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Passenger tires inflated with nitrogen age slower

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Executive summary

There has been a substantial amount of interest in N_2 inflation of tires over the years. N_2 tire inflation is used in the aerospace and racing industries and is beginning to make inroads into the long haul trucking industry. Some of the main benefits of using N_2 as an inflation medium are: higher air pressure retention due to lower permeability than O_2 through IIR, NR and SBR compounds (which leads to improved gas mileage); linear volume expansion with temperature because of nitrogen's inherently low water absorption characteristics; and the expected improvement in structural durability due to a significant reduction in rubber oxidation (oxidation caused by air from the cavity being forced into the tire carcass). With the advent and commercialization of polymer membrane separation techniques, N_2 generation has become much more affordable and easier to maintain than in the past. This paper will investigate the effect N_2 inflation has on the oven aging performance of passenger tires. Results from field aging studies, along with oven aging studies using air and a 50/50 mixture of N_2/O_2 as inflation media, show significant changes in the tire rubber properties with time. When N_2 is used as the inflation media, the change in rubber properties is slowed down significantly or even halted.

N_2 tire inflation is common to several industries. The aerospace industry uses nitrogen because of its consistent inflation pressure retention and reduction of oxidation in the rubber compounds. Auto and motorcycle racing use nitrogen because it is inherently dry compared to compressed air. Depending on the humidity of the inflation air, tire pressure can change dramatically (and non-linearly) during the heat build caused by racing. Nitrogen performs predictably as an ideal gas because it does not readily absorb or carry water. Large tires used on off-road vehicles in the mining industry, for example, use nitrogen to prevent auto-ignition of the tires due to the high temperatures and thick treads.

TECHNICAL NOTEBOOK
Edited by Harold Herzlich

Adoption of nitrogen tire inflation into passenger and truck tires has been much slower. Some reasons for the slower adoption rate of nitrogen inflation into mainstream applications are: 1. accessibility to nitrogen inflation systems, 2. cost of nitrogen inflation systems, both to the provider and the user, and 3. dearth of information as to the benefits of nitrogen inflation for either the fleet owner or average consumer. One benefit of using N_2 is claimed to be higher air pressure retention because of the lower permeability of N_2 than O_2 through IIR, NR and SBR compounds. While this is true in controlled laboratory tests of pressure retention in tires, the benefit to the real world consumer could be somewhat less. Pressure loss due to leakage around the rim flange seal of the tire to the rim and also the valve seal to the wheel (plus pressure loss through the valve itself) could account for some of the air loss experienced by the typical consumer, for example. The characteristic linear volume expansion with temperature because of nitrogen's inherently low water absorption characteristics is no benefit to the average driver because the handling requirements for daily commuting are nowhere near as demanding as for racing; the improvement would be negligible and imperceptible.

The expected improvement in structural durability due to a significant reduction in rubber oxidation, however, could be a tremendous benefit to both the fleet owner and consumer. It is believed that rubber oxidation in the interior of a tire is caused by air from the cavity being forced into the tire carcass.[1] The National Highway Traffic Safety Administration recently completed a study into the physical and chemical properties of field aged tires, including the mechanism of aging.[2] The NHTSA study included "cut tire" analysis of approximately 150 tires retrieved from the field manufactured by Bridgestone/Firestone, Goodyear and Michelin. To quote from the study:

"The general pattern of change indicates that cross-link density evolution due to aerobic and thermal aging is the dominant aging factor."

The tires that were the focus of the NHTSA study were found to be defective in part because the physical properties of the rubber in the steel belt area had deteriorated due to oxidative aging. Studies conducted by this laboratory confirm the NHTSA findings.[3] Further work has demonstrated that accelerated oxidative aging of tires can be accomplished by use of an oven and the mechanism of aging is identical to tires obtained from the field.[4,5]

If the use of nitrogen as the inflation media can slow down or retard the oxidative degradation of tire rubber, then the durability of the tire should be improved. One mechanism for how tire durability could be improved is by reducing the oxidative aging of the wedge rubber.

The wedge rubber in a steel-belted radial tire is added to help prevent belt edge separations from occurring. It is for this reason that the wedge rubber is one of the most important tire components; the wedge rubber helps determine the durability of a tire. As a tire goes

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Fig. 1. Tire nomenclature used in this paper.

