

# CORRELATION OF RUBBER PROPERTIES BETWEEN FIELD AGED TIRES AND LABORATORY AGED TIRES

DAVID R. BAUER, JOHN M. BALDWIN,\* KEVIN R. ELLWOOD  
FORD MOTOR COMPANY, DEARBORN, MI

## ABSTRACT

The kinetics of aging of key tire properties both in the field and in oven exposures at different temperatures has been interpreted by using a combination of empirical models and accelerated shift factors. Crosslink density and rubber modulus increase with aging while peel strength and elongation-to-break decrease. In the case of oven aging, the rate of property change increases from 40 °C to 70 °C and then decreases. In the case of field aging, the rate of property change is greatest in hotter climates such as Phoenix and is slower in cooler climates such as Detroit. Spare tires age at a rate that is ~70% as fast as on-road tires. Below 70 °C, the rate data for all of the aging changes can be fit to an Arrhenius relationship with an activation energy of ~69 kJ/mole, a value that is consistent with the aging process resulting from diffusion limited oxidation. The measured acceleration factor of oven aging at 70 °C relative to on-road aging in Phoenix is independent of the property change measured confirming that it is possible to chemically age tires in ovens. It takes 6-7 weeks of oven aging at 70 °C to produce a tire that is aged 4 years in Phoenix. Field results show that the rate of tire aging varies by over a factor of 5 for the different tire types and brands studied in this work. The implications for tire durability testing are discussed.

## INTRODUCTION

In previous papers, we have reported results on rubber property changes with aging in tires both obtained from the field and aged in laboratory ovens at different temperatures.<sup>1-5</sup> A single tire type and brand was aged for up to 12 weeks at temperatures ranging from 40 °C -100 °C. Property measurements included swelling ratio, modulus, peel strength and elongation-to-break in the skim and wedge regions of the tire. Swelling ratios were used to estimate relative crosslink densities using the standard Flory-Rehner relationship. Similar measurements were made on a number of different tire types and brands obtained at various times in service from different cities. The following summarizes the preliminary conclusions of those studies:

1. The crosslink density of rubber from both the skim and the wedge regions of all tires increases with aging time. The modulus at 100% strain also increases with aging time. The peel strength of the skim rubber and the elongation-to-break of the wedge rubber decrease with time. For a given tire, the different property changes are strongly correlated with one another independent of how the tires are aged. These changes are consistent with aging caused by oxidation.
2. The extent of rubber degradation during oven aging increased with increasing temperature up to 70 °C. Above 70 °C, the extent of aging in the wedge and skim decreased. The data at different temperatures obeyed time-temperature-superposition. The acceleration shift factors at the different temperatures (70 °C and below) obeyed an Arrhenius relationship with an activation energy of ~69 kJ/mole. This activation energy is consistent with diffusion limited oxidation. The reduction in aging above 70 °C can be attributed to oxygen starvation in the skim and wedge regions of the tire at the higher temperatures. This effectively limits the maximum oven aging temperature to 70 °C and below.
3. The relative property changes observed after field aging correlated well with those observed after oven aging (up to 70 °C). Property changes were larger in hotter cities

\* Corresponding author. Ph: 313-322-3284; Fax: 313-323-1129; email: jbaldw11@ford.com

(e.g., Phoenix). These results strongly suggest that field aging is also controlled by diffusion limited oxidation and that it should be possible to age tires under controlled laboratory conditions that will have the same "chemical" age as those found in the field.

In this paper, we extend the comparison of oven and field aged tires to include a detailed kinetic analysis of the property changes that occur under different exposure conditions. We first present empirical kinetic expressions that are useful in extracting relative rate constants for the different property changes. We compare the different property change rates as a function of oven temperature and field environment. We confirm that tire aging is controlled by diffusion limited oxidation. The temperature dependence of relative rates at 70 °C and below can be fit by a single activation energy and oven aging reproduces the changes observed in the field. Finally, we use the same kinetic analysis to compare field aging rates for different tire classes and brands and discuss possible methods to evaluate performance of aged tires.

## EXPERIMENTAL

### PHYSICAL PROPERTIES

*Peel Strength.* - Samples were prepared by cutting 2.5" (63.5 mm) wide radial sections, bead to bead. The sample was then sectioned into two 1.25" (31.75 mm) radial strips, which were each cut circumferentially at the centerline of the tread resulting in four test specimens (2 DOT side and 2 non-DOT side). Each sample was cut with a razor knife for a length of 1" (25.4 mm) from the skim end of the test strip, midway between the belts, to facilitate gripping the ends in the T-2000 Stress/Strain Tester jaws. The sides of each specimen were scored midway between the belts, to a depth of 1/8" (3.175 mm) radially from the end of the gripping surface to the end of belt #2 in the shoulder area, providing a 1" wide peel section. The peel test was performed at 2" per minute (50.8 mm/minute) at 24 °C.

*Tensile and Elongation.* - Samples of the belt wedge interply rubber, located between belts 1 and 2, were removed from both shoulders (DOT side and non-DOT side) of aged tires and buffed to a uniform thickness of 0.5 to 1.0 mm. Care was taken so that no significant heat was introduced to the samples by the buffing. Specimens were die-cut using an ASTM D 638 Type V dumbbell die and tested per ASTM D 412. Results obtained included modulus values @ 25%, 50%, 100%, and each 100% thereafter, ultimate elongation and tensile strength. Samples were tested at 20" per minute (50.8 cm/minute).

*Swelling Ratio.* - Measurements were made on skim rubber samples swollen to equilibrium in toluene after 24 hours. Five specimens were tested for each sample. The swelling ratio of the compound in the swollen gel was measured at equilibrium swelling. The swelling ratio of the rubber compound was not corrected for the presence of fillers.

*Crosslink Density.* - Crosslink density measurements were determined on samples swollen to equilibrium in toluene after 24 hours. Five specimens were tested for each sample. The volume fraction of polymer in the swollen gel was measured at equilibrium swelling and the crosslink density determined using the Flory-Rehner equation.<sup>6</sup> The polymer-solvent interaction parameter  $\chi$  with toluene as the swelling media for natural rubber, is 0.391.<sup>7</sup> The values were not corrected for filler content. It is recognized that the absolute value of the crosslink density calculated by this procedure may not necessarily be correct, however, the relative change in crosslink density should be more correct. Since the crosslink density values for any given tire construction are only compared within its group (*i.e.* not across manufacturers, for example) the

comparisons are valid. Moreover, it is often pointed out that if corrections for filler type and volume fraction (along with chain end corrections, accounting for non-contributing 'loops' and trapped physical crosslinks, *etc.*) are not made, then the value of the crosslink density, *per se*, is meaningless. In the research presented in this paper, however, the modulus and crosslink density are closely correlated. For a given sample, there is good agreement between the modulus change and the calculated crosslink density change, confirming the use of the Flory-Rehner equation in this application. The uncorrected, calculated crosslink density correctly predicts the experimental stress-strain curve up to 100% modulus, again validating the use of the uncorrected value of the crosslink density calculation.

