RUBBER OXIDATION AND TIRE AGING - A REVIEW

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ABSTRACT

While a new tire may have excellent resistance to crack initiation and propagation between the steel belts, an aged tire of the exact same construction can exhibit dramatically reduced crack growth resistance, which in some cases may contribute to tire failure. This article will review the research that has gone into quantifying the rate of oxidation the steel belt rubber oxidizes in different climates from tire samples retrieved from consumers' vehicles. The information obtained from the field is then compared to data collected from various resources attempting to develop accelerated tire aging protocols. Finally, methods for potentially improving tire aging are reviewed.

INTRODUCTION

The composite foundation of most passenger and light truck tires (both radial and bias) is built on diene-based elastomers such as NR, SBR and BR. The rubber calendered onto the steel belt plies of radial tires, for example, is almost exclusively NR based. It is this 'belt skim' rubber with which this article will mostly concern itself. The belt skim rubber of the tire is what bonds the steel belts together, Figure 1. Additionally, the belt skim also bonds the steel belt package (there are a minimum of two steel belts in a radial tire) to the body ply cord rubber below and the tread package rubber above. A common failure mode in tires occurs when a propagating separation in the belt skim between the steel belts progresses to a point where the centrifugal force at highway speed is sufficient to result in the tread and top belt detaching from the tire carcass, Figure 2. This type of failure mode can and does occur in the field, as evidenced by one of the largest tire recalls in automotive history.[1] As will be discussed in more detail below, one cause of the tread separations was found to be oxidative aging of the skim and wedge rubber inside the tire. When the skim and wedge rubber oxidize, they lose elasticity and peel strength. During operation, cracks form inside the tire at the edge of the two steel belts. Crack growth rates increase dramatically in oxidized rubber, so as mileage and chronological age increase, the cracks can propagate between the belts, potentially resulting in a tread separation.[2,3] The oxidation that leads to the chemical and physical changes in the belt skim is termed "tire aging". Unlike tread wear (the traditional measure of tire life) or other damage (punctures, ozone cracking, *etc.*), the rubber oxidation that leads to tread separations is typically not visible to the average consumer.

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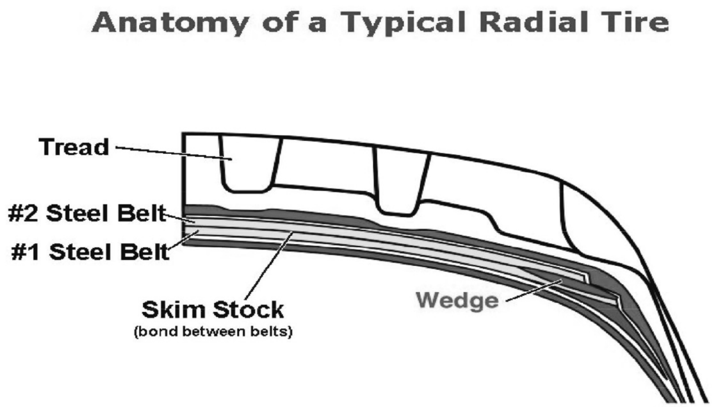

FIG. 1. — Anatomy of a typical radial tire showing skim and wedge rubber.

FIG. 2. — Tire carcass after a complete tread separation. (reprinted from Ref. 1 – the NHTSA ODI report EA 23).

One result of the previously mentioned tire recall is that the United States Congress required NHTSA (the U.S. Dept. of Transportation's National Highway Traffic Safety Administration) to research new regulations for aged tires. To support this requirement, NHTSA has performed significant research into the various physical and chemical changes that occur during tire aging, both in the field and in an accelerated, laboratory setting. Along with NHTSA, several other entities have published research on various aspects of tire aging, including field studies; oven aging of new tires; roadwheel aging of tires; and ultimately, tire performance tests developed from this body of work. This review describes that research. The authors hasten to add that the idea of developing laboratory aging tests for tires is not new. In 1929, Nellen and Sellers of the Lee Tire Company published an article on the correlation of Geer oven aging to the 'natural aging' of certain tread and carcass stocks.[4] Their research revealed that accelerated aging conditions can yield both representative and non-representative properties in the test samples, when compared to identical rubber compounds cured into tires shelf aged for up to 3 years. This review will update their research with examples from modern tire construction and technology. First, there will be a summary of the analysis of the recalled tires that led to the link between tread separations and rubber oxidation. Then, a description of the basics of rubber oxidation and early work on measurements of aging in tires will be reviewed. From that baseline will follow a discussion of the research regarding measurements of rubber oxidation in tires, aged both in the field and in different accelerated laboratory tests, demonstrating that oven aging can produce tire properties in a manner consistent with that observed in the field. Finally, it is shown that a tire test developed by NHTSA for assessing new tire durability can be used to evaluate the performance of oven aged tires. The concluding remarks will discuss various approaches to potentially improve tire aging performance.

ANALYSIS OF RECALLED TIRES

The tread separations that resulted in the 2000/2001 tire recalls involved a number of different tires manufactured in three different plants. The tires were used predominantly on sport utility vehicles (SUV's) produced from 1991-2001. The cumulative rate of claims as a function of time in service has been reported by NHTSA and is shown in Figure 3 for tires manufactured in the different plants.[1] Several factors are worth noting. First, the failure rates are reported in parts per million. Second, the failure rate varies widely with manufacturing plant for nominally the same tire. This implies that manufacturing processes played a key role in the factors that led to tread separations. By far the most important finding in Figure 3 is that the failure rate has a clear induction period even for the poorest performing tire. This suggests that aging is a key factor in the failure mode. This finding does not necessarily rule out manufacturing variability as the source of the failures, but it does suggest that it is related somehow to an aging phenomenon in the tire. It should also be noted that the reason that the increase in failures slows down at long times is that relatively few tires are still in service after 7-8 years. Tires are replaced for a number of reasons including tread wear, punctures, etc. One final important finding was that the large majority of failures occurred in so-called "hot" states. Failure rates were highest in Arizona, New Mexico, Texas, Florida, and Southern California. Very few failures were reported in the northern states.

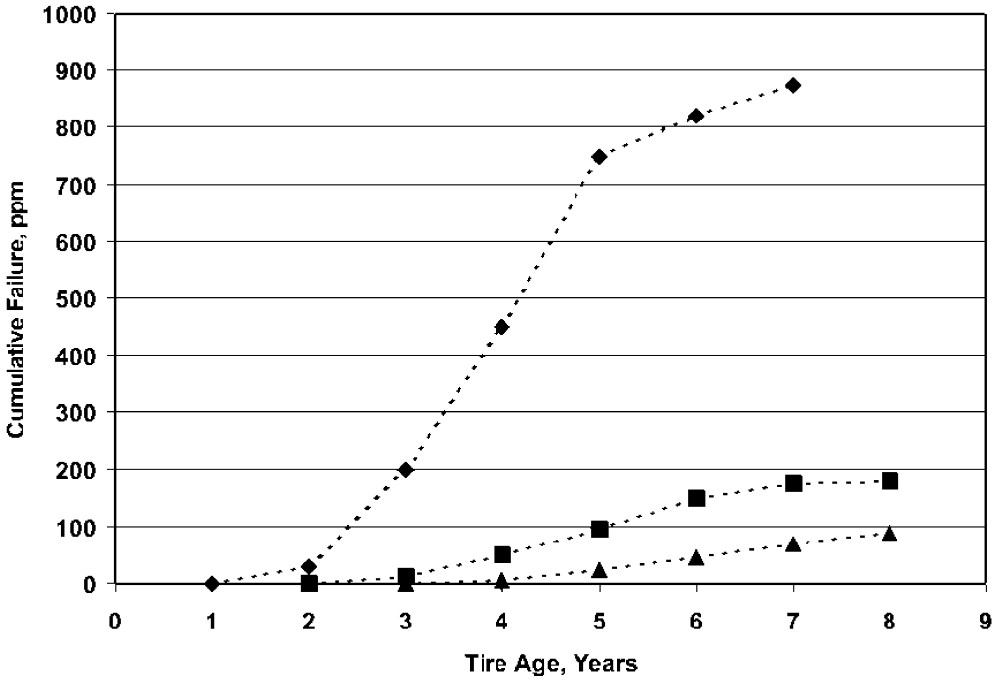

FIG. 3. — Cumulative failure frequency for a recalled tire manufactured in 3 different plants.

