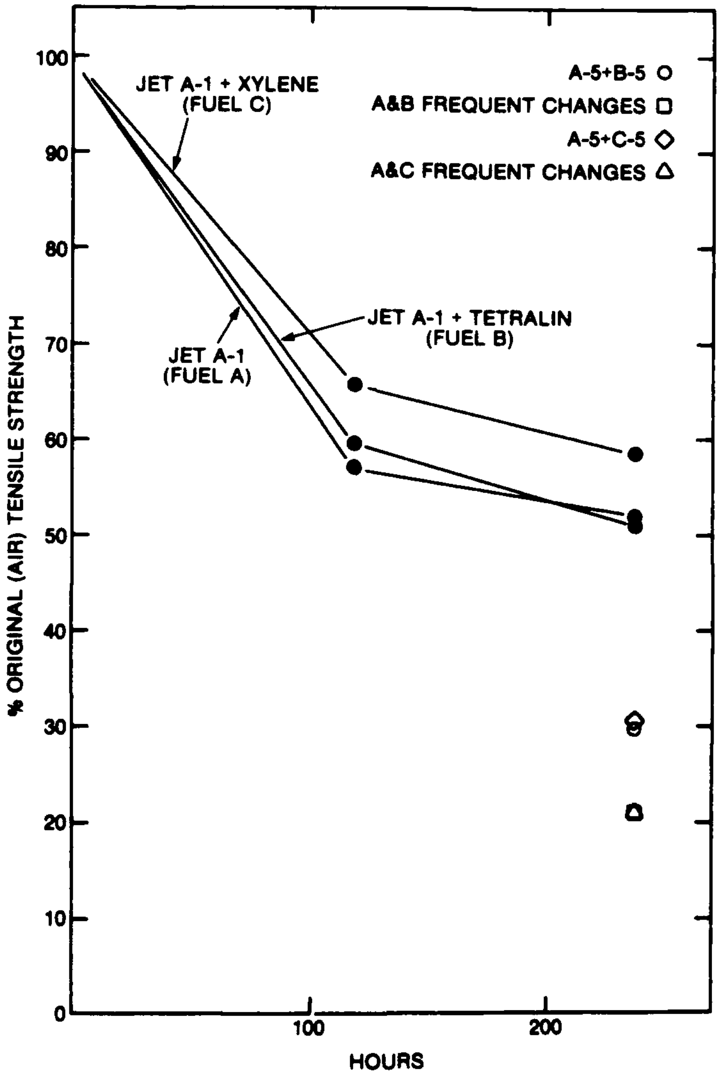

Fig. 8 Effect on tensile strength of cycling at 120°C between two fuels.