#### MATERIALS

One tire type was used in the oven aging study, a Goodyear Wrangler AP<sup>®</sup> LT245/75R16 (DOT Code: MD11APWV4102 for Phase 1 and MD11APWV4003 for Phase 2). Tires were mounted and inflated to the maximum pressure listed on the sidewall prior to oven aging: 450 kPa (65 psi). In the case of tires inflated with the 50/50 blend of N<sub>2</sub>/O<sub>2</sub>, the atmospheric air present was not purged; the blend was added on top of it yielding a tire cavity concentration of approximately 44% O<sub>2</sub>. Two separate experiments were conducted. In Phase 1, tires were aged in air circulating ovens for 2, 4, 6, and 8 weeks @ 70 °C, 80 °C, 90 °C and 100 °C. In Phase 2, tires were aged in the same ovens for 3, 6, 9, and 12 weeks @ 40 °C, 50 °C, 60 °C and 70 °C. New tires were analyzed unaged and used as the baseline condition. The ovens were calibrated per ASTM E 145 with an A2LA approved, modified, method for temperature uniformity, consistency, air flow exchanges and airflow velocity.

#### KINETIC MODELS

Rubber aging has been studied extensively.<sup>6-7</sup> Aging can be divided between aerobic and anaerobic. Aerobic aging is controlled by the rate of oxidation, which in turn is a function of the permeation rate of oxygen to the location of interest and the rate of reaction of oxygen with that rubber. This is typically termed diffusion limited oxidation. At the rubber surface, permeation limits do not apply and the rate is just a function of oxygen reaction kinetics. In general the activation energy for oxidation is higher (90-110 kJ/mole) than that for permeation (30-35 kJ/mole). This means that at higher temperatures all oxygen may be consumed by reaction before it reaches a particular interior location. Under these conditions, degradation is dominated by anaerobic reactions. We have previously shown that for all field samples and for oven aging at 70 °C and below, aging of the rubber skim and wedge regions of tires is dominated by diffusion limited oxidation.<sup>1-5</sup> Studies of laboratory aging using different fill gases confirm this result and suggest that the oxygen is diffusing through the tire inner liner to reach these locations. Using nitrogen as a fill gas dramatically reduces property change at a given temperature while increasing the oxygen content of the fill gas or the inflation pressure increases the rate of property change. The kinetic models presented below are based on the assumption of aerobic oxidation.

The kinetics of aerobic oxidation in different rubber materials have been studied extensively by Gillen *et al.* through measurements of oxygen consumption rates, modulus profile, and elongation to break over a wide range of temperature and time. These studies demonstrated that under constant, controlled conditions, the oxygen consumption rate depended strongly on rubber composition, but for a given material, was relatively constant for long periods of time.<sup>8-11</sup> The rate of oxygen consumption increased with increasing temperature consistent with typical oxidation activation energies mentioned above (for these experiments, diffusion limitations were not an issue). The relative rates of oxygen consumption at different temperatures were consistent with accelerated shift factors derived from property change measurements such as modulus and

elongation to break implying that the property changes were controlled by the extent of oxidation over the whole temperature range. At low extents of oxidation, the increase in modulus was proportional to the extent of oxidation. At high oxidation levels, the modulus increased exponentially with oxidation. Crosslink density and modulus are strongly correlated. At relatively low oxidation levels, the number of reactive sites is large compared to number of sites that have reacted (oxidized). Thus, one would expect that the change in crosslink density (and modulus) would be proportional to the extent of oxidation. Over the range of aging observed in our studies, we find that both the modulus and crosslink density of the skim and wedge rubber in tires can be fit to a simple linear equation in time,

$$A(t) = A(0)(1 + \alpha t) \quad (1)$$

where the rate constant  $\alpha$  reflects the oxidation rate and its effect on modulus or crosslink density. Thus,  $\alpha$  will depend on the intrinsic oxidation rate of the rubber material of interest, the permeation rate of oxygen between the rubber sample and the oxygen source, and composition factors that influence the exact products of oxidation (crosslinking vs. scission). We expect the values of  $\alpha$  to be different for different rubber compositions in the same tire and even for the same composition in different locations within the tire. For similar locations, the values of  $\alpha$  for modulus and crosslink density should be similar (this is the reason that we have chosen to analyze crosslink density rather than swelling ratio). It should be noted that crosslink density and modulus are affected not only by oxidation but also by state of cure. Post-curing reactions that occur after molding typically increase the crosslink density and modulus by 5-10% after molding. Post-curing is rapid relative to oxidation. Formally, the initial values in equations 1 and 2 represents the values after post-cure but before any oxidation has occurred. In practice, the time zero values are not included in the fit since they may not have been fully post-cured.

For properties such as peel strength and elongation to break, which decrease with oxidation, a different empirical relation has to be used. Gillen *et al.* have used the accelerated shift factor technique to determine the time dependence of the loss of elongation to break for typical rubbers out to less than 5% property retention.<sup>11</sup> We have found the this data can be fit to the following expression,

$$B(t) = \frac{B(0)}{(1 + \beta t)} \quad (2)$$

where the rate constant  $\beta$  reflects the oxidation rate and its effect on loss of elongation. The fit of Equation (2) to typical experimental data of Gillen *et al.* is shown in Figure 1. Equation (2) matches the experimental data almost exactly from 5% to 90% property loss. This is a significantly larger range of property loss than we observe in the tire aging studies. Based on the excellent agreement shown in Figure 1, we will use Equation (2) to determine the rate of loss of elongation-to-break in the wedge rubber of tires under different exposure conditions. We will use the same expression to determine the rate of loss of peel strength of skim rubber. Note that in previous work, peel retention data were fit to a logarithmic dependence on time. From Figure 1, it is clear that Equation (2) can be fit to a function that is linear in  $\log(\text{time})$  over much of the range of the data. The advantage of Equation (2) over the earlier logarithmic fits is that it correctly fits the short time data.