In order to evaluate what aging process was responsible for the tread separations, a large number of recalled tires were dissected by NHTSA and rubber properties measured. Some of the specific measurements will be described in more detail below, however, it is important to note that novel techniques had to be developed to measure properties of critical rubber components in the tire. For example, it was possible to measure stress-strain properties of the wedge rubber (an insert rubber strip in between the steel belts at their edges) by cutting samples from the belt edge. The skim rubber, which bonds the two belts together, is typically too thin to obtain samples for stress-strain measurements. To evaluate the mechanical properties of the skim rubber, a peel test was employed to measure the peel strength between the two belts. It was also possible to measure relative crosslink densities of the rubber by swelling measurements. It was found that the crosslink density of the skim and wedge rubber increased with aging time while the strain to break and peel strength decreased.[1] Following earlier work of Ahagon (also discussed in more detail below), these results clearly indicated that the skim and wedge rubber were undergoing oxidation.[5-7] Oxidation has a strong temperature dependence, which is consistent with the observation of the importance of temperature in tire aging.

OXIDATION BASICS AND EARLY WORK ON TIRE AGING MEASUREMENTS.

Conventional tests of tire durability discussed openly in industry are generally based on the premise that durability (including aging) is solely a function of driving. That is, tire aging is either a direct result of mechanical damage from fatigue cycling or caused by oxidation due to the higher temperatures in the tire during driving. Oxidation during stationary periods was ignored. For example, one automotive company has developed an Accelerated Endurance Test (ATE) that involves placing tires on vehicles and driving for 45,000 miles on various roads in Texas and Mexico. The test takes roughly 11 weeks to complete. A large tire manufacturer developed a laboratory road wheel test (termed the LTDE test) that was designed to insure that tires would pass the ATE test. This test uses a standard 67” road wheel with tires inflated to 40 psi (or other pressures depending on tire type) with a 50/50 blend of O_2/N_2. Tires are loaded to 111% of maximum load.[8] Tires tested in this manner did exhibit failures consistent with tread separation, however, they did not show significant oxidation in the belt edge region.[9] Earlier work described road wheel test results comparing nitrogen inflation vs. air inflation regarding time to failure in a durability test.[10] Another study related the effects of shelf life storage to the force and moment properties of tires.[11]

The tests described above focus on evaluating tire mechanics rather than oxidation. The only test available that related to rubber oxidation even indirectly was the air permeability test.[12] In this test, air loss through the rubber innerliner (usually a halo-butyl based rubber) was measured as a % loss / month. Tires with better innerliner compositions or thicker liners exhibit lower losses of air.[8] While improved innerliners will be a key approach in improving tire aging life, the link between air loss and oxidation rate is indirect and other factors can influence rubber oxidation and loss of tire performance. To understand the factors that control rubber oxidation inside the tire, it is necessary to describe diffusion limited oxidation (DLO).

The basics of oxidation in rubber have been extensively reviewed.[13-15] The different chemical reactions will not be discussed further here. What will be discussed are the factors that control oxidation kinetics in tire rubber and how oxidation changes the different properties of rubber. Because tires are relatively thick, of primary interest is the oxidation of the internal rubber materials. Diffusion limitations are of critical importance to understanding oxidation kinetics in tire rubber. Diffusion limitations arise from the fact that oxidation occurs throughout the rubber, consuming oxygen that has to diffuse from the surface. If the oxidation rate is high enough, the oxygen can be consumed before it diffuses entirely through the rubber material. This leads to concentration gradients, which in turn leads to a gradient in oxidation through the material. Gillen *et al.* have carried out extensive studies of diffusion limited oxidation through measurements of oxygen uptake and oxygen permeability.[16-18] For constant conditions, the oxidation rate is relatively constant with time. The basic auto-oxidation scheme leads to the following relationship between oxygen consumption oxygen concentration and temperature:

$$d[O2]/dt = - \rho(T) * ([O2]/(1+a[O2])) \quad (1)$$

The rate of oxygen consumption is proportional to oxygen concentration at low concentration, but is independent of oxygen concentration at higher concentrations. The oxygen concentration is controlled by the rate of consumption and the permeability of oxygen. The permeability is also a function of temperature. The temperature dependence of oxygen permeation and reactivity, ρ, is shown in Figure 4.[19] At high temperatures the reactivity increases faster than permeability leading to increased oxygen starvation inside the rubber. For tire oxidation, the permeability of both natural rubber and the butyl rubber used in the innerliner has to be considered. Butyl rubber has a much lower permeability than natural rubber and is used in innerliners to reduce the loss of air through the tire. Ellwood *et al.,* have developed a finite element model of oxidation in tires that can predict the concentration gradient and oxidation rate throughout the different layers of the tire.[20,21] Typical results for oxygen concentration and oxygen consumption are shown in Figures 5 and 6. Since the partial pressure of oxygen is much larger in the tire cavity than outside it, the innerliner is critical in reducing oxidation of the skim and wedge rubber. This model is used later to validate and interpret experimental measurements on tire aging.

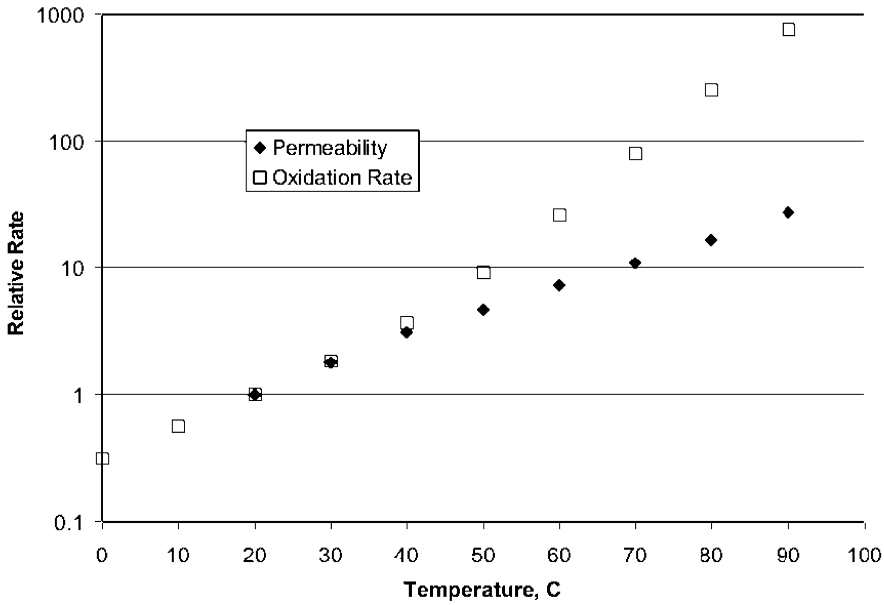

FIG. 4. — Relative temperature dependence of permeability and oxidation rate for natural rubber.

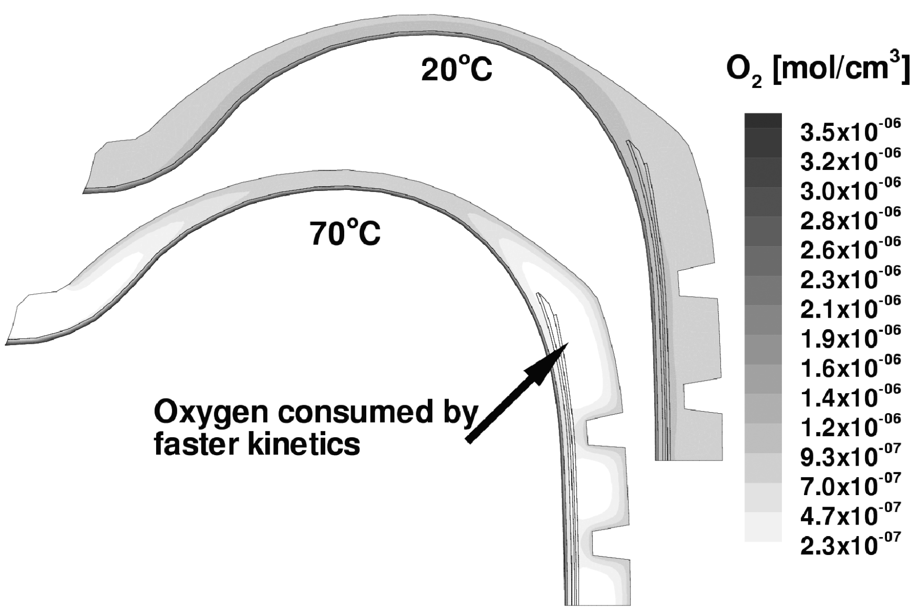

FIG. 5. — Distribution of oxygen concentration in a tire at different temperatures. The lack of oxygen in the thick sections of tread in the tire at 70 °C is due to consumption of oxygen in the rubber nearest the air cavity by diffusion limited oxidation.