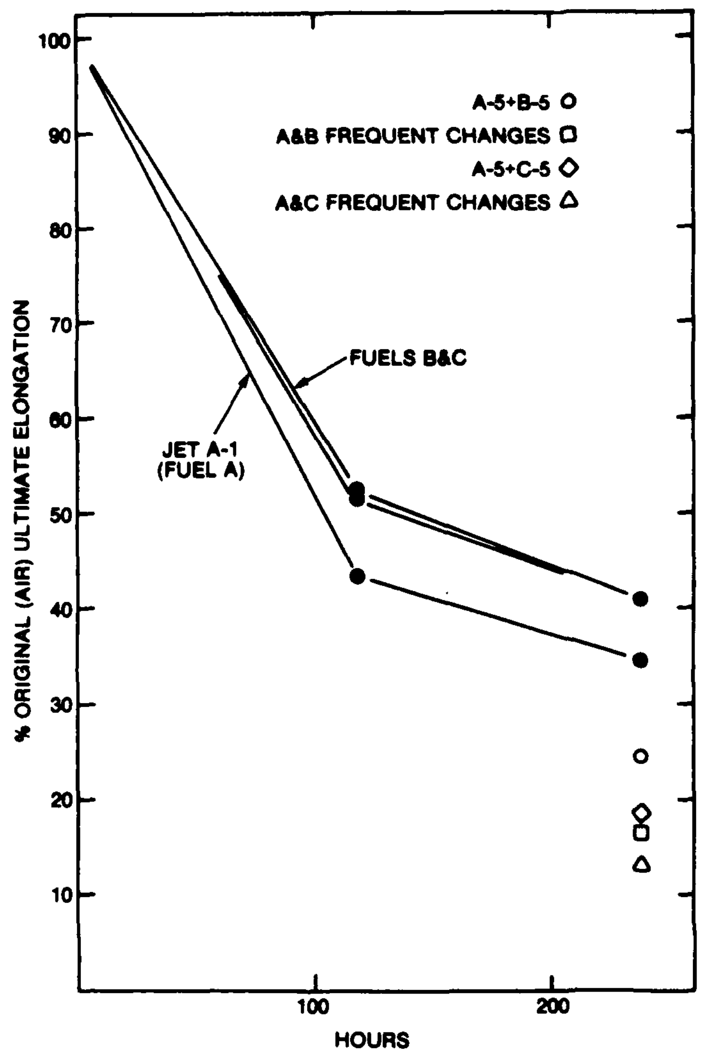

Fig. 9 Effect on ultimate elongation of cycling at 120°C between two fuels.