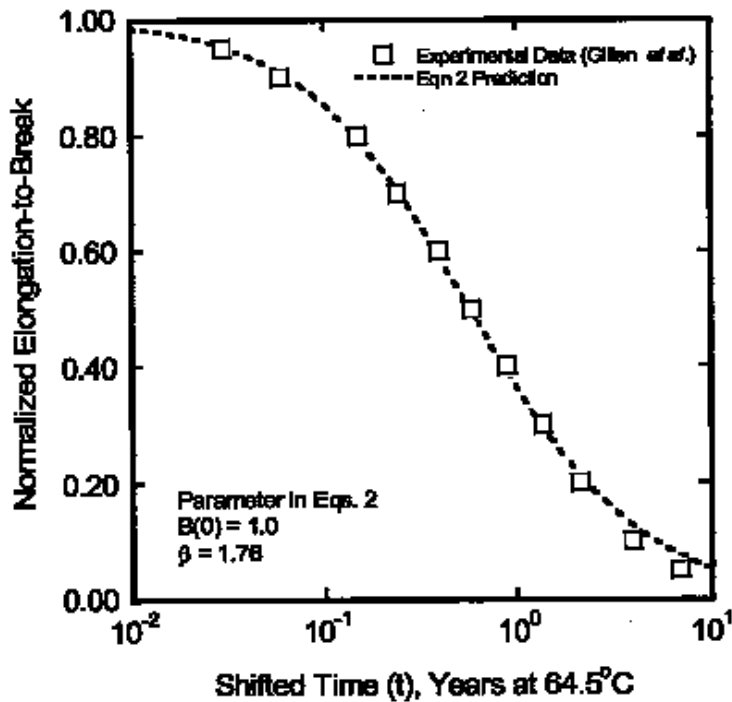


FIG. 1. — Elongation-to-break versus shifted time for nitrile rubber. The data is interpolated data taken from Figure 3 from Ref.<sup>11</sup>. The solid line is the best fit to Equation 2. Note the log scale in time.

In previous work, we have used the accelerated shift factor approach to derive relative rate constants. The shift factor approach makes no a priori assumptions regarding the shape of the aging curve. It requires, however, accurate values for the initial properties and overlapping measurements for different conditions. For the oven aging studies the accelerated shift factor approach and the use of Equations (1) or (2) yield essentially identical results. In fact combining the two approaches (*i.e.*, using the analytic form to guide the shifting) improves the precision of the somewhat limited data sets available. In the case of field data, a combination of uncertainty due to possible changes over time of the initial values and limited range of aging in many locations makes the accelerated shift factor approach difficult to apply. In particular, it is difficult to compare results from different tire sets. By fitting to an analytic form (Equations (1) or (2)), it is possible to compare more easily the different field results with one another and to compare field results with the oven results.

## RESULTS AND DISCUSSION

### LABORATORY OVEN AGING

The kinetics of laboratory oven aging are shown in Figures 2-5 for skim crosslink density, wedge modulus, wedge elongation-to-break, and skim peel strength. Data are shown for temperatures from 40 - 70 °C and for fill gasses of air and a 50-50 blend of oxygen and nitrogen (in the absence of purging, this effectively doubles the initial concentration of oxygen in the tire) at a pressure of 450 kPa (65 psi). The shift factors for the different temperatures are adjusted to yield the best fit to Equations (1) or (2). For these cases, using Equations (1) or (2) to guide the determination of the shift factors does not significantly affect the results that would have been

obtained using the shift factor approach alone. As we shall see, the value of the use of the empirical expressions is in relating the rates in the oven with the rates in the field for different locations and tire types. The values for the rate constants  $\alpha$  and  $\beta$  are given in Figures 2-5 for the different property changes at 40 °C. As expected, the rate constants for crosslink density and modulus change on aging are similar. The rate constants for loss of elongation and peel strength are 3-4 times larger than those for crosslink density and modulus suggesting that oxidation has a larger relative effect on loss of elongation and peel strength than on increase of modulus or crosslink density. The data shown in Figures 2-5 include both air and 50/50 oxygen/nitrogen fill gasses. It was assumed that the effect of fill gas composition was independent of temperature. The use of a 50-50 blend of oxygen-nitrogen effectively increases the oxidation rate by a factor of  $1.4 \pm .05$  versus air for the different property changes. (The fact that doubling the oxygen concentration does not double the oxidation rate is consistent with the basic model of rubber oxidation)<sup>11</sup> The relative rates at different temperatures are shown in the Figures. Aging at 70 °C is roughly 11 times faster than aging at 40 °C. An Arrhenius plot of the relative rate constants versus temperature is shown in Figure 6. The activation energy for all of the property change rates is ~69 kJ/mole. As discussed in the Introduction, this is consistent with previous analysis of this data. The measured activation energy falls in between those measured for rubber oxidation and permeation. This is consistent with the prediction for the total flux of oxygen into a semi-infinite slab.<sup>4,12</sup> For this case, the flux can be shown to be given by,

$$f_{O_2} = C_0(Dk)^{\frac{1}{2}} \quad (3)$$

where  $D$  is the diffusivity of oxygen;  $k$  is the first order rate constant for oxidation; and  $C_0$  is the equilibrium oxygen concentration at the sample surface. The activation energy for a flux given by Equation (3) is just the average of the activation energies for diffusion and oxidation. It is interesting to note that this average value ranges from 60-73 kJ/mole, which is consistent with our measured value.

Relative rates for field data from different cities for a tire that is the same size as that used in the oven aging experiments are also shown in Figure 6. A discussion of these results will be presented below.

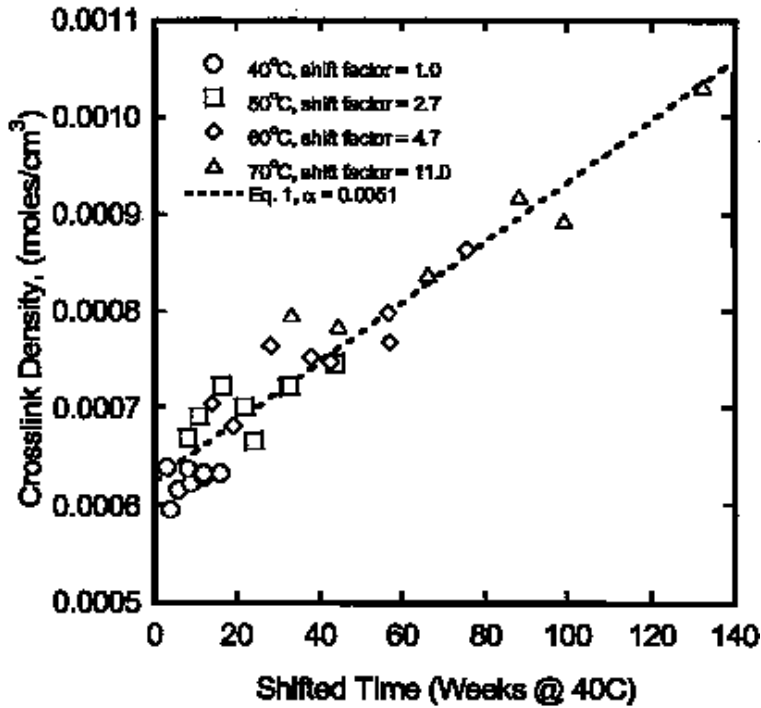


FIG. 2. — Skim crosslink density versus oven aging time for temperatures from 40 °-70 °C. The acceleration shift factors are shown in the legend. The solid line is the fit to Eq. (1), with the rate constant in weeks<sup>-1</sup> at 40 °C.

