

ACCELERATED AGING OF TIRES, PART III

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ABSTRACT

The purpose of this research is to determine the conditions whereby a new tire can be artificially aged in an accelerated manner, in order to duplicate the actual mechanism of chemical aging observed in field-aged tires. The ultimate goal of the study is to age tires to a desired level, say equivalent to 4 years old, and then test the tires in durability, high speed, and performance tests. The previous paper described various oven aging methodologies and the data analysis techniques used. This paper will build on the previously described data analysis techniques developed for elongation at break measurements and apply them to swelling ratio data and peel strength data.

By utilizing the method initially developed by Gillen and modified by this laboratory for use with tires, it has been shown that the skim rubber of tires oxidatively ages at oven temperatures between 40 °C and 70 °C when mounted and inflated with either air or a blend of 50/50 N₂/O₂. The methodology has been successfully extended from elongation at break data to peel strength and swelling ratio data. The calculation of the Arrhenius activation energy for diffusion of oxygen through new and aged rubber was also determined. The effect of aging on permeability is to reduce the permeability of oxygen and increase the activation energy. These results have important implications when attempting to model the diffusional aging characteristics of inflated tires. The effect of changing the partial pressure of oxygen and its concomitant effect on the acceleration of aging was also investigated. The results indicate that by doubling the partial pressure of oxygen, the rate of oxidation is increased by approximately 1.5 times. This result is entirely consistent with the theory of diffusion limited oxidation.¹

INTRODUCTION

This paper reports the effects of static oven aging on tire rubber properties and extends the work of the two previous papers.^{2,3} This paper seeks to further refine the methodology developed for utilizing shift factors to determine the kinetics and mechanism of accelerated aging. The approach uses the shift factor method developed by Gillen, *et al.* to analyze the kinetics of peel strength decay and swelling ratio change.^{4,6} The method was used to determine if the aging of the skim rubber is limited by the diffusion of oxygen and whether the results obey the Arrhenius equation. The Arrhenius plots were constructed using the shift factors empirically determined from the plots of peel strength or swelling ratio vs. time in the oven at temperatures ranging from 40-70 °C. The permeability of a model body ply coat compound was measured to determine the energy of activation of oxygen diffusing through a filled rubber compound. The measured value was then used to determine the mechanism of degradation for the properties of peel and swelling ratio. The shift factor methodology was also used to determine the acceleration factors for oxidation of oven aged tires where the pressure was increased to 1.5 and 2 times the maximum listed on the sidewall.

EXPERIMENTAL

MATERIALS

One tire type was used in the study, a Goodyear Wrangler AP[®] LT245/75R16 (DOT Code MD11APWV4003). Tires were mounted and inflated to the following pressures prior to oven aging: 450 kPa (65 psi), 675 kPa (97.5 psi), and 900 kPa (130 psi). In the case of tires inflated with 100% O₂ or a 50/50 blend of N₂/O₂, the atmospheric air present was not purged; the blend was added on top of it yielding a tire cavity concentration of approximately 86% or 44% O₂, respectively. Tires were aged in air circulating 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

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were calibrated per ASTM E 145 with an A2LA approved, modified, method for temperature uniformity, consistency, air flow exchanges and airflow velocity.

TABLE I
RECONSTRUCTED SKIM COMPOUND FOR TIRES TESTED IN STUDY

Ingredient	PHR	Extractables	Ash	Volume
Polyisoprene	100	1.0		107.5
Carbon black (N326)	61			33.9
Zinc oxide	6.7		6.7	1.2
Calcium carbonate	1.0		1.0	0.4
Diocetyl adipate	1.0	1.0		1.0
Hydrocarbon oil	5.4	5.4		5.5
Cobalt naphthenate	0.5	0.1	0.1	0.5
Wax	1.0	1.0		1.0
Stearic acid	1.0	1.0		1.2
Santoflex 6PPD	2.0	2.0		1.7
Misc. extractables ^{a)}	1.0	1.0		1.1
Santocure NS	1.5	0.3		1.0
Sulfur	2.3			1.2
Total	184.4	12.8	7.8	157.2
Calculated ash content (by wt.)	4.2%			
Calculated extractables (by wt.)	6.9%			
Calculated carbon black (by wt.)	33.1%			
Calculated density (mg/ml)	1.173			

^{a)} Formulation may contain processing aids, waxes, etc.