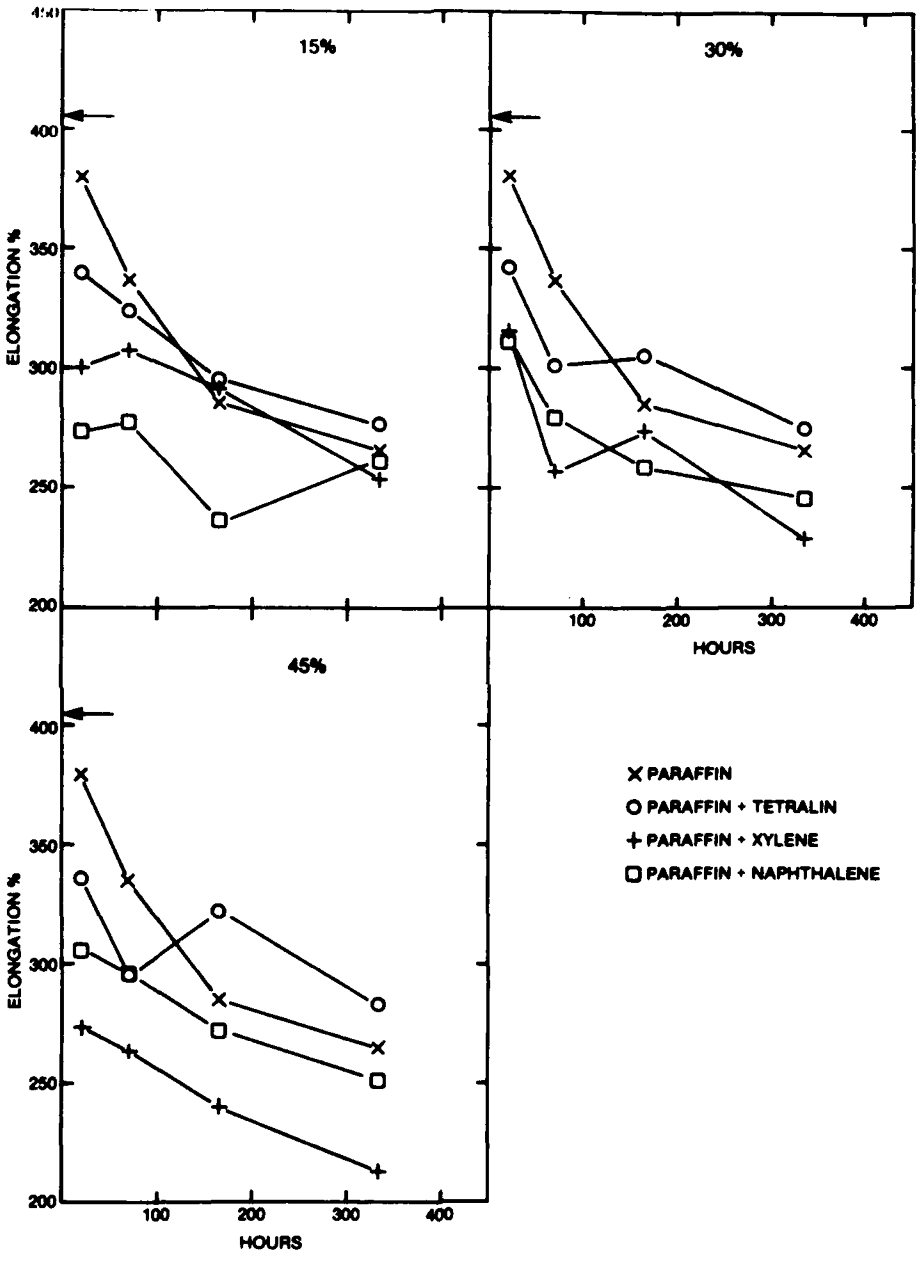

Fig. 10 Ultimate elongation as a function of incubation time at 100°C, in paraffin with aromatic additions at three levels. Arrow indicates initial (air) value of property.