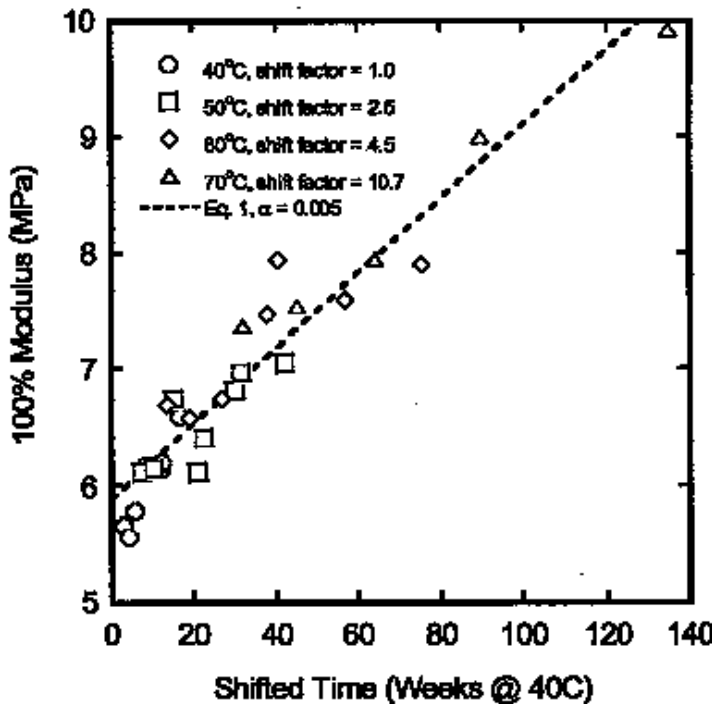


FIG. 3. — Wedge modulus versus oven aging time for temperatures from 40 °-70 °C. The acceleration shift factors are shown in the legend. The solid line is the fit to Eq. (1), with the rate constant in weeks<sup>-1</sup> at 40 °C.

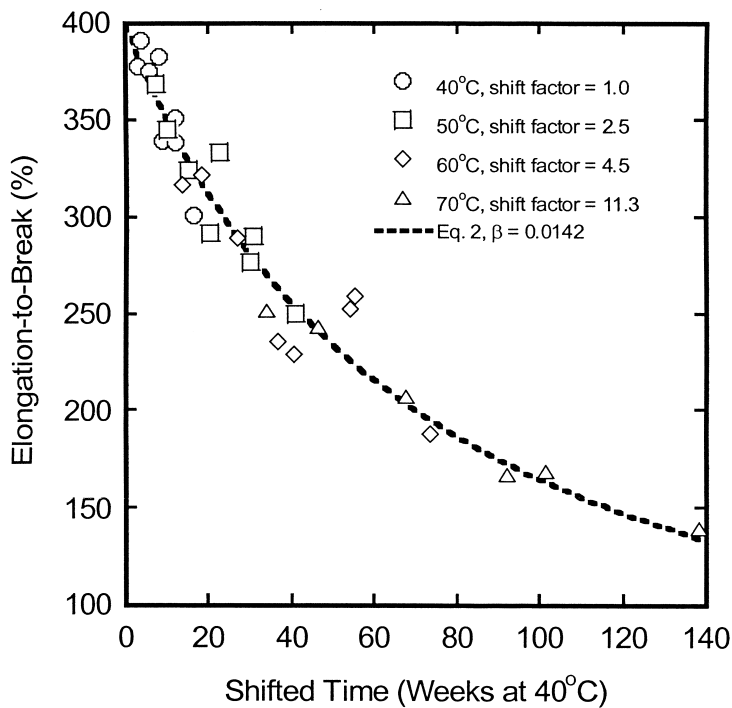


FIG. 4. — Wedge elongation-to-break versus oven aging time for temperatures from 40 °-70 °C. The acceleration shift factors are shown in the legend. The solid line is the fit to Eq. (2), with the rate constant in weeks<sup>-1</sup> at 40 °C.

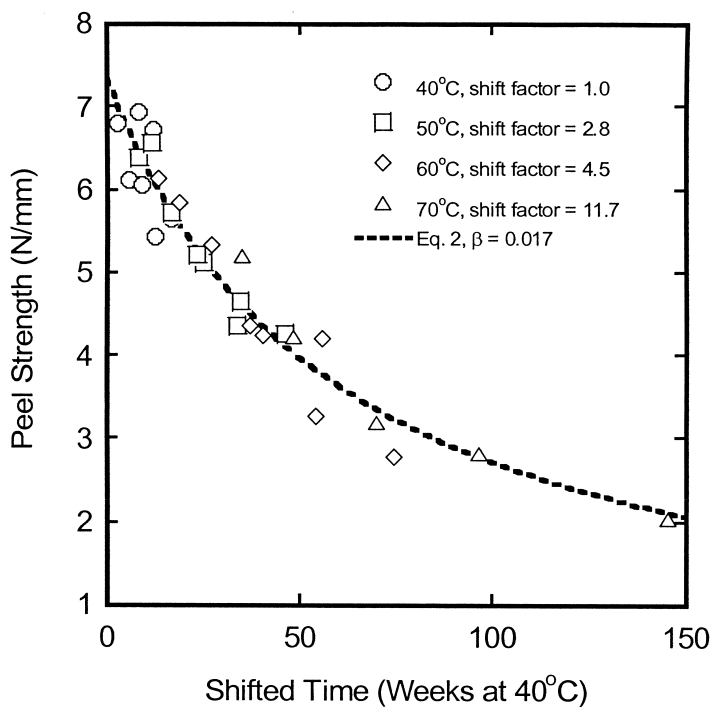


FIG. 5. — Skim peel strength versus oven aging time for temperatures from 40 °-70 °C. The acceleration shift factors are shown in the legend. The solid line is the fit to Eq. (2), with the rate constant in weeks<sup>-1</sup> at 40 °C.