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 $\frac{1}{8}$ " (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) at 24 °C.

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.

Reconstruction of Skim/Wedge Rubber Chemical Formulation. — An attempt was made to reconstruct the formulation. As the reader is undoubtedly aware, chemical reconstruction of a

thermoset rubber is difficult and the precise formulation is known only to the compounder. Nevertheless, it is important to understand, at least generally, the chemical make-up of the compound one is studying. Table I contains the reconstructed formula. It is also important to realize that the formula represents the rubber *as tested*, not necessarily as formulated.

Permeability Testing. — Permeability testing was performed on a model plycoat compound (Table II) at 4 different temperatures, 30 °C, 45 °C, 60 °C, and 75 °C. The method used was ASTM D1434.

TABLE II
MODEL PLYCOAT COMPOUND USED IN PERMEABILITY MEASUREMENTS

Raw Material	PHR
Emulsion SBR (23 % styrene)	50
Natural rubber	50
N660 carbon black	60
Paraffin oil (Sunpar 150)	10
Zinc oxide	3
Tall oil rosin (NovaRes 1179)	2
Antioxidant(mixed diaryl-phenylenediamines)	0.5
Antioxidant [N-phenyl-N-(1,3-dimethylbutyl)-p-phenylenediamine]	0.5
Accelerator, (N-cyclohexyl benzothizole-2-sulfenamido)	1
Insoluble sulfur	2.5

RESULTS AND DISCUSSION

The chemical aging of natural rubber (NR) is generally divided into two types: aerobic and anaerobic. Aerobic aging can be further separated into two mechanisms. Both aerobic kinetic schemes involve the initial step of oxygen cleaving the unsaturated polymer main chain. Depending on the temperature and oxygen concentration, the newly formed main chain radical can either propagate through other double bonds, thus increasing the modulus and lowering the strain at break value, or not propagate and rearrange into stable products which lowers *both* the modulus *and* the strain at break value. It has been shown that the propensity for chain scission to dominate over crosslinking increases as the temperature and/or the oxygen concentration increases.⁷⁻⁸ Typically, the predominance of anaerobic aging is associated with relatively high temperatures, e.g. above 100 °C, and is characterized by the breaking and rearranging of the sulfur crosslinks. The physical characteristics of anaerobically aged rubber are lower modulus with retention or even an increase in the strain at break value. The reason for either the aerobic or anaerobic mechanism to dominate in any particular article is design and application dependent. Since oxygen must diffuse through the rubber, a thicker article will exhibit less aerobic aging toward its middle, farther away from the oxygen source. The reason the middle of a thicker rubber article is less affected by oxidation is because oxygen reacts with the rubber along the way, thus starving the interior of oxygen. Even relatively thin samples will show a gradient of oxidation from surface to middle, however, if the temperature is sufficiently high. This mechanism is referred to as Diffusion Limited Oxidation (DLO) and becomes significant when the rate of oxygen consumption in the rubber is greater than the rate which oxygen can be resupplied through diffusion.⁹ It has been shown that the belt package rubber of passenger car tires in the North American market oxidatively age, therefore care must be taken that the laboratory acceleration

mechanism is also oxidative.^{10,11}

Investigation into accelerated aging was done by using mounted, inflated tires statically aged in ovens at various times and temperatures. The reason behind mounting the tires was twofold; one, to more closely duplicate the actual condition of a tire in the field and two, because it has been reported that the inflating air permeates the halobutyl innerliner and is the source of oxygen for the belt package region of the tire.¹² Oven aging was chosen because it is well known that increased temperatures accelerate oxidative aging of NR. Three filling gases, air, a 50/50 blend of N_2/O_2 , and 100% O_2 were used. In the case of tires inflated with either 100% O_2 or the 50/50 blend of N_2/O_2 , the atmospheric air present was not purged; the blend was added on top of it yielding a tire cavity concentration of approximately 86% or 44% O_2 , respectively.