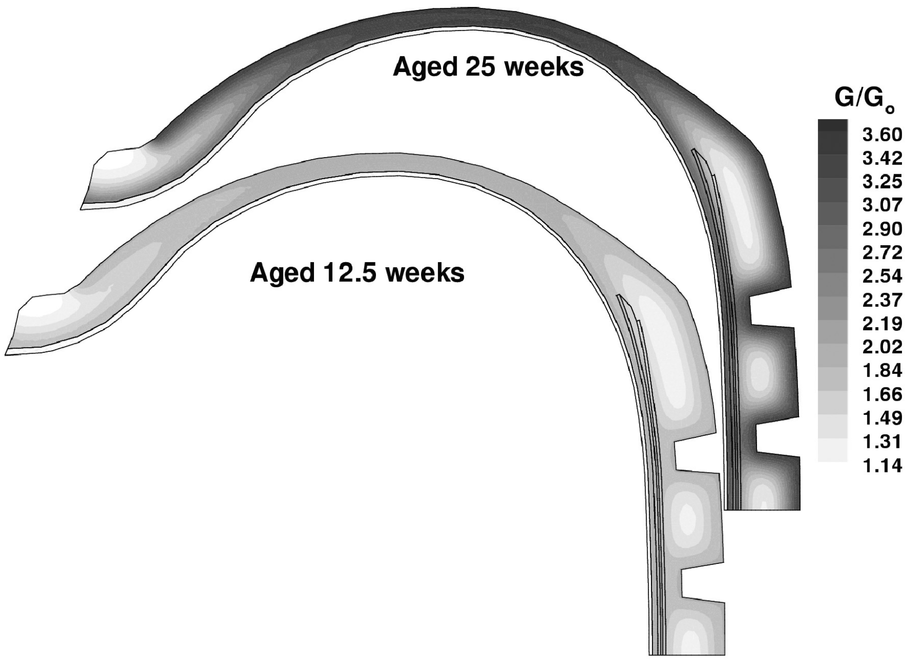

FIG. 6. — Distribution of changes in rubber modulus with oxidation at 70 °C. The lack of change in modulus in the thick sections of tread indicates oxygen starvation in this region. Note that the skim and wedge rubber is oxidizing at 70 °C.

There are a large number of parameters that can be measured to track the extent of oxidation in rubber. The most direct measure is oxygen uptake. Oxygen uptake measurements have been described in detail by Gillen *et al.*[16-18] This measurement can provide a highly sensitive and accurate measure of the extent of oxidation in a rubber sample. Unfortunately, it has to be carried out under controlled laboratory conditions and cannot be used to analyze samples "after the fact." Oxidation in aged rubber samples can also be measured by measuring the difference in oxygen concentration inside the rubber before and after aging. This technique, though widely used, suffers from a few practical difficulties. For rubber compounds widely used in tires, the initial concentration of oxygen is ~2-3%. Typically rubber properties are very poor after an oxidation that is equivalent to an uptake of ~1%. Thus, the background oxygen concentration can make accurate oxidation measurements difficult. In addition, some of the oxidation products (as well as some of the original oxygen containing compounds) may be volatile at higher temperatures. This makes comparison of oxidation rates at higher temperatures problematic. Since one of the goals of tire aging studies is to evaluate oven aging as an accelerated test, it is necessary to look at other measures of oxidation.

The process of oxidation leads both to crosslink scission and to crosslink formation. For the rubber compounds used in tire skim and wedge formulations, oxidation leads to a net increase in the crosslink density. Thus, it is possible to use crosslink density as a relative measure of oxidation. Crosslink density can be measured by swelling.[22] It is important to note that tire rubber compounds are all highly filled with carbon black. This complicates the analysis of relating a swelling measurement to absolute crosslink density, however, relative measurements are still valid indicators. It is important to insure that oxidation is the only source of changes in crosslink density. In many cases, the rubber does not reach a maximum (non-oxidative) crosslink density right out of the mold. Post-cure has to be considered in using crosslink density changes as a measure of oxidation. Fortunately, post-cure effects are usually small (5-10%) and occur early in the aging exposure.

One of the key questions in evaluating any accelerated test for oxidation is whether the test induces the same kinds of chemical changes as seen during service.[23] One method that has been proposed to evaluate chemical change as a function of test condition is measurements of the distribution of sulfur crosslink structures. There are procedures to determine the concentration polysulfidic, di-sulfidic, and mono-sulfidic crosslinks in cured rubber.[24] These tests indicate that as the temperature of the exposure increases, the crosslink distribution changes. This result has been used to argue against the use of higher temperatures to accelerate oxidation. It is important to note, however, that the test itself was not designed to separate the carbon-carbon or carbon-oxygen crosslinks that are formed during oxidation. Depending on the type of crosslink formed, it may be counted as a mono-, di-, or poly-sulfidic crosslink. As noted above, higher temperatures can volatilize oxidation fragments. It is also likely that higher temperatures convert less stable peroxy crosslinks to carbon-carbon crosslinks. This would not necessarily invalidate the use of higher temperatures to accelerate oxidation. As long as the overall crosslink density and other property changes vary in a similar manner, the use of elevated temperatures to accelerate oxidation may be allowed.[25]

For diffusion limited oxidation, it is critical to establish the maximum temperature that can be used without oxygen starvation. That is, for a given sample, there will be a temperature above which the degradation process will change from aerobic oxidation to anaerobic degradation. Ahagon has developed a procedure to evaluate how test conditions influence the degradation process.[5-7] The procedure involves comparing changes in modulus versus changes in strain-to-break. When these quantities are plotted in a log-log plot, the data fit on a straight line with a slope that is roughly -0.75 for a sample undergoing aerobic oxidation. Raising the temperature results in deviations from linearity and ultimately in a completely different behavior. Instead of the modulus increasing and the strain-to-break decreasing with increasing oxidation, for anaerobic degradation both the modulus and strain-to-break decrease with increasing degradation. These observations are completely consistent with the basics of aerobic and anaerobic degradation process. Oxidation causes in overall increase in crosslink density and a decrease in elasticity (strain-to-break). In contrast, anaerobic degradation typically results in crosslink scission. This leads to both a decrease in modulus and elasticity. Similarly one would expect that plots of peel strength retention versus crosslink density would show similar trends as a function of test conditions. Ford researchers have used the Ahagon approach to evaluate aging mechanisms in both field aged tires and laboratory aged tires.[26-29]

The failure rate plot of Figure 3 used time as the key aging parameter, rather than mileage. As noted above, conventional wisdom was that aging was caused by driving. If this premise were correct, mileage, not time would be the correct variable for aging. To develop and validate a laboratory test for tire aging, it was first necessary to determine the nature and kinetics of aging of non-recall tires in the real world. Along with measurements of rubber aging, it is also necessary to relate tire aging to actual tire performance metrics. Finally, if tire aging was found to be a general phenomenon, it would be important to establish how rubber composition and tire construction influence aging rates. Answering these questions drove the next phase of research on tire aging.