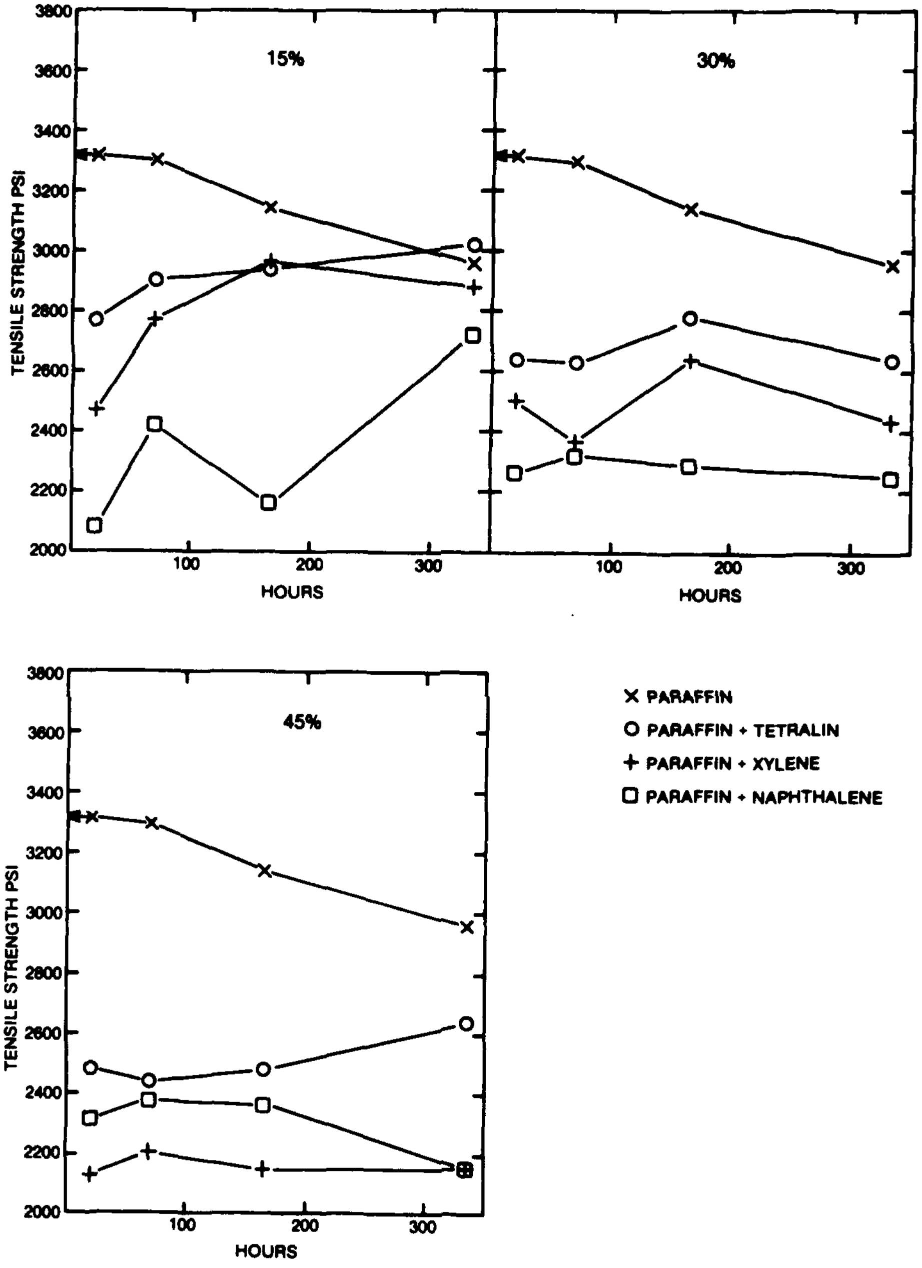

Fig. 11 Tensile strength as a function of incubation time at 100°C, in paraffin with aromatic additions at three levels. Arrow indicates initial (air) value of property.

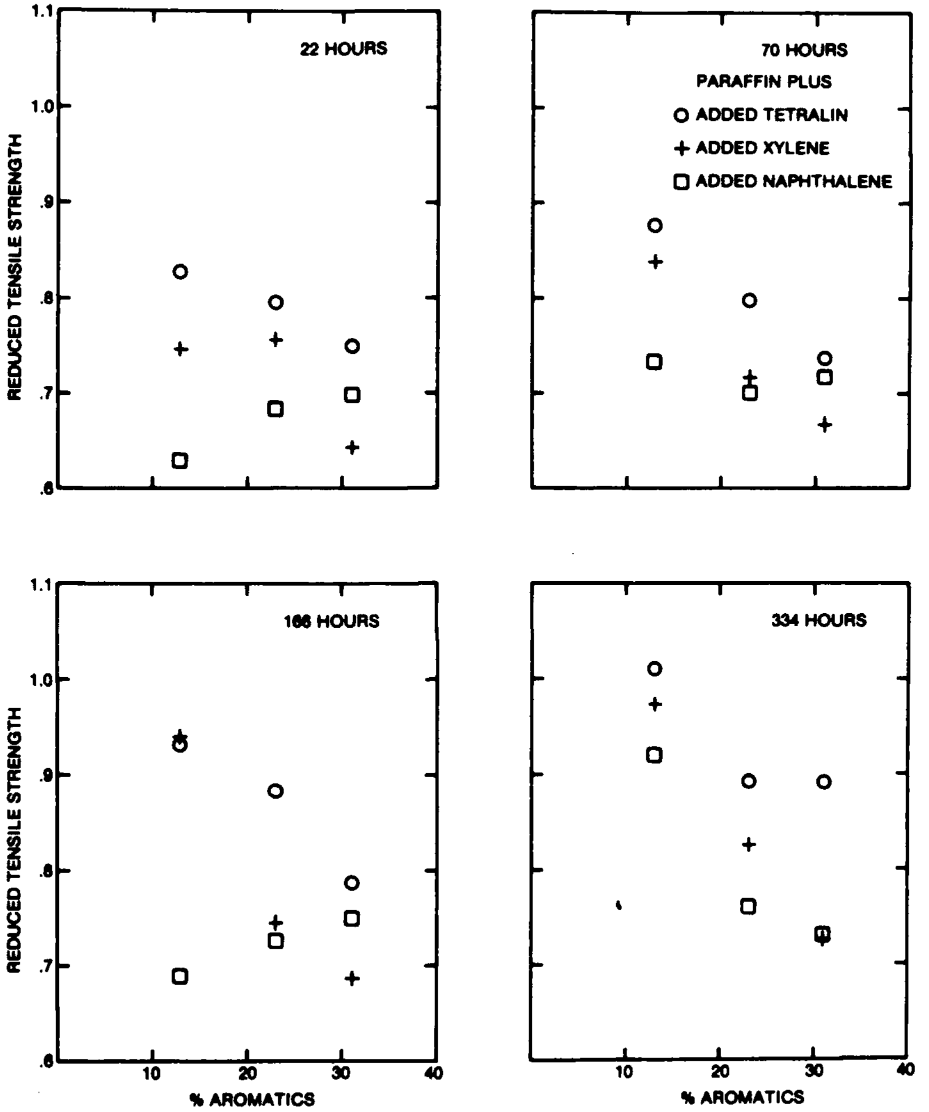

Fig. 12 Tensile strength of rubber exposed to various fuels, relative to that of rubber exposed to paraffin for the same periods.