The method employed to analyze the data obtained from the skim rubber was that of Gillen,^{4,6} *et al.*, who employed the classic time-temperature superposition approach using strain at break data. The method will be used to analyze the kinetics of aging in order to determine both if the aging of the skim rubber is diffusion limited and whether or not the results obey the Arrhenius equation. Arrhenius plots will be constructed using the shift factors (a_t) empirically determined from the plots of peel strength vs. time and swelling ratio vs. time. Figure 1 is a plot of the peel strength vs. time. Figure 2 is the plot of swelling ratio vs. time. It is customary to shift the data along the X-axis from the higher temperatures on to the lowest temperature tested, in this case 40 °C. Figure 3 is the plot of the shifted data for peel strength and Figure 4 is the plot of shifted data for the swelling ratio data (the shift factors (SF) for each data set are included in the legend of the Figures). This data also falls on a logarithmic regression fit. It should be noted that the logarithmic fits were performed *after* the empirical shift factors were determined and are added to aid the reader's eye.

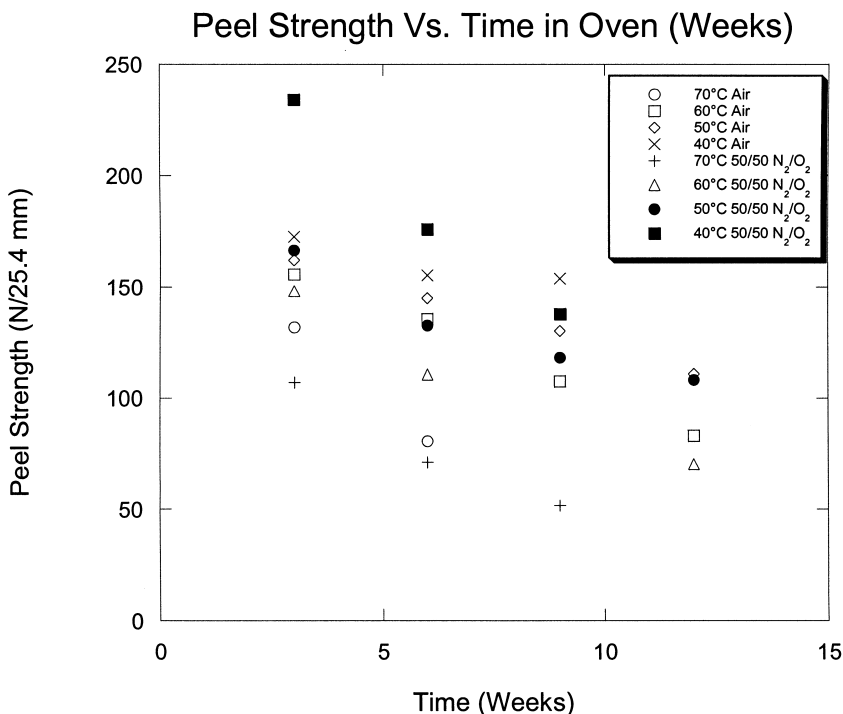


FIG. 1. — Peel strength vs. time in oven. Tires were inflated with either air or a blend of 50/50 N_2/O_2 .