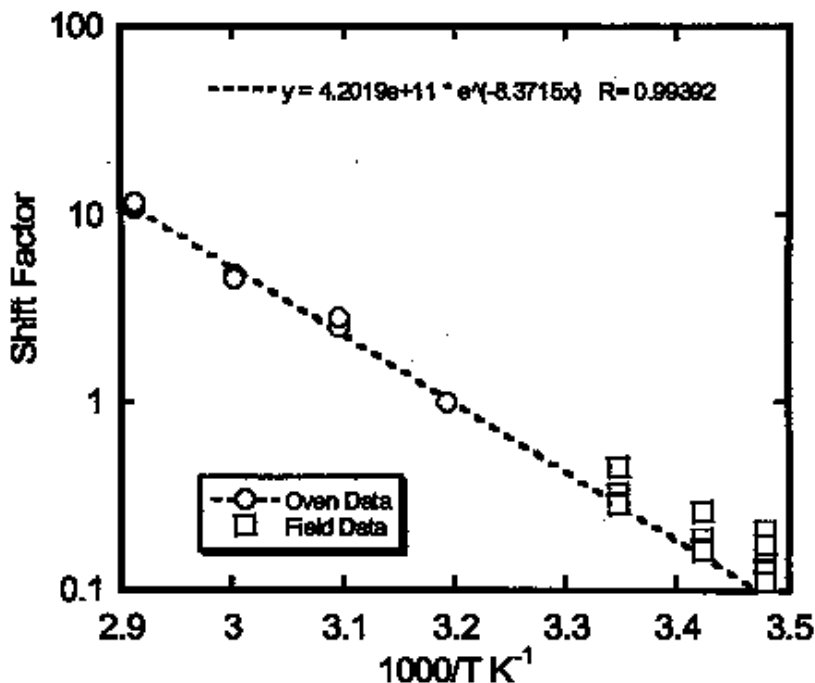


FIG. 6. — Shift factor versus  $1/T$  for the different property changes. The shift factors have been normalized to  $40^\circ\text{C}$ . The oven data cover the range  $40^\circ\text{C}$  to  $70^\circ\text{C}$ . The activation energy is  $69\text{ kJ/mole}$ . The field data are from Phoenix, Los Angeles, Detroit, and Hartford.

#### FIELD AGING

In order to quantitatively understand the effects of mileage, age, environmental conditions, and vehicle interactions on the steel belt package of a radial tire, a study was conducted to retrieve and analyze tires from end-users. Once the owner was interviewed about driving and maintenance habits and the tires were accepted into the study, shearographic analysis of the tires were performed along with other non-destructive testing. The tires were then dissected and analyzed for tensile and elongation properties of the rubber at the belt edges. Crosslink density measurements were made across the belt skim rubber, along with the peel adhesion force required to separate the two steel belts. The complete study involved tires from six cities: Detroit, Phoenix, Los Angeles, Hartford, Miami, and Denver. Vehicle types ranged from small cars to pick-up trucks and encompassed both passenger and light truck tires from three OE tire manufacturers. The environmental factors used to choose the cities were average temperature, ozone concentration, and road roughness. Approximately 2,500 tires were collected from the field, of which around 1,500 were dissected and analyzed.

As will be seen below, field aging data exhibits significantly more variability than the laboratory oven aging data. There are several possible reasons for this higher variability including variations caused by customer use, vehicle variability, and variability in the tires themselves. This latter seems likely to be the most important source of variability. Tires of a given type and brand evaluated in this study were produced over a  $>4$  year time period at different plants. It is to be expected that both the initial property values and factors that influence oxidation rates (such as inner liner composition and thickness) may vary significantly over such a time period even for manufacturing processes that are reasonably controlled.

In order to determine the effects of environment (*i.e.* city) and on-road versus spare tire aging, it is advantageous to study tires that age the fastest, to utilize as many tries as possible,

and to compare properties that change the most. Figure 7 shows the loss of peel strength for a set of two tire types for four different cities. The tires are from the same manufacturer, are similar in size, and have been found to age nearly identically. Again, we have used the approach of shifting the data from the different cities onto a single master curve (Equation (2)). It is clear that tires age fastest in Phoenix and slowest in Detroit and Hartford, with Los Angeles falling in between. This correlates with the ambient temperatures in the four cities. Other factors such as ozone concentration or humidity do not appear to be important in the aging of these properties. If ozone had been an important factor, aging in Los Angeles should have been larger. It is not surprising that ozone does not have an effect on the skim or wedge rubber in tires. Ozone is so reactive that it does not have the opportunity to diffuse into the tire. Limited tire aging data was obtained for Miami. The aging rates were similar to those for Phoenix suggesting that humidity is not an important factor. All of the tires in Figure 7 were on-road tires. Aging of spares are compared with on-road tire aging in Figure 8. On-road tires age roughly 1.25 times faster than spare tires independent of property. That is, the ratio of the rates of crosslink density increase and peel strength loss are the same independent of whether or not the tire is a spare. This suggests that the difference in rate is due to the fact the on-road tires see a somewhat higher temperature history than spare tires due to a combination of sun load and tire heating during driving. It is important to note that on-road tires are typically driven around 5% of the time. Even though the skim/wedge region may see a significant temperature rise (20-40 °C) during a drive cycle, the overall effect is still relatively small due to the small fraction of time the tire is exercised. Similarly, sun load would be expected to have a relatively minor effect, since the vehicle shades most of the tire.

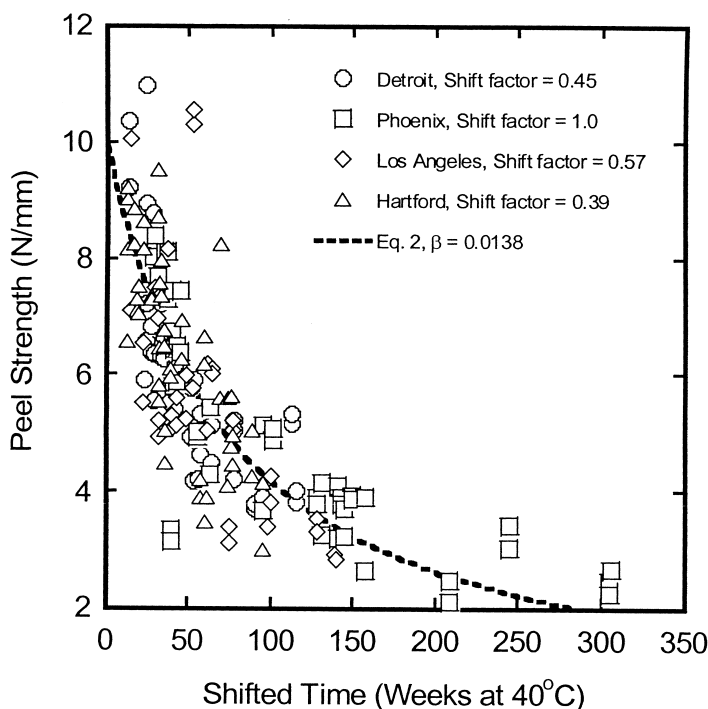


FIG. 7. — Loss of peel strength versus shifted time in Phoenix for a combination of tires AA and BA. Detroit and Hartford age more slowly than Phoenix with Los Angeles being intermediate.

As noted earlier, the tire types in Figure 7 and 8 age relatively rapidly compared to other tires in the study. Field aging behaviors for tire DC are shown in Figures 9-12. This tire has an aging rate that is roughly in the middle of the tires evaluated in this study. Data from on-road tires for all four cities has been used using the same city shift factors in Figure 7. Despite the large variability in the field data, it is possible to extract average aging rates for the different property changes. One of the most important results of the field study is the comparison of aging rates of different tire types and brands. Typical behavior for three different tires is shown in Figure 13. Some tires age very slowly, while others lose properties significantly at 4 years in Phoenix. The average rate of peel strength loss and elongation to break for all of the tires studied here are shown in Figure 14. The relative aging rates for different tires vary by a factor of 6.