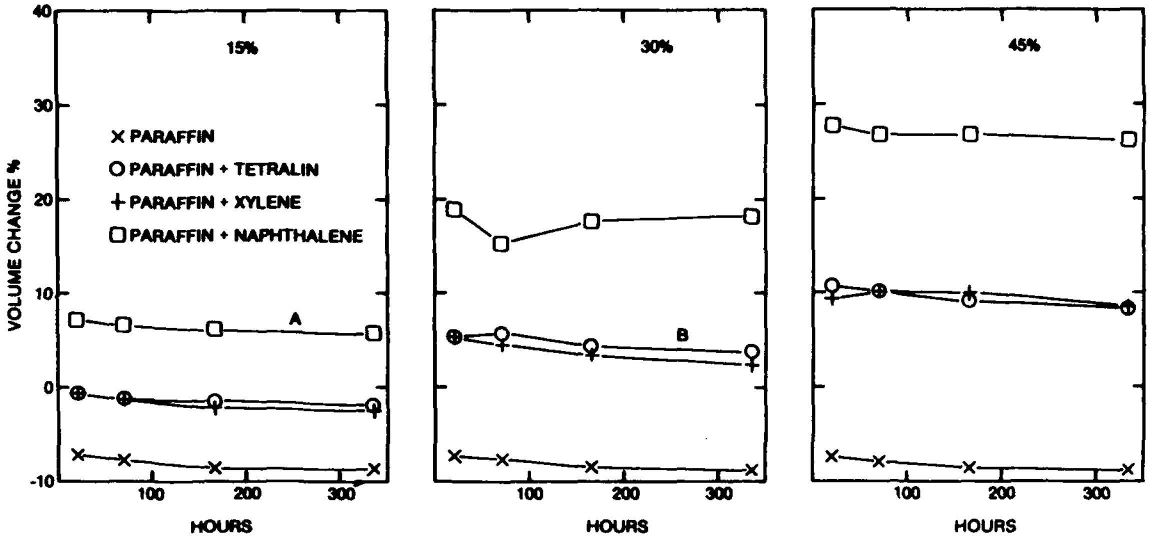

Fig. 13 Swelling as a function of incubation time at 100°C, in paraffin with aromatic additions at three levels.