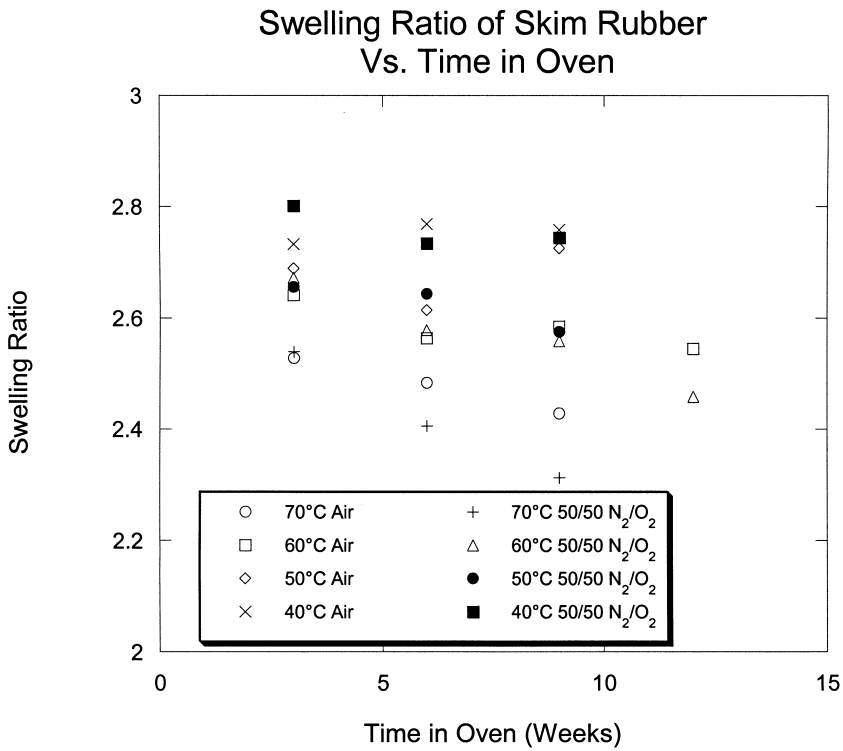


FIG. 2. – Swelling ratio vs. time in oven. Tires were inflated with either air or a blend of 50/50 N₂/O₂.

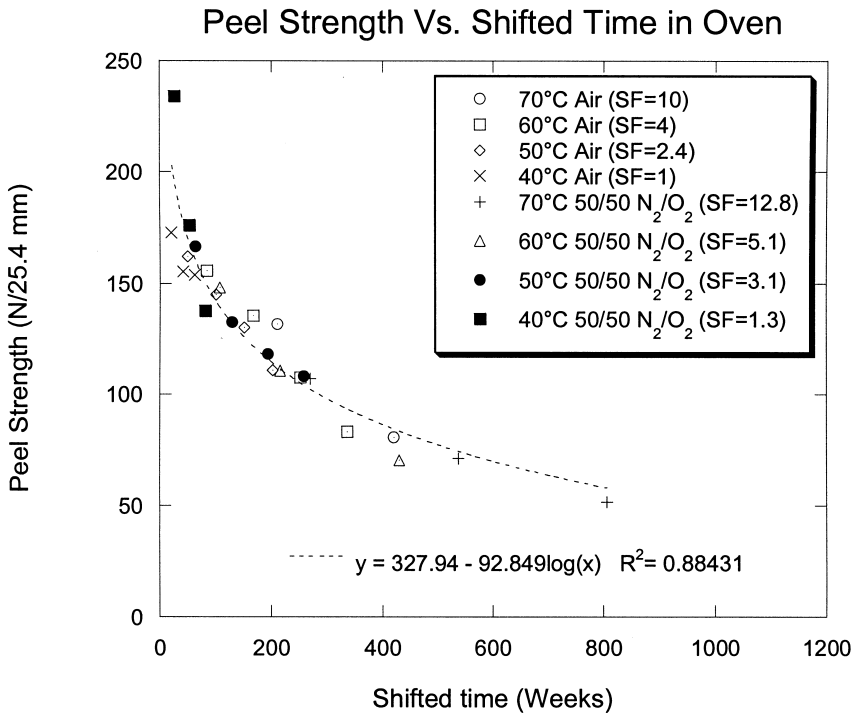


FIG. 3. – Peel strength vs. shifted time in oven. Shift factors are in the legend, designated by SF. All data was shifted onto the results for 40 °C inflated with air.