STUDIES ON AGING OF TIRES RETRIEVED FROM THE FIELD

Besides the analysis of field retrieved recall tires described above, both NHTSA and the Ford Motor Company carried out tire retrievals on non-recalled tires from a variety of manufacturers and sizes. The NHTSA study comprised 6 different tires collected from Phoenix, AZ. Tires ranged in size from a small car tire (P195/65 R15 to a load range E light truck tire (LT245/75 R16). The tires were all on-road tires (no spares). Care was taken to insure that the tires spent all of their life in the Phoenix region. Tires that had been repaired or damaged were excluded from the roadwheel testing portion of the study. A variety of measurements of rubber property change and tire performance were made. Test measurements included crosslink density, modulus, elongation to break, peel strength and crack resistance. Tire evaluations included shearography as well as both stepped up speed and stepped up load roadwheel testing. The results are available on the NHTSA website.[30]

The Ford retrieval study involved collecting tires from 15 different tire-vehicle combinations and 6 different cities. The 15 tire-vehicle combinations involved 6 different vehicle types and 3 different tire manufacturers. Four of the cities, Phoenix, AZ; Los Angeles, CA; Detroit, MI; and Hartford, CT were chosen to evaluate temperature effects. Two other cities, Denver, CO and Miami, FL were added to evaluate road conditions and in the case of Miami, determine if humidity played a role in aging. Relatively fewer tires were obtained from Denver and Miami. Tires ranging in age from 2 weeks to 6 years were collected. An attempt was made to collect tires of a given age with low and high mileage to separate the effects of time and mileage on tire aging. Both on-road and spare tires were collected. Over 1500 tires were analyzed. Tires were inspected and some subjected to shearography. Rubber property measurements included skim rubber crosslink density and peel strength and wedge rubber modulus and elongation-to-break. These properties were also measured by NHTSA using the same procedures so that the results from the two studies can be compared. Analysis of the Ford results included a DOE analysis of the main factors that contributed to aging and a specific kinetic analysis of the aging rates for individual tires.[31]

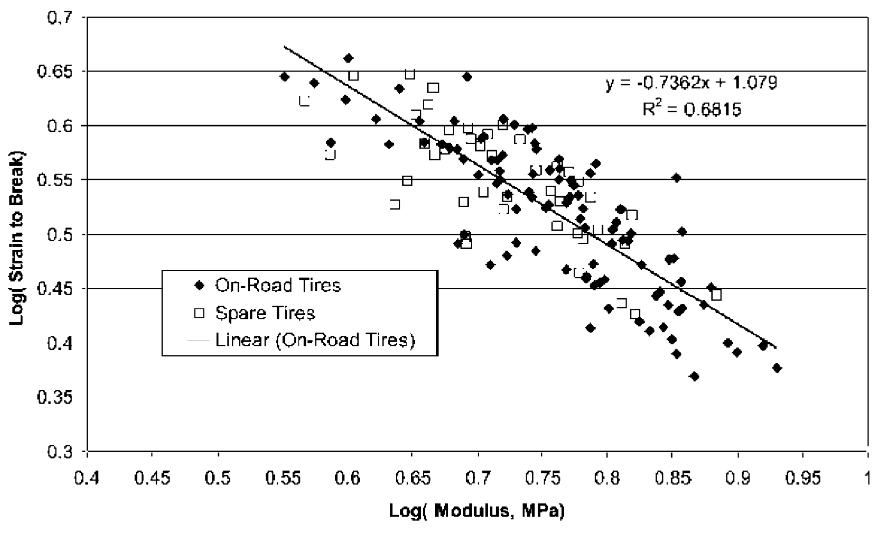

FIG. 7. — Ahagon plot of on-road and spare tires retrieved from the field. Both data sets indicate oxidative aging.

The most important finding of the two field retrieval studies was that all tires age, albeit at different rates. The mechanism of aging in the field retrieval tires can be confirmed to be aerobic oxidation by use of Ahagon plots, Figure 7. As expected for aerobic oxidation, the modulus increases with aging while the strain-to-break decreases leading to an Ahagon plot that is linear with a slope that is roughly -0.75. Similar results were found for all tires. Interestingly, the Ford study revealed that spare tires age by aerobic oxidation the same as on-road tires. Both Ford and

NHTSA also found that the crosslink density and modulus of the skim and wedge rubber increase with age while the elongation-to-break and the peel strength decrease. The crosslink density and modulus increase linearly with time, consistent with a relatively constant oxidation rate. The loss of peel strength is the same at the belt edge and the center of the belt suggesting that the rate of oxidation (and thus temperature) is independent of location along the belt.

The NHTSA study was limited by the relatively small number of tires in each data set. The larger number of tires in the Ford study allowed for more detailed kinetic analysis. For example, Figure 8 shows peel strength retention data for one of the Ford tires from 3 different cities (note that Detroit and Hartford have been combined). The data from different cities can be combined using shift factor analysis, Figure 9. Analysis of peel strength indicated that this data could be fit to the following equation:

$$\text{Peel (t)} = \text{Peel (0)}/\ (1+ b^*t) \qquad (2)$$

where b is a measure of the aging rate. This equation has also been found to fit the elongation-to-break data from the Ford and NHTSA experiments and extensive laboratory aging elongation-to-break data of Gillen *et al.*[32] Gillen *et al.* have also published procedures to determine relative aging rate using shift factors. Ford employed a similar analysis to interpret their aging data. For example, analysis of the aging data from a single tire type collected from different cities suggests that aging was fastest in Phoenix and that the rates in Los Angeles and Detroit/Hartford were 57% and 42% as fast as Phoenix. DOE analysis of all the tires and of all the property changes confirmed that Phoenix was by far the harshest location.[31]

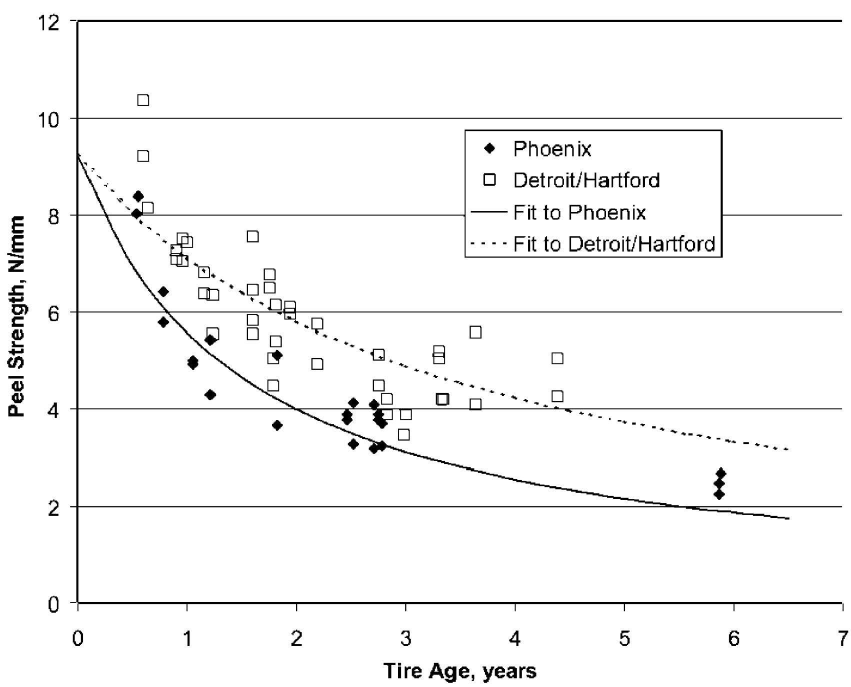

FIG. 8. — Loss of skim rubber peel strength versus aging time for a single tire type retrieved from different locations.