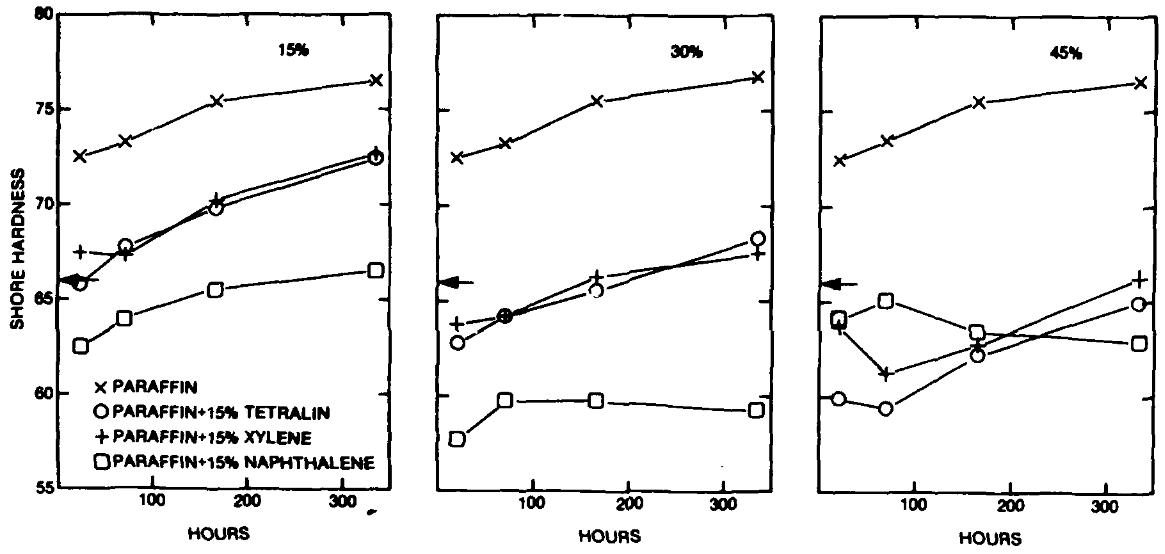

Fig. 14 Hardness as a function of incubation time at 100°C, in paraffin with aromatic additions at three levels. Arrow indicates initial (air) value of property.

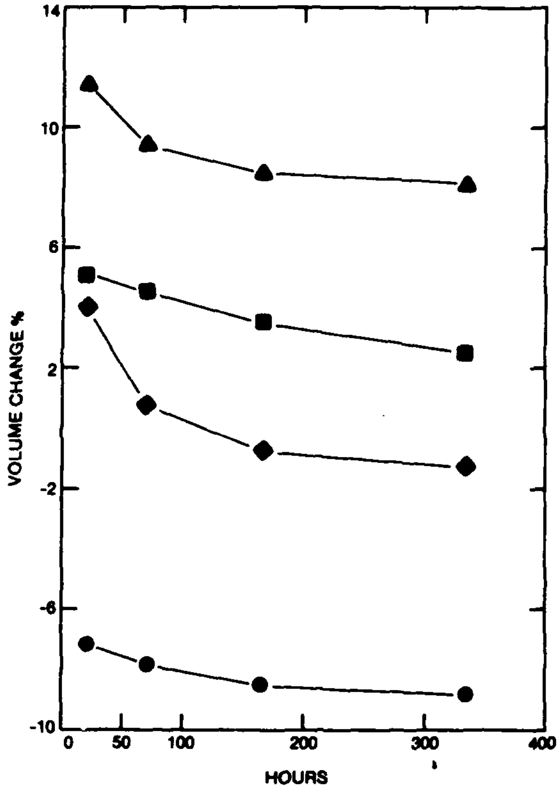

Fig. 15 Swelling as a function of exposure at 100°C to paraffin and to decane, with and without addition of xylene.

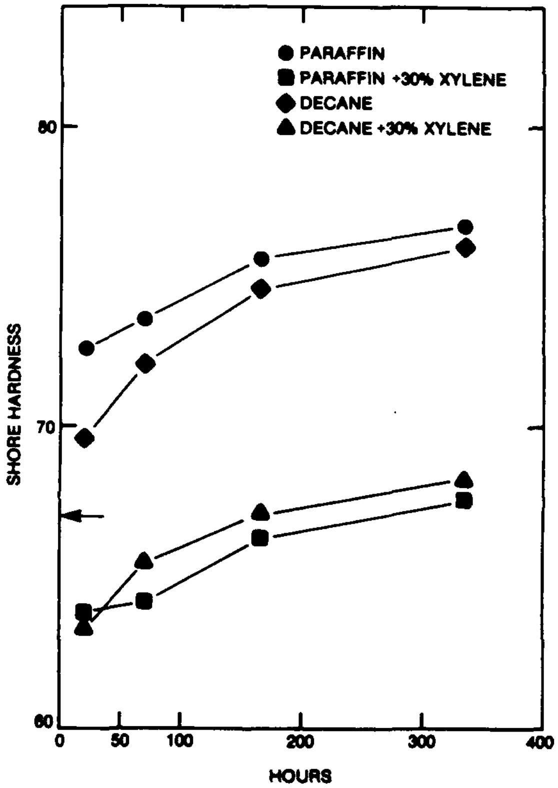

Fig. 16 Hardness as a function of exposure at 100°C to paraffin and to decane, with and without addition of xylene. Arrow indicates initial (air) value.