In order to extract the apparent activation energy due to oxidation kinetics, ΔE_k , from the shift factors, it is necessary to understand and estimate the contributions of diffusional effects to the aging process. The process of O_2 diffusion can be reflected by an additional contribution to the overall apparent activation energy, ΔE , by an amount related to the activation energy for the diffusion of O_2 , ΔE_d . An inherent assumption in determining how these quantities are calculated is the implication that a measured quantity (such as swelling ratio or peel strength, for example) is linearly related to the total amount of O_2 reacted into a sample. Given this assumption, one only needs to examine the O_2 flux, f_{O_2} , at the surface of a semi-infinite slab:¹³

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

where D and k are the diffusivity and first order rate constant for O_2 , respectively. Inserting the Arrhenius temperature dependency for D and k results in:

$$f_{O_2} = C_0(D_0k_0)^{\frac{1}{2}} \exp\left(-\frac{\Delta E_k + \Delta E_d}{2RT}\right) = C_0(D_0k_0)^{\frac{1}{2}} \exp\left(-\frac{\Delta E}{RT}\right) \quad (2)$$

where, D_0 , and, k_0 , are pre-exponential factors, R , is the universal gas constant, and, T , is the temperature. Thus, a measured overall apparent activation energy can be related to the more fundamental diffusional and kinetic energies by:

$$\Delta E = \frac{\Delta E_k + \Delta E_d}{2} \quad (3)$$

Therefore, a plot of $\text{Log}(a_t)$ vs. $1/T$ yields:

$$\text{Slope} = \frac{\Delta E_k + \Delta E_d}{2} \quad (4)$$

The permeability of oxygen through a model plycoat compound was run at four different temperatures to determine the apparent energy of activation for diffusion of oxygen (formulation shown in Table II). The resulting Arrhenius plot is shown in Figure 5. The data represents two measurements; the first measurement was made on a freshly cured sample, the second measurement was made on a sample aged for 9 days at 90 °C. The sample thickness was below 1mm to ensure homogeneous oxidation occurred (this was confirmed with indentation modulus profiling along the cross section of the sample). The apparent energy of activation for oxygen diffusion through the fresh sample was calculated to be 30 kJ/mole, and for the aged sample the value was 31 kJ/mole. These numbers agree with the previous literature value of ΔE_d for the diffusion of O_2 through natural rubber, 34 kJ/mole.¹⁴ The value of ΔE_d for the aged sample will be used in the calculation of ΔE_k .