The relative aging rates in the other cities were independent of tire type and of type of property change. This means that all the tires age by the same single mechanism; namely oxidation of the skim and wedge rubber. This conclusion includes spare tires as well as on-road tires. In fact, spare tires age at a rate only slightly slower than on-road tires (~70-80%). DOE analysis confirms that mileage was a relatively unimportant factor in aging compared to time. Thus time, not mileage, is the correct metric for tire aging. The analysis determined that other factors such as vehicle type, ozone, humidity, and road conditions were unimportant to oxidation of the belt package. The only significant factors for tire aging rate were ambient temperature and tire type. Tire aging rates in the different locations are consistent with the relative rates predicted by the temperature dependence for rubber oxidation shown in Figure 4. The relative rates of aging (as determined by averaging the rates of loss of peel strength and elongation-to-break) for the different tires in the Ford and NHTSA tire study vary by over a factor of 5. Note that this metric for tire aging is just one of the many possible metrics that could be used. Other metrics include the time to reach a particular skim rubber peel strength value or wedge rubber elongation-to-break value. Use of these metrics lead to somewhat different rankings but a similar variation in aging performance. Besides variations from manufacturer to manufacturer, tire size, or more specifically, tire aspect ratio seems to effect the tire aging rate. Tires with higher aspect ratios age faster than tires with lower aspect ratios.[31]

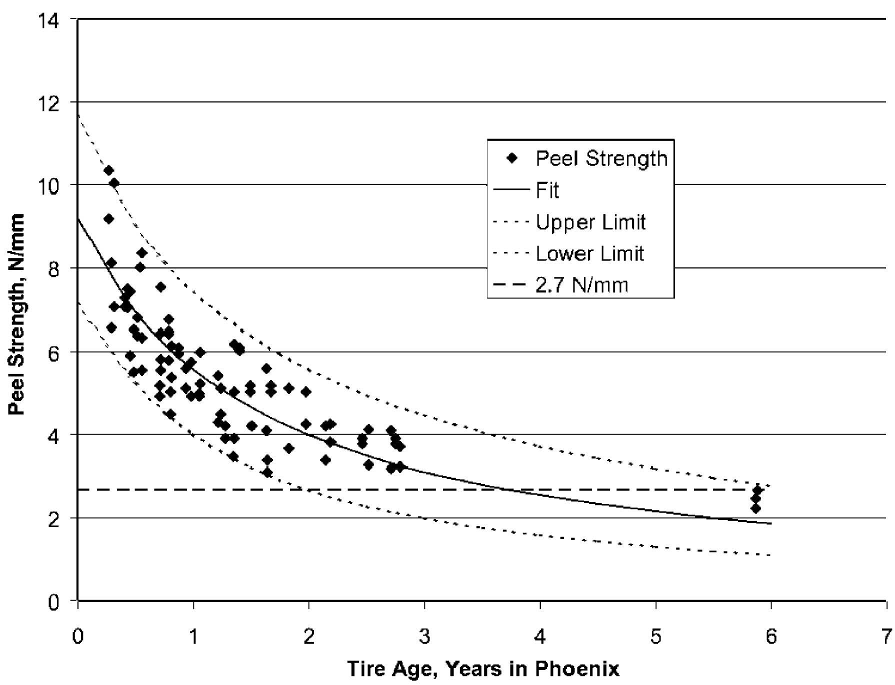

FIG. 9. — Tire aging results from a single tire. Data from different locations have bee n combined using shift factor analysis. The data can be fit to Equation 2 to derive an aging rate for that particular tire. The variability of field aging is also illustrated in this figure.

One important factor that is apparent from the field aging data (see Figure 9) is that that field aging behavior is highly variable. The average values for peel strength and elongation-to-break can be calculated from their average initial values and the average aging rate using Equation 1. The variability that is observed can be accounted for by considering variations in both the initial properties and, what is more important, in the aging rate. The upper and lower limits can be estimated by assuming that both the initial properties and the aging rate are distributed normally about their average values with standard deviations of ~8% and 17% respectively. These upper and lower limits are shown in Figure 9. The lower limit value is particularly important since this represents the "worst-case" tire at any given age. It is this worst-case tire that will likely fail first. An average tire has to be aged almost twice as long as the worst-case tire. This result will be important in the development of accelerated tests to predict tire aging failures.

It is also important to determine the sources of these variabilities. The sources for variations in initial properties include measurement error and manufacturing variations. The manufacturing variations are larger than would be determined from a set of new tires since the tires were manufactured over a large span of time. Variations in aging rate can be ascribed to manufacturing variations (*e.g.*, variations in innerliner or antioxidant package) and variations in time-temperature exposure history. Since the geographic location is the same, the variations in temperature must be due to variations in customer parking or driving habits. Since the variability and average aging rate for spare tires is almost as large as for on-road tires, the effect of driving habits must either be relatively small or be the same for both on-road and spare tires. Driving, especially aggressive driving, would increase the temperatures of the on-road tires. Another factor that would affect both on-road and spare tire temperatures is parking habits. Parking in full sun on a black asphalt road would lead to significantly higher tire temperatures that parking in a shaded garage or parking structure.

LABORATORY TIRE AGING STUDIES

Laboratory tire aging studies have been carried out by researchers at Ford Motor Company, NHTSA, and ASTM. Most of the studies have involved evaluations of oven aging, though NHTSA and ASTM also carried out evaluations of road wheel aging (recall the early assumption that tire aging was caused by driving). Kinetic analysis of the data from ASTM road wheel aging clearly showed that the belt edge was oxidized more than the belt center.[33] This is consistent with the known temperature distribution of tires on a road wheel but is not consistent with behavior observed in the field. As a result, proposed procedures for accelerated aging of tires are now all based on oven aging.

Early studies by researchers at Ford concluded that because of the higher oxygen partial pressure on the inside of tires mounted on wheels, most of the oxidation that occurs in the skim and wedge is due to oxygen permeating through the innerliner from the inside air cavity.[34] This result has been confirmed by finite element models of tire oxidation (see the oxygen concentration profiles in Figure 5). Thus, to replicate actual field aging conditions, it is necessary to mount the tire on a wheel and inflate it. The first goal of research on oven aging was to demonstrate that it did in fact age tires in a manner that was consistent with the field results. This means that the aging that results from oven exposures must induce aerobic oxidation of the skim and wedge rubber. In addition, the rate of oxidation must be the same from the center of the belt to the belt edge consistent with results found for field aging. Critically, the acceleration factor between the laboratory test and field results should not depend on tire construction. The test with the highest acceleration factor (consistent with the above constraints) will lead to the shortest testing time. The acceleration factor for oxidation will depend on temperature and oxygen concentration. For this reason, research has focused on varying temperature, pressure, and fill gas composition.

Ahagon plots can be used to determine the oven aging conditions where the wedge rubber undergoes aerobic oxidation. The wedge rubber has the longest path from the inside of the tire and finite element models indicate that it will be more sensitive than the skim rubber to effects of diffusion limitation. Figure 10 shows an Ahagon plot for oven aging up to 70 °C of an LT metric tire. An LT tire being relatively large should be more sensitive to the effects of diffusion limitations than a small car tire. The LT metric tire was filled to its maximum sidewall pressure of

65 psi with either air or a 50/50 blend of O2/N2. The tires were aged up to 12 weeks at temperatures ranging from 40-70 °C. The results show that the wedge undergoes aerobic oxidation with either air or the 50/50 blend of O2/N2 up to a temperature of 70 °C. Note that the slope while different from –0.75, is within the range found for tires from the field study. At long exposure times at 70 °C, there is some evidence for deviation from aerobic oxidation in this tire. Finite element modeling and measurements of cavity air composition suggest that this deviation is a result of oxygen depletion in the tire air cavity. For this reason more recent oven aging studies have included periodic replenishment of the oxygen in the air cavity. Above 70 °C, there is clear evidence for oxygen starvation. The plots no longer follow the behavior indicated for aerobic oxidation.[27,35]

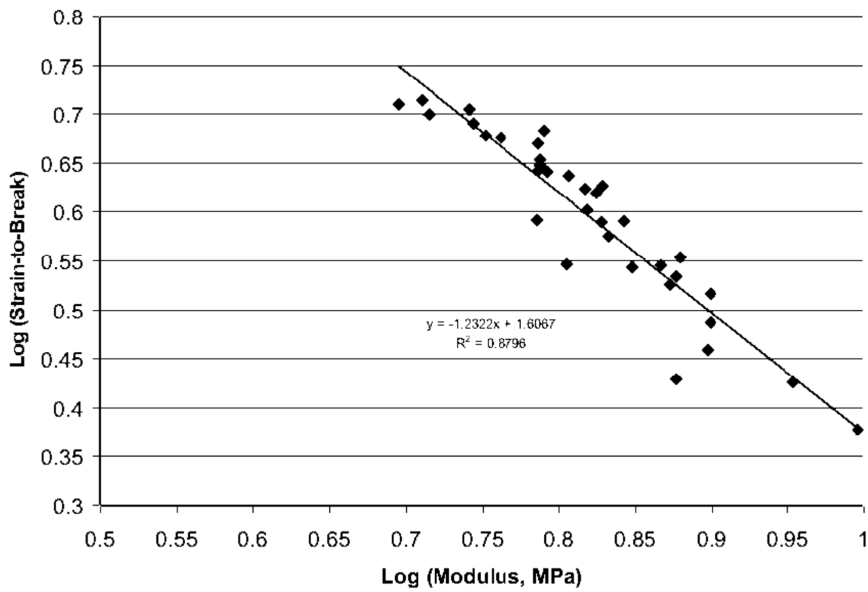

FIG. 10. — Ahagon plot of oven aged tire.