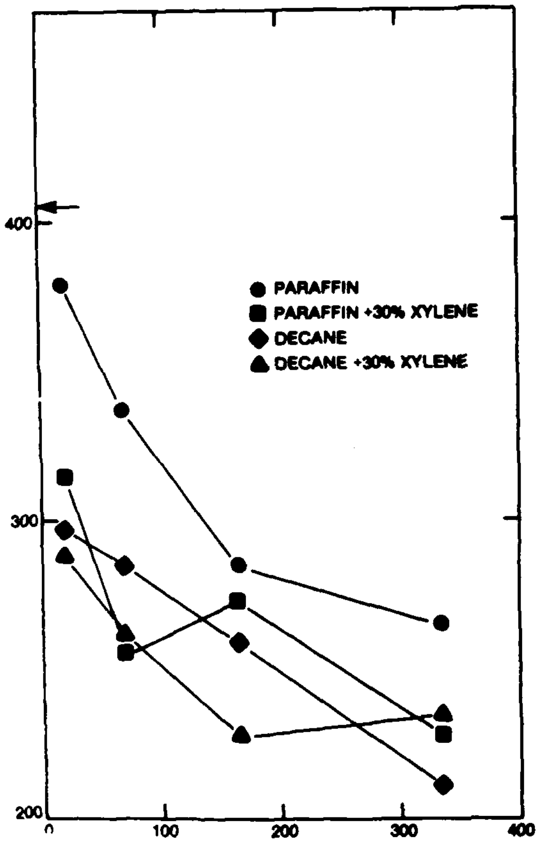

Fig. 17 Ultimate elongation as a function of exposure at 100°C to paraffin and to decane, with and without addition of xylene. Arrow indicates initial (air) value.

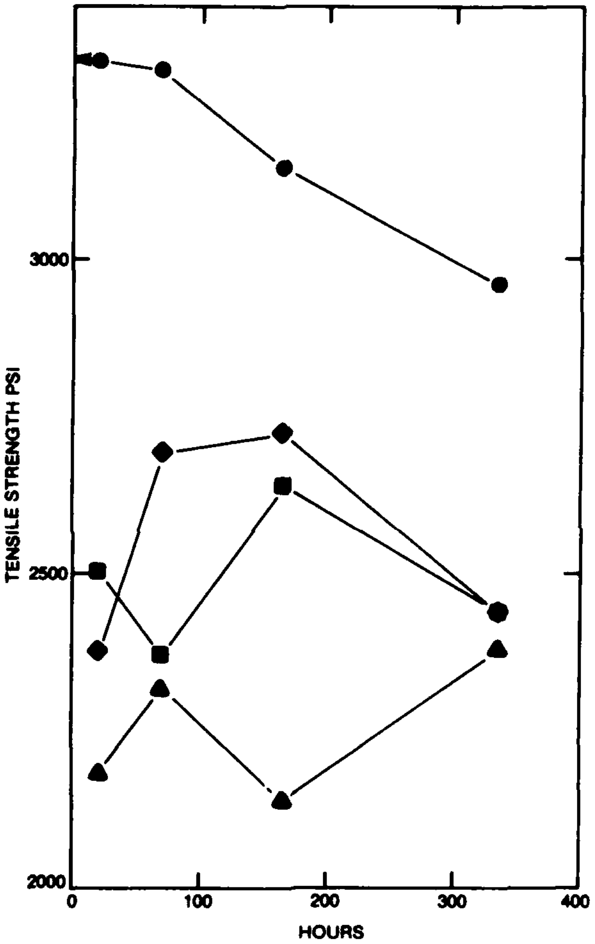

Fig. 18 Tensile strength as a function of exposure at 100°C to paraffin and to decane, with and without addition of xylene. Arrow indicates initial (air) value.

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13 ABSTRACT - UNCLASSIFIED

A nitrile rubber was incubated in fuels to which model aromatic compounds had been added at several levels. Changes in the rubber were determined by standard elastic property determinations after various periods of incubation. The main determinant of attack by the fuel was its aromatics level. Naphthalene was particularly effective in promoting swell and softening, but had about the same effect on elastic properties as mononuclear aromatics at the same level. Cycling of the nitrile rubber between two fuels of considerably different aromatics level degraded tensile properties to a greater extent than did exposure to either fuel alone for the same total period of time.

KEY WORDS

Nitrile Rubber
Fuel
Hydrocarbon
Physical Property
Compatibility

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