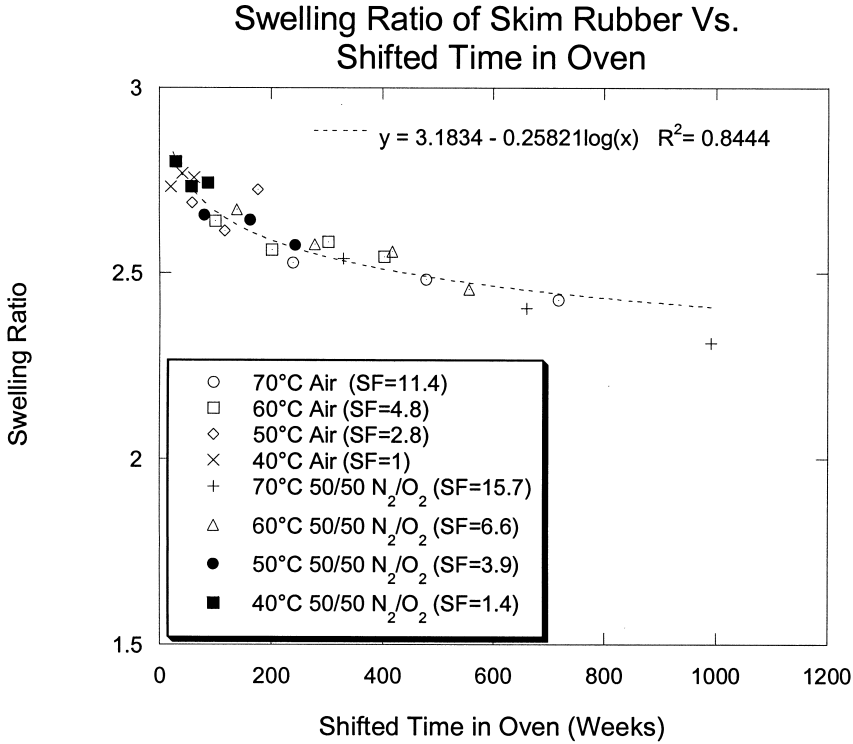


FIG. 4. – Swelling ratio vs. shifted time in oven. Shift factors are in the legend, designated by SF. All data was shifted onto the results for 40 °C inflated with air.

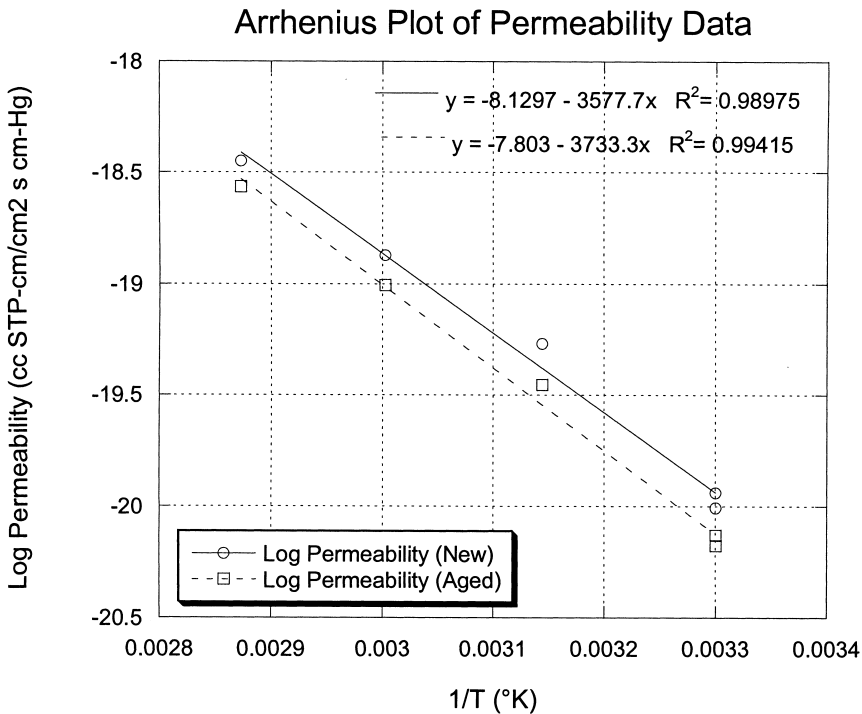


FIG. 5. – Arrhenius plot for permeability measurements made on model plycoat compound. The aged data represents rubber that has been aged in an oven at 90 °C for 9 days.

Figure 6 is a graph of log shift factor vs. $1/T$ for the peel strength and swelling ratio (For air inflated tires only. The slopes for the respective enriched oxygen inflated tires are identical). The apparent activation energy (that is, the energy of activation calculated from just the value of the slopes from Figure 6) over this temperature range is ~ 70 kJ/mole for both inflation media. Inserting the value of ΔE_d and the slopes from Figure 6 into Eq. (4) yields the correct energy of activation for the property changes with respect to time and temperature. For peel strength, the energy of activation is calculated to be 101 kJ/mole, and the energy of activation for the swelling ratio is 109 kJ/mole. These values are in excellent agreement with the activation energies reported in the literature for the oxidation of crosslinked natural rubber.¹⁵ This method of analysis confirms that the mechanism of aging for the skim rubber in these tires is aerobic in the temperature range from 40 °C to 70 °C.