Kinetic analysis of oven aging of the small car tire carried out by the ASTM (the same tire as studied in the field by NHTSA) confirms that the oven aging behavior of the different skim and wedge rubber properties behaves in a manner that is similar to that observed in the field.[33] The crosslink density of the skim and the modulus of the wedge rubber increase linearly with time, while the elongation-to-break and the peel strength decrease. In addition, aging of the skim rubber is relatively constant from the center of the belt to the belt edge. The rate of aging increases with increasing temperature from 55 to 75 °C. Indentation modulus studies of the extent of oxidation on the small car tire do indicate that the oxidation profile is distorted at the highest temperature (75 °C) relative to the profiles found in the field aged tires. This result is contradicted, however, by research conducted by an individual tire manufacturer claiming that 80 °C is the optimum temperature for oven aging tires.[36]

Oven aging research carried out at Ford covered a wider temperature range and many more tire constructions than the ASTM study.[26,27,34,35] Ford researchers measured aging rates as a function of temperature (40-100 °C), fill gas (100%N2 to 100%O2) and pressure (up to 2x the maximum sidewall pressure) for one tire construction (the LT metric tire) as well as less extensive studies on tires of different sizes from different manufacturers. The variability of property changes with oven aging is much less than that for field aging, and it is possible to determine the rate of aging as a function of test condition by fits of peel strength versus time to Equation 2. The temperature dependence can be determined from shift factor analysis as shown in Figure 11. As shown in Figure 12, the rates of property change increase steadily with increasing temperature reaching a maximum around 70 °C and then begin to decrease. The theoretical prediction based on finite element analysis of tire oxidation is also shown. The data in Figure 12 include not only data from the LT metric tire but from other tires as well varying in size from SUV/minivan tires to a small car tire. The consistency in the temperature dependence with different tires suggests that it should be possible to consistently age tires in the oven at temperatures up to 70 °C with an acceleration factor that is independent of tire size or construction. This will be confirmed in the next section. The data in Figure 12 also includes both air and the 50/50 blend of O2/N2 as fill gas. The use of the 50/50 blend effectively doubles the concentration of O2 in the cavity. This leads to an increase in oxidation rate of ~40%. The acceleration that results from using the 50/50 blend is independent of test temperature or tire type. Higher pressures or higher oxygen concentrations can also be used to further accelerate the oxidation, however, the gain in rate is small and for safety reasons pressures above the maximum sidewall pressure or oxygen concentrations above 50% are not recommended. In the next section, results comparing oven aging to field aging for tires of various sizes will be presented.

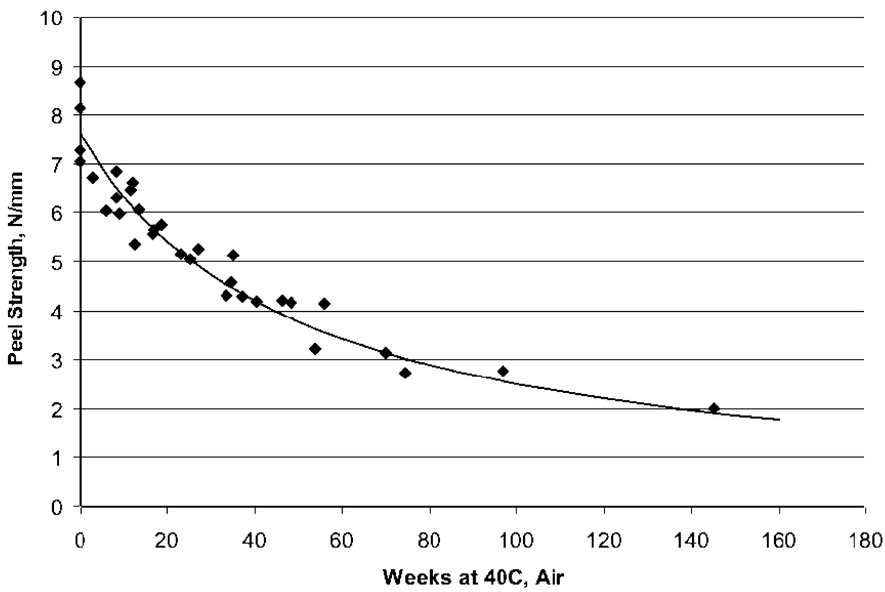

FIG. 11. — Peel strength versus aging time at 40C, air inflation. The shift factors for 50, 60, and 70 °C are 2.8, 4.5, and 11.7 respectively. The shift factor for 50/50 N_2/O_2 is 1.38.

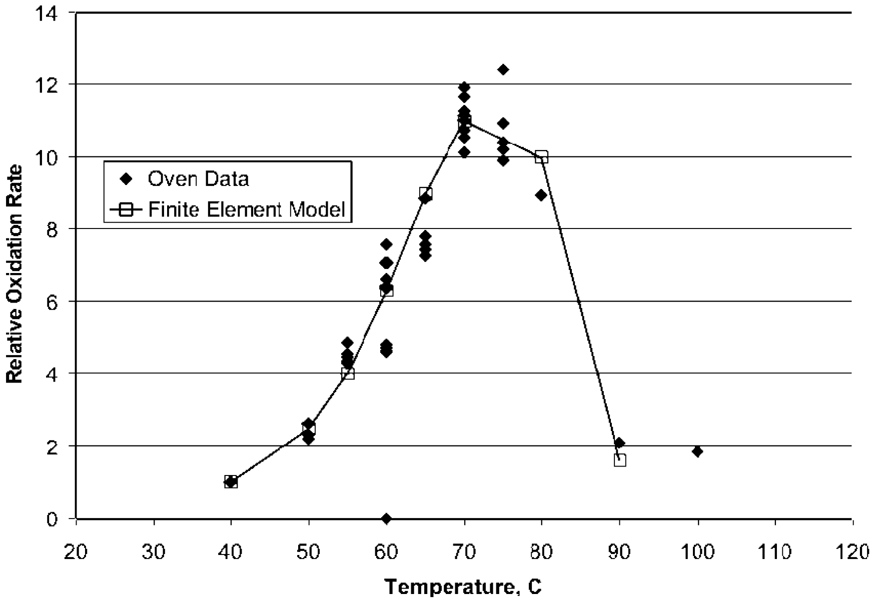

FIG. 12. — Dependence of rubber oxidation on oven temperature.

CORRELATION OF OVEN AND FIELD AGING AND DETERMINATION OF ACCELERATION FACTORS

A correlation between oven aging and field aging can be established by comparing aging rates for different tire sizes and constructions. If the ratio of aging rates is independent of tire type for a particular test, then that test can be used to reliably age tires. One important factor that must be considered in the comparison is to establish that the tires that are tested in the accelerated test have the same composition and manufacturing process as the tires that were evaluated in the field. This is a serious issue since the tires that were evaluated in the field by both Ford and NHTSA were manufactured during the period 1996-2002 while the tires tested in the oven studies were manufactured in and after 2004. Some of the tires that were evaluated in the field study were no longer being produced to the same specifications. In general, specific, time dependent compositional data for the different tires was not available. The only way to determine whether the skim and wedge rubber behaved the same for tires in the field set and in the oven set was to compare initial properties and to compare aging behavior using Ahagon plots. If the initial peel strength or elongation-to-break were significantly different in the oven and field tire sets, a compositional change likely occurred which would render comparison of aging rates in the two sets meaningless. Even if the initial properties were similar, if the slopes of the Ahagon plots were different, it is likely that the aging behaviors were also different.