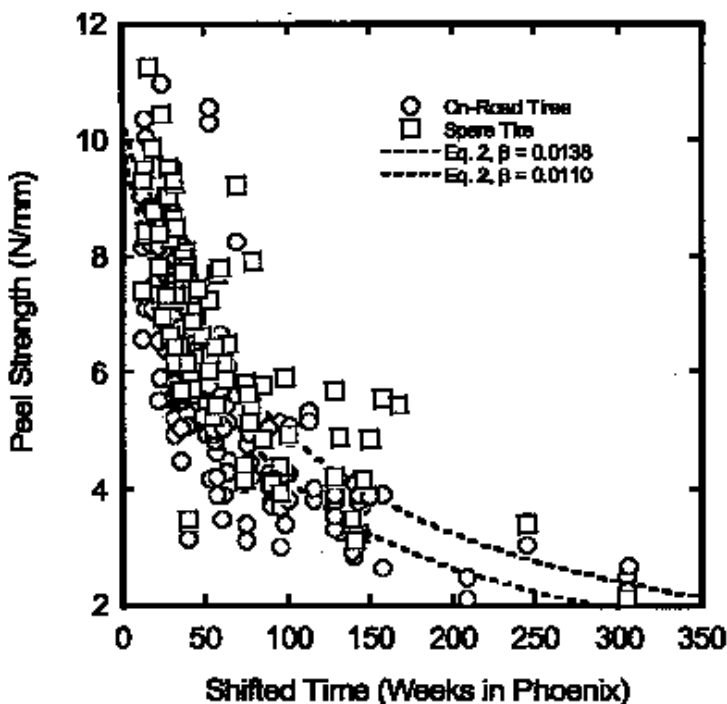


FIG. 8. — Comparison of loss of peel strength for spare and on-road tires. The tires were AA or BA and the city shift factors were the same as for Figure 7.

None of the tires in the field study represent exactly the tire used in the oven aging study. The tire in the field study that most closely matches the oven aged tire for size and initial properties is tire AC. While the field data for tire AC is not as extensive as that for other tires in the field study, it is sufficient to extract reasonable estimates for the different property aging rates (see Figure 13, for example). The rate constants for the different property changes in the field for Tire AC are compared with those for oven aging at 70 °C in Table I. For these tires the correlation of rate of property change in the oven and Phoenix are remarkable considering the significant variability of the field data and the fact that the tires are not identical. This together with the previous analysis<sup>2</sup> strongly suggests that it should be possible to chemically age tires that are representative of tires aged in the field using conventional air circulating ovens. A ratio of ~34 suggests that 6-7 weeks at 70 °C produces a tire that is equivalent in age to a tire that has been on the road in Phoenix for 4 years. That this acceleration is simply due to temperature can be confirmed by calculating an “activation energy” weighted temperature for each city using monthly

ambient average temperature data. The weighted ambient temperatures range from 25.5 °C in Phoenix to 14.2 °C in Detroit and Hartford. The relative rates for aging in the field are compared to those in the oven in Figure 6. The field data exhibit a temperature dependence that is reasonably similar to the oven data consistent with diffusion limited oxidation being the basic aging mechanism in both field and oven. Field aging appears to be roughly 10-50% faster than that predicted by extrapolation of the oven aging. This can be accounted for by the fact that the temperatures are based on ambient data. The field data is for on-road tires whose temperature history will be somewhat higher than ambient for a number of reasons including heating from driving, sun load, and convective heating from the road surface. A factor that compensates in part for the higher on-road temperature relative to ambient is the pressure of the tires in the oven aging test. The oven test used a pressure of 450 kPa (65 psi), which is likely to be higher than that for the field tires. A higher pressure would lead to a slightly higher aging rate.

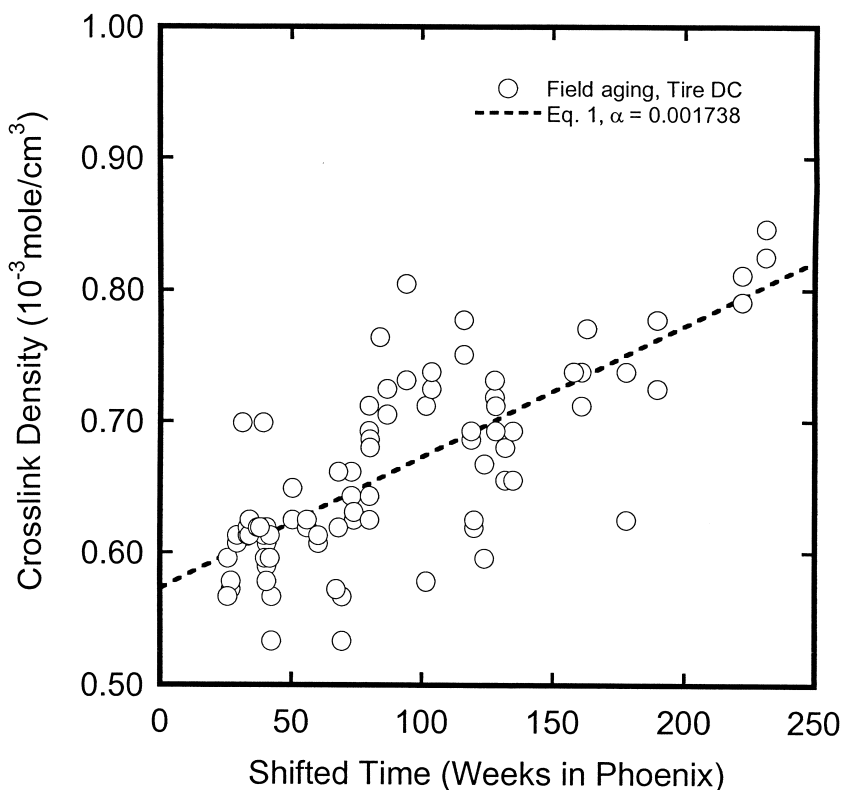


FIG. 9. — Skim crosslink density versus field aging time (weeks in Phoenix) for tire DC. The shift factors for aging in the different cities were the same as for Figure 7. The rate constant (weeks<sup>-1</sup>) for the fit to Equation (1) is shown in the legend.