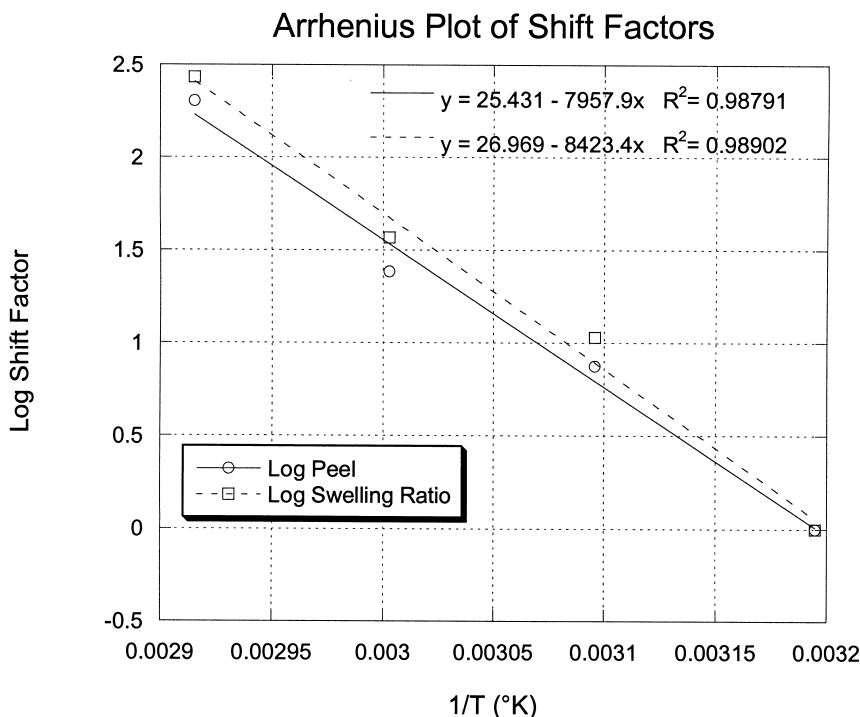


FIG. 6. – Arrhenius plot for the shift factors (for tires inflated with air) from Figures 3 and 4.

Another experiment was performed to quantify the acceleration effect by increasing the partial pressure of oxygen in the tire cavity. All tires were aged at 60 °C for 3-12 weeks in the oven. The partial pressure was changed in two ways; by increasing the pressure of air or 50/50 blend of N_2/O_2 to 1.5 and 2 times the maximum sidewall inflation pressure, or by increasing the concentration of oxygen at the normal pressure (1.0 times the maximum sidewall inflation pressure). Figure 7 shows the data for the swelling ratio vs. the shifted time in the oven (the data was shifted onto the 60 °C air inflation data at 1.0 times the maximum sidewall inflation pressure). The data set for nitrogen inflated (reported previously) tires was also included for reference.¹⁶ The shift factors plotted against the partial pressure of oxygen are shown in Figure 8. Partial pressure was calculated by taking the measured oxygen concentration at the beginning of aging and multiplying by the measured pressure. The results show a good relationship between the oxygen partial pressure and the swelling ratio shift factors. This means that the greater the oxygen concen-

tration in the tire cavity, the faster the belt package rubber oxidizes. The rate, however, is not doubled with a doubling of the oxygen concentration. This result is entirely consistent with the theory of diffusion limited oxidation.¹