Oven aging was carried out on 5 OE tires for which field aging data was available. The tires include 3 SUV/minivan tires with different field aging rates, a large car tire and a small car tire.[32,37-39] Four different tire manufacturers were represented. The small car tire (evaluated by NHTSA and the ASTM) was represented by the manufacturer to have remained consistent over this time period. This was confirmed through analysis of the initial rubber properties. By contrast, there was clear evidence for compositional changes in some of the rubber in the other tires. For the three SUV/Minivan tires, the skim rubber was consistently the same, however, the wedge rubber in the newer tires had a significantly higher elongation to break and lower modulus for all three manufacturers. By contrast, the elongation-to-break of the wedge rubber for the large car tire was the same in the two sets but the skim rubber properties were different. Ahagon analysis of the aging behavior in the oven and field sets were consistent with the conclusion that all of the properties of the small car tire could be used for comparison but that only the skim rubber properties could be compared for the SUV/Minivan tires and only the wedge rubber elongation-to-break could be used for the large car tire.

Analysis of the property retention data from the field (Phoenix) and from oven aging studies for these different rubber properties yield an acceleration factor of ~25 and ~31 for exposures at 65 and 70 °C, respectively, using air as the fill gas. The corresponding acceleration factors for 65 and 70 °C using a 50/50 blend of O_2/N_2 as the fill gas are ~36 and ~44. This implies that 8 weeks of exposure at 65C using the 50/50 blend of O_2/N_2 as the fill gas should produce a tire that is ~5.5 years old in Phoenix. It should be noted that this particular test did not include oxygen replenishment. Including oxygen replenishment would result in a small further acceleration. These acceleration factors are consistent with an extrapolation of the temperature dependence of the oven aging data to ambient temperatures in Phoenix (see Figure 12). These results establish that oven aging at temperatures ~65-70 °C can age tires in a manner that is consistent with the field. The acceleration factor is independent of tire size or field aging rate. It is now possible to produce tires of a specific age (in years of average exposure in Phoenix). The next step is to evaluate tests of tire performance as a function of aging.

TIRE DURABILITY TESTING OF FIELD AND OVEN AGED TIRES

Researchers at NHTSA applied their stepped-up-speed (SUS) test (performed on a 1.7m indoor road wheel) to the 6 tires that they retrieved from the field. Most of the tires show no dependence of SUS failure time on aging.[30] In contrast the rubber properties of these tires declined significantly with age. Only one tire, tire E, shows a definite decline in SUS failure time with aging and even for this tire, the correlation coefficient is less than 0.5. Tires with a higher speed rating tend to perform better in the SUS test as expected. One of the higher speed rated tires (tire C) actually increases in SUS performance with aging. Increases in SUS failure time with aging are also seen with oven aged tires. One explanation for this result is that oxidation increases the hardness of the different rubber components in the tire. In particular, oven aging increases the hardness of the tread compound in addition to rubber on the interior of the tire. As a result, oven aged tires run cooler on the high speed test than do new tires. This likely accounts for their improved performance. Field aged tire performance on aged tires is likely determined by a balance of the increase in hardness versus the formation of cracks in the belt edge of the tire as exhibited by tire shearography. Oven aging does not induce cracks at the belt edge. It appears that SUS testing does not provide a suitable means to evaluate tires after aging.

NHTSA also evaluated the performance of the 6 Phoenix aged tires in a stepped-up-load (SUL) test (performed on a 1.7m indoor road wheel). The first 34 hours of the test correspond to the tire durability requirement for new tires, Federal Motor Vehicle Safety Standard (FMVSS) 139.[40] If no tire failure has occurred at 34 hours, the load is increased by 10% every 4 hours until failure occurs. The results for the 6 tires are shown in Figure 13. The two high speed rated tires show a small decrease of SUL failure time with aging. The failure times for the unaged tires with higher speed rates are significantly higher than those for the S and Q rated tires. In addition, the S and Q rated tires all show a more significant decrease in SUL failure time with aging. The decrease in failure time is approximately linear with age, though there is a great deal of scatter in the data, due no doubt, to the natural variability of field aging as discussed above. For the S and Q rated tires, there is a reasonable correlation of aging rate with loss of rubber properties though the limited number of tires and the large scatter in the data make it difficult to draw unambiguous conclusions.

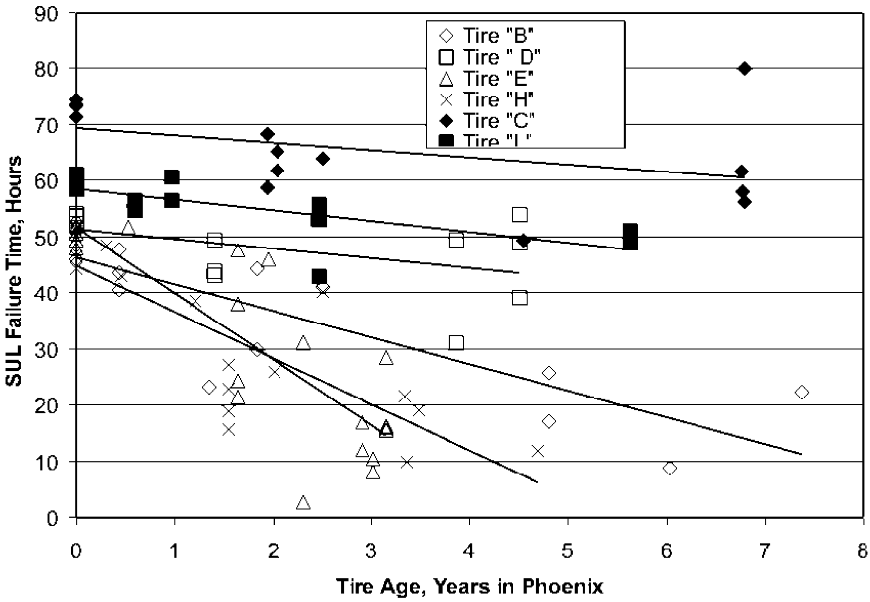

FIG. 13. — Time to failure in stepped-up-load (SUL) testing versus aging time in Phoenix.

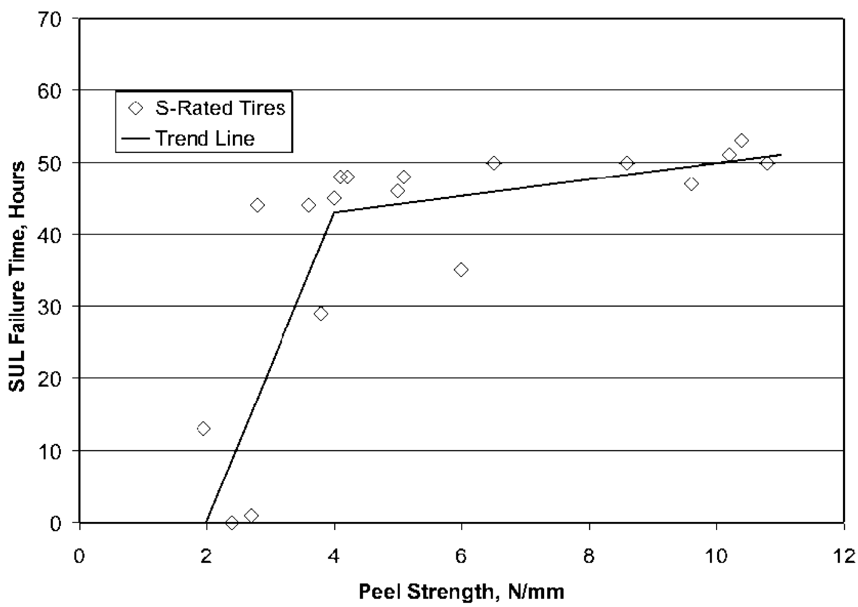

FIG. 14. — Correlation of SUL time to failure and peel strength after oven aging.