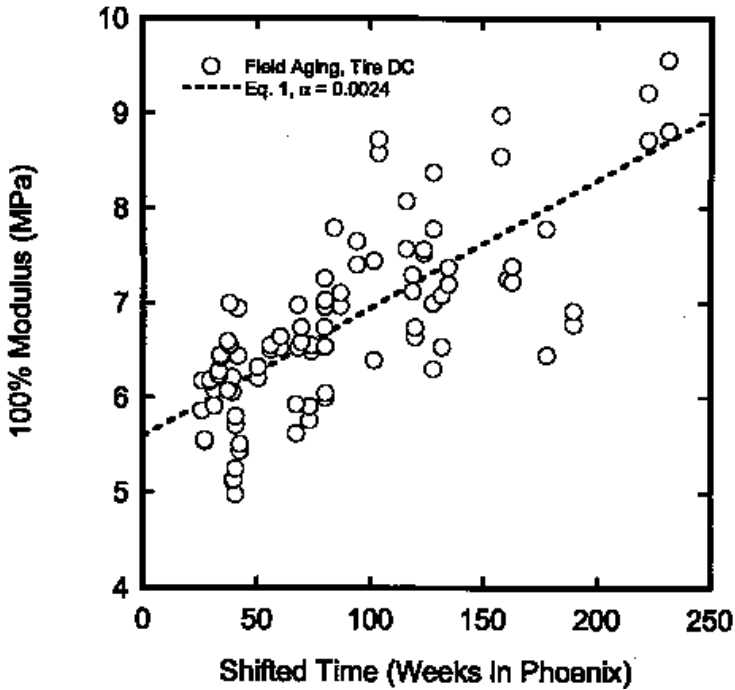


FIG 10. — Wedge modulus versus field aging time (weeks in Phoenix) for tire DC. The shift factors for aging in the different cities were the same as for Figure 7. The rate constant (weeks<sup>-1</sup>) for the fit to Eq. (1) is shown in the legend.

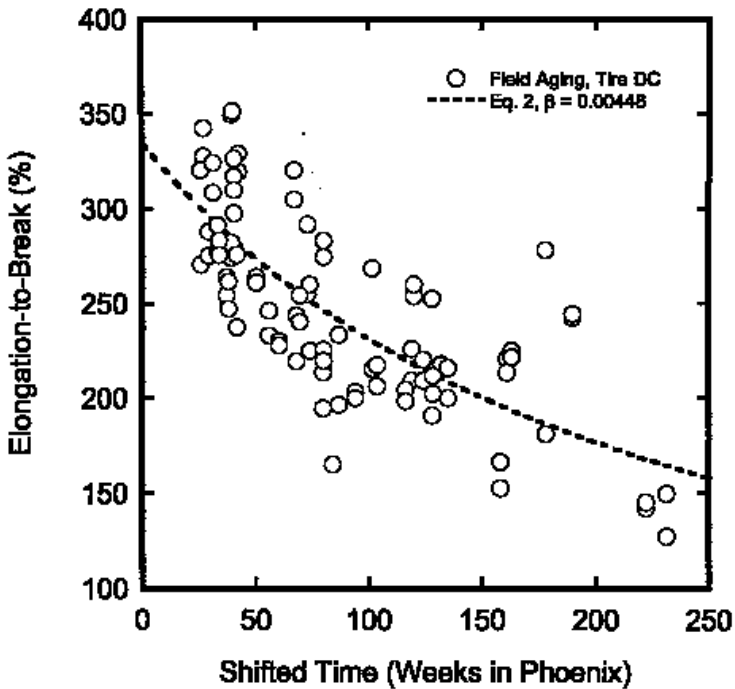


FIG 11. — Wedge elongation-to-break versus field aging time (weeks in Phoenix) for tire DC. The shift factors for aging in the different cities were the same as for Figure 7. The rate constant (weeks<sup>-1</sup>) for the fit to Eq. (2) is shown in the legend.

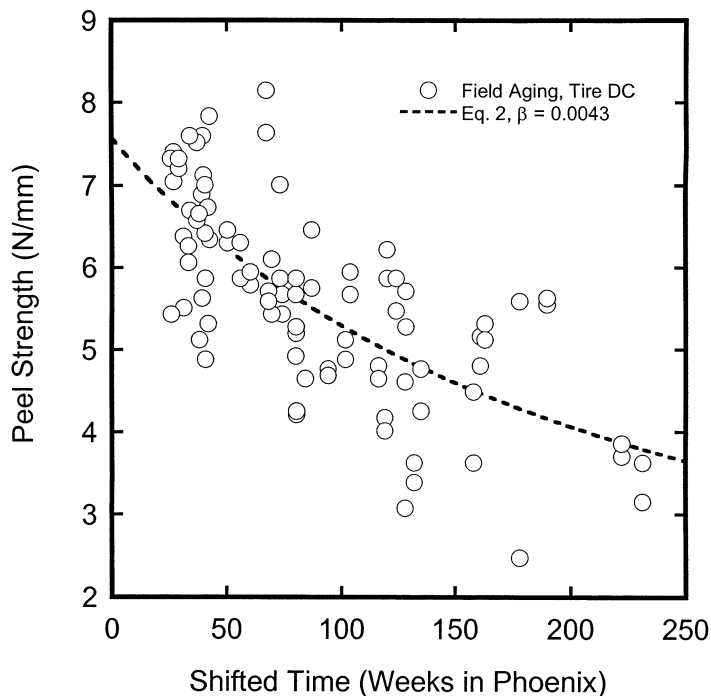


FIG. 12. — Skim peel strength versus field aging time (weeks in Phoenix) for tire DC. The shift factors for aging in the different cities were the same as for Figure 7. The rate constant (weeks<sup>-1</sup>) for the fit to Eq. (2) is shown in the legend.

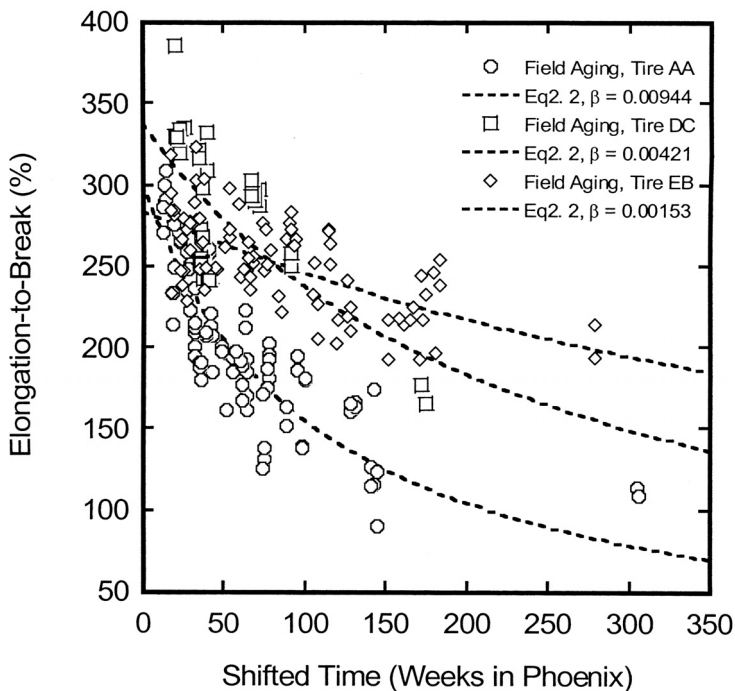


FIG. 13. — Comparison of loss of elongation-to-break with aging time for 3 different tires. The shift factors for aging in the different cities were the same as for Figure 7. The rate constants (weeks<sup>-1</sup>) for the fits to Eq. (2) for the different tires are shown in the legend.