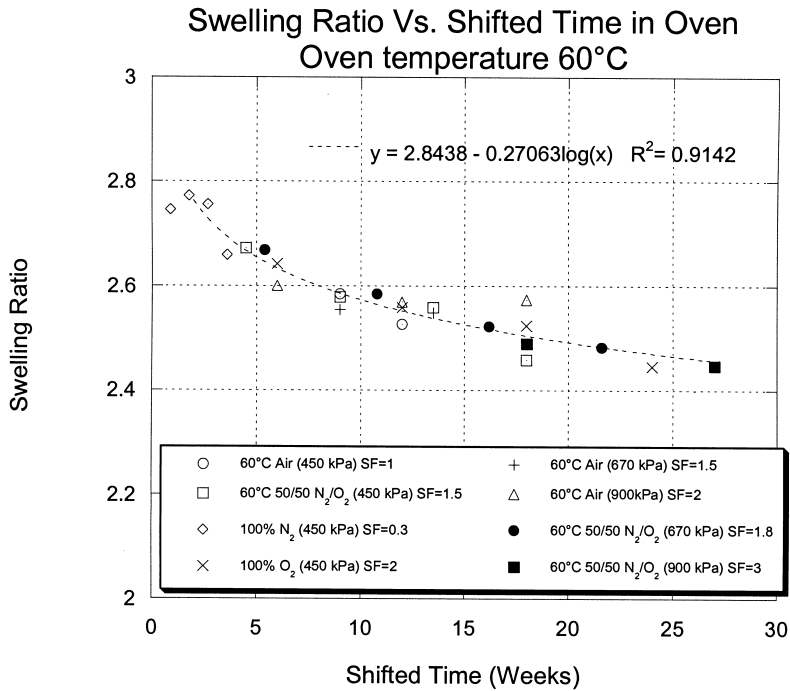


FIG. 7. – Swelling ratio vs. shifted time in oven for tires aged at 60 °C with various partial pressures of oxygen.

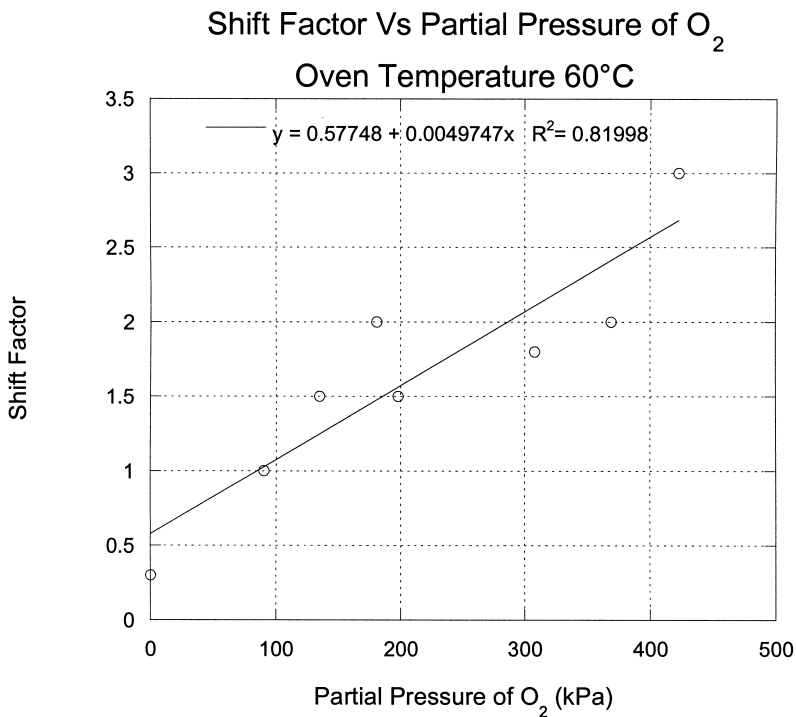


FIG. 8. – Shift factors vs. partial pressure of oxygen.

CONCLUSIONS

By utilizing the method initially developed by Gillen and modified by this laboratory for use with tires, it has been shown that the skim rubber of tires oxidatively ages at oven temperatures between 40 °C and 70 °C when mounted and inflated with either air or a blend of 50/50 N₂/O₂. The methodology has been successfully extended from elongation at break data to peel strength and swelling ratio data. The calculation of the Arrhenius activation energy for diffusion of oxygen through new and aged rubber was also determined. The effect of aging on permeability is to reduce the permeability of oxygen and increase the activation energy. These results have important implications when attempting to model the diffusional aging characteristics of inflated tires. The effect of changing the partial pressure of oxygen and its concomitant effect on the acceleration of aging was also investigated. The results indicate that by doubling the partial pressure of oxygen, the rate of oxidation is increased by approximately 1.5 times. This result is entirely consistent with the theory of diffusion limited oxidation.¹

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