The variability of oven aging is much less than that for field aging.[32] To establish whether a clear correlation exists between SUL failure times and skim and wedge rubber property retention, Ford measured these properties after oven aging for a number of different tire constructions.[37] Again, the tires separated themselves by speed rating. Higher speed rated tires had longer SUL failure times and did not show a strong dependence with loss of rubber properties. The S-rated tires were relatively independent of rubber property loss until that loss reached a critical value at which point the SUL drops abruptly with decreasing peel strength and/or elongation-to-break. The result for peel strength is shown in Figure 14. Once the value for peel strength drops below its critical value, and the failure time begins to decrease, the failure time rapidly drops below 34 hours, which is the requirement for new tires in FMVSS 139. Thus, requiring an aged tire to pass the 34 hour requirement insures that the rubber properties remain above the critical value. Superimposing the NHTSA field data onto the oven trend lines indicates that the SUL failure time in the field aged tires is lower than in the oven aged tires at any given level of aging (as defined by property loss). This is most likely a result of the formation of cracks at the belt edge during field aging that do not occur in oven aging. Due to the strong correlation between skim and wedge rubber oxidation, it is not clear whether the loss of one of the properties is more important or if both are important in determining tire aging behavior. It is also not clear whether % retention or absolute values correlate better with SUL. Nevertheless, SUL testing of oven aged tires can provide a means to rank tire aging performance.

IMPROVING TIRE AGING

There are many possible ways to improve the aging performance of tires. One of the most basic approaches is to compound anti-oxidants into the rubber and is an entire field of research unto itself. With the myriad of approaches and chemistries available to the individual tire compounder, keeping in mind that each manufacturer has its own institutional knowledge of what has worked and what will work best for their own needs, this paper will not discuss the detailed use of anti-oxidants.[41] Suffice it to say that it is assumed that an appropriate level of anti-oxidant is compounded into the belt and wedge rubber; the rest of this section than, will discuss other approaches to improving tire aging.

Since oxidation of the skim and wedge rubber is one of the key degradation pathways that can lead to tread separations and since most of the oxygen responsible for rubber oxidation comes from the inside of the tire, one way to reduce the oxidation of the skim and wedge rubber is to replace the oxygen with nitrogen.[34,42] Filling tires with nitrogen rather than air is widely used to improve reliability of tires used in demanding applications such as aerospace, racing and over-the-road trucks. It is now being marketed to passenger car consumers. The major selling point is that nitrogen has a lower permeation rate than oxygen and thus improves inflation pressure retention. Studies of oven aging at 60 °C suggest that filling the tire cavity with pure nitrogen can reduce the rate of loss of peel strength and elongation-to-break by over 70% relative to air. It is important to note that practical considerations limit the reduction in oxygen level by nitrogen inflation to about 5% (versus 21% in air). To reduce the oxygen content further, it is necessary to purge the original air in the cavity several times and to use highly purified nitrogen which is not readily available to most consumers. The finite element model described above predicts a similar dependence of oxidation rate on oxygen content that is found during oven aging, Figure 15. With the model validated by experimental measurements, researchers at Ford have used finite element analysis of tire oxidation to estimate the degree of reduction of oxidation as a function of oxygen content under more realistic temperature conditions.[43] The use of nitrogen does improve inflation pressure retention and the use of dry nitrogen versus air may have other benefits, however, in the field, the effects of nitrogen inflation may be hard to quantify.

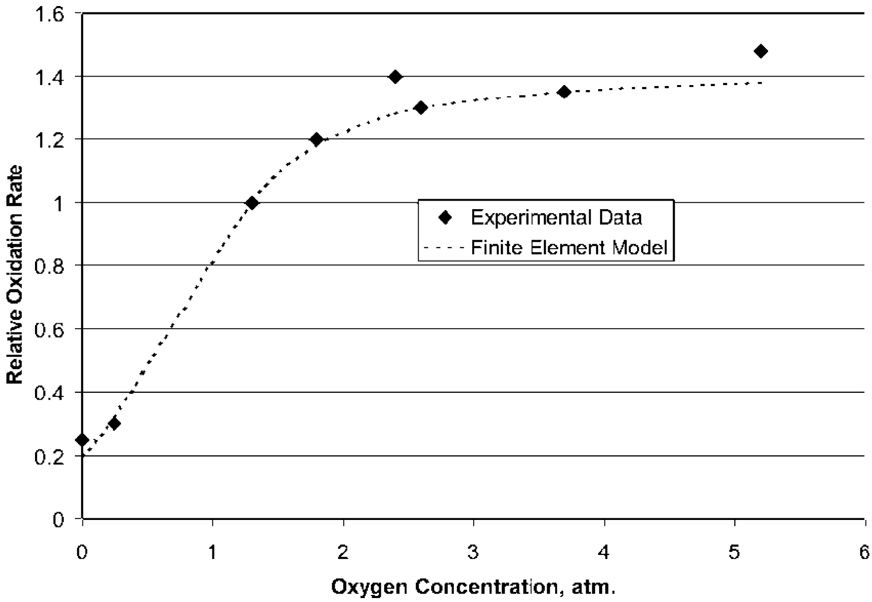

FIG. 15. — Relative oxidation rate of skim rubber versus oxygen concentration. The data is normalized to air inflation.

One of the most important components of the tire vis-à-vis oxidation resistance is the innerliner. The innerliner is designed to limit the permeation of air through the tire to provide acceptable inflation pressure retention. Innerliner performance depends on its thickness and on its composition. In particular, Waddell *et al.* have reported that increasing the percentage of halobutyl rubber in the innerliner from 60/40 (the remainder being natural rubber) to 100/0 results in a decrease in permeation of over at least a factor of 2.[44-47] They also report that use of 100% halo butyl innerliners improve the time to failure in FMVSS 139 load test by over 60% relative to the use of a 60/40 innerliner. In this particular test, the load was increased following FMVSS 139 up to 100% of rated load and then held at that load until failure. Failure times ranged from 360 to 580 hours. This test is qualitatively similar to the load durability test evaluated by ASTM and discussed above. Test times are also similar. In is important to note that the ASTM test and most likely the FMVSS 139 test as performed in these experiments age the belt edge more than the rubber in the center of the belt. Thus, these tests results do not insure that similar improvements will be seen in the field. Nevertheless, based on the fact that the innerliner reduces permeation over the whole skim and wedge region more or less uniformly, one would expect to see improvements in tire aging performance with reductions in permeability. The observed improvements in tire life are consistent with the effects of a two-fold reduction of oxygen transport on the oxidation rate as estimated from finite element modeling.[20,21] Along with reducing the extent of oxidation, improved innerliners also reduce the intracarcass pressure in the tire. High intracarcass pressure can lead to stresses that shorten tire life. These effects may be most significant for high inflation pressure LT-metric tires. It should be noted that some load range E tires (maximum inflation pressure of 80 psi) exhibit sidewall bulges and other failure modes after extensive oven aging and fail almost immediately on road wheel testing.[30] Reducing intracarcass pressure in these tires would be expected to improve both the extent of oxidation and the retention of mechanical integrity. An innerliner with a rubber content that has significant halobutyl rubber content is currently the state of the art for innerliners, however, technologies with even lower oxygen permeation may soon be available. For example, Rogers *et al.* have reported that a nanocomposite innerliner reduces permeation by 40% relative to a 100% bromobutyl innerliner.[48] More specific barrier technologies have also been proposed by Exxon Chemical and Yokohama Tire involving the use of a rubber/polyamide vulcanizate in place of a traditional butyl innerliner.[49]

CONCLUSION

Despite the significant effects of field variability on rubber aging in tires, it is possible to derive reasonable estimates of aging rates for key rubber properties in tires. In addition, various conditions can be defined for oven aging of tires: mount tires on wheel, inflate tire with air or 50/50 N2/O2 to the maximum sidewall pressure and expose at 60-70 °C. Depending on the specific conditions, it is possible to produce tires in 7-10 weeks that appear to be equivalent to tires aged in Phoenix for 6 years independent of tire size or brand. It is possible to meaningfully evaluate the resulting artificially aged tires. SUL testing of oven aged tires can provide a means to rank tire aging performance.

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