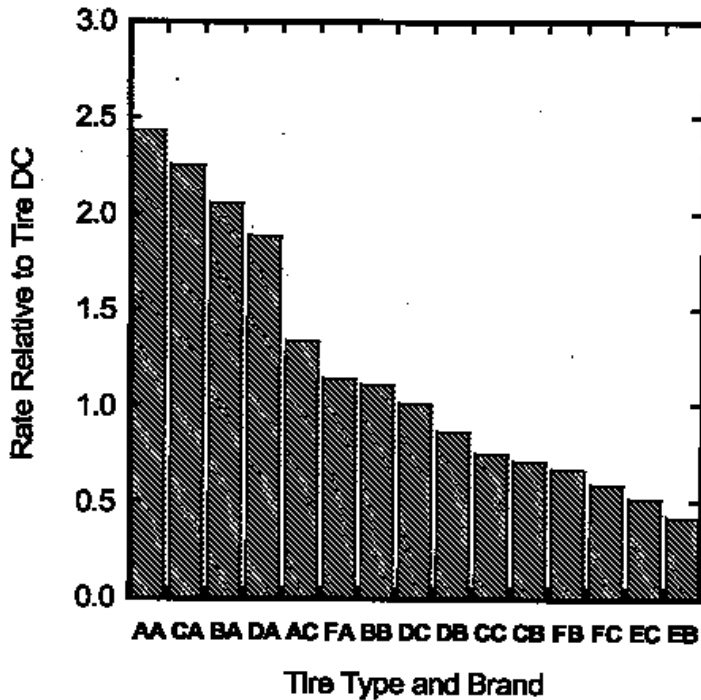


FIG. 14. — Relative aging rates for 15 different tires. The tires vary by type and brand. Aging rates are an average of the rates for loss of elongation and peel strength based on field aging results.

While the correlation established in this work is promising, for oven aging to be a useful predictor of field aging, it is necessary to establish a correlation in aging rates for different tire sizes and brands. This study is underway and will be the subject of future reports. The next question is how to evaluate aged tires. There are several possible approaches. One approach would be to measure key properties related to the failure modes of interest and to set property retention requirements after a given amount of aging. For example, in the case of belt-to-belt separation, peel strength is a key material parameter. One could choose to set peel strength retention of 50% after the equivalent of some years of aging in Phoenix. Another approach would be to develop a road wheel test for aged tires. An important consideration in this approach is the observation that even though oven aging is chemically equivalent to on-road aging, it is not mechanically equivalent. On-road tires invariably contain microcracks that are not present after oven aging alone. One of the components of the road wheel test would have to induce such cracks prior to other testing. Finally, it should be possible to evaluate the performance of aged tires using vehicle durability tests. We are currently exploring all of these options.

TABLE I  
COMPARISON OF OVEN AGING OF GOODYEAR WRANGLER AP® LT245/75R16 TO FIELD AGING (PHOENIX) OF TIRES AC

Property	Rate at 70 °C	Rate in Phoenix	Acceleration factor
Skim crosslink density	0.059	0.00175	34
Wedge modulus	0.061	0.00166	37
Wedge elongation-to-break	0.168	0.0042	40
Skim peel strength	0.216	0.0084	26
		Average	34+6

Note: The rates at 70 °C were determined from the rate at 40 °C and the shift factor at 70 °C using the data in Figures 2-5. The rates in Phoenix for tire AC have been analyzed in a manner similar to that shown for Tire DC in Figures 9-12.

## CONCLUSION

We have used simple empirical expressions and the shift factor method to compare property changes in key tire materials as a function of oven aging temperature and field location. We find that crosslink density and modulus increase, while elongation-to-break and peel strength decrease with aging. These changes are consistent with aging that results from diffusion limited oxidation. For a given tire and property change, the rate of aging is determined by the temperature of the tire. The activation energy is ~69 kJ/mole. Comparison of rates in the oven and in the field suggest that 6-7 weeks of oven aging at 70 °C is equivalent to 4 years on the road in Phoenix. The exact temperature and fill gas that provides the most consistent acceleration factor will be determined from oven aging studies of a number of different tire types and brands. The field aging studies indicate that different tire types and brands age at dramatically different rates. We are in the process of developing aging tests that combine oven aging with mechanical testing to predict tire durability.

## REFERENCES

- <sup>1</sup>J. M. Baldwin, "Accelerated Aging Of Tires, Part I," Paper #34, presented at a meeting of the Rubber Division, American Chemical Society, Cleveland, OH, October 14-16, 2003.
- <sup>2</sup>J. M. Baldwin, D.R. Bauer, and P.D. Hurley, "Field Aging Of Tires, Part II," Paper #29, presented at a meeting of the Rubber Division, American Chemical Society, Columbus, OH, October 5-8, 2004.
- <sup>3</sup>J. M. Baldwin, D. R. Bauer, and K. R. Ellwood, "Accelerated Aging Of Tires, Part III," Paper #30, presented at a meeting of the Rubber Division, American Chemical Society, Columbus, OH, October 5-8, 2004.
- <sup>4</sup>J. M. Baldwin, D. R. Bauer, and K. R. Ellwood, "Accelerated Aging Of Tires, Part II," presented at a meeting of the Rubber Division, American Chemical Society, Grand Rapids, MI, May 17-19, 2004.
- <sup>5</sup>J. M. Baldwin, M.A. Dawson, and P.D. Hurley, "Field Aging Of Tires, Part I," presented at a meeting of the Rubber Division, American Chemical Society, Cleveland, OH, October 14-16, 2003.
- <sup>6</sup>J. R. Shelton, *RUBBER CHEM. TECHNOL.* **56**, G71 (1983).
- <sup>7</sup>R. W. Keller, *RUBBER CHEM. TECHNOL.* **58**, 637 (1985).
- <sup>8</sup>K. T. Gillen, M. Celina, and R. Bernstein, *Polym. Degrad. Stab.* **82**, 25 (2003).
- <sup>9</sup>K. T. Gillen, et al., *Trends Polym. Sci.* **5**, 250 (1997)
- <sup>10</sup>J. Wise, K. T. Gillen, and R. L. Clough, *Polym.* **38**, 1929 (1997).
- <sup>11</sup>K. T. Gillen, and M. Celina, *Polym. Degrad. Stab.* **71**, 15 (2001).
- <sup>12</sup>J. Crank, "The Mathematics of Diffusion," Second Edition, Oxford University Press, New York (1975).