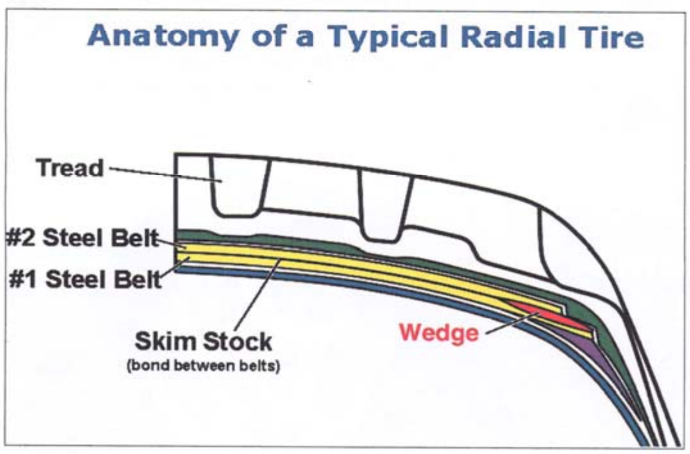
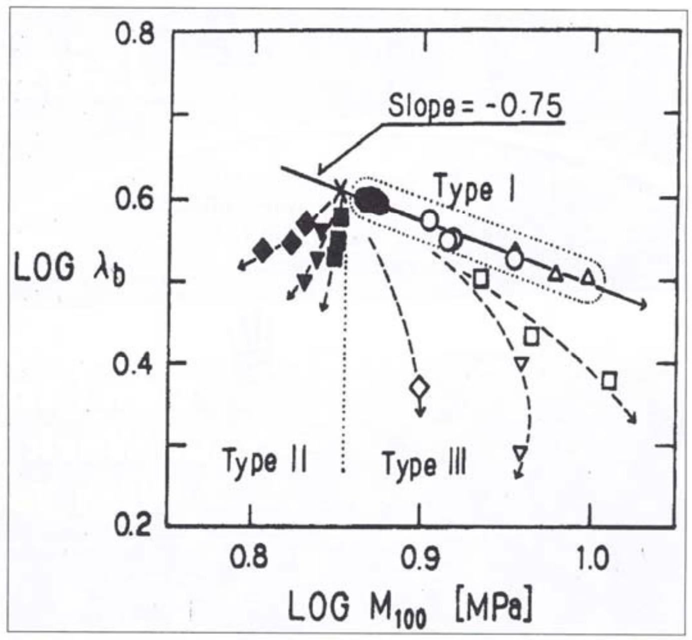


Fig. 2. Data analysis ("Ahagon Plot") used to understand aging mechanism of wedge rubber. The plot is of the log of the strain ratio at break vs. the log of the modulus at 100-percent strain. Linear Type I aging is considered normal, oxidative aging. Type II aging is considered high temperature, anaerobic aging. The mechanism for Type III is high temperature oxidative aging, which also could be called diffusion limited oxidation (DLO).



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through repeated stress cycling during its lifetime, the strains are the greatest at the belt edge. When the wedge rubber aerobically ages, the material begins to stress harden. This stress hardening lowers the elongation at break and may lower its resistance to crack growth during the stress cycles. This is important because tread and belt delaminations start with cracks growing from the wedge inward between the steel belts. Nitrogen inflation could prevent the wedge from stress hardening, thus improving the crack growth resistance, which in turn would improve tire durability. Earlier work done on tube-type bias ply tires and roadwheel tested steel-belted radials has shown improvements in durability compared to air-inflated tires.[6,7]

The research presented in this paper will concentrate on the effect nitrogen tire inflation has on the change in rubber properties around the steel belt of the tire. Tires inflated with 96 percent and 99.9 percent nitrogen were oven aged at 60°C for three to 12 weeks. For comparison, tires inflated with either air or a 50/50 mixture of N_2/O_2 were oven aged alongside the nitrogen-inflated tires. After aging, tires were cut and a number of tests were performed. These included the measurement of peel force between the first and second steel belt, which is a measure of the tearing energy of skim rubber. Tensile and elongation properties also were obtained from samples of the wedge rubber located between the steel belts in the shoulder.

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 maximum pressure listed on the sidewall prior to oven aging: 450 kPa (65 psi). In the case of tires inflated with the 50/50

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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 44 percent O_2. For tires inflated to 96 percent nitrogen, 99.9 percent pure nitrogen was added on top of the atmospheric air present in the tire cavity, thus yielding the 96 percent concentration. The tires yielding 99.9 percent pure nitrogen cavities were inflated and purged 10 times each with 99.9 percent nitrogen. Tires were aged in the same ovens for three, six, nine and 12 weeks at 60°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.

Physical properties

Tensile and elongation—Samples of the belt wedge rubber (**Fig. 1**), located between belts 1 and 2 were removed from both shoulders of unaged and 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 stresses at 25-percent, 50-percent, 100-percent strain and each 100-percent strain thereafter, ultimate elongation and tensile strength. Samples were tested at 2.0 inches per minute (50.8 cm/minute).

Peel strength—Samples were prepared by cutting 2.5 inch (63.5 mm) wide radial sections, bead to bead. The sample was then sectioned into two 1.25 inch (31.75 mm) radial strips, which were each cut circumferentially at the centerline of the tread, resulting in four test specimens (2-SS and 2-OSS). Each sample was cut with a razor knife for a length of 1 inch (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 inch (3.175 mm) radially from the end of the gripping surface to the end of belt #2 in the shoulder area, providing a 1 inch wide peel section. The peel test was performed at 2 inches per minute (50.8 mm) at 24°C.

Reconstruction of skim and 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 makeup of the compound one is studying. **Table I** contains the re-

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Fig. 3. Ahagon plot for tires oven aged at 60°C with air, 50/50 N_2/O_2, 96 percent nitrogen and 100 percent nitrogen as the inflation media. The tires inflated with more than 95 percent nitrogen do not appear to change very much from the new tires, even after 12 weeks in the oven, whereas tires inflated with the oxygenated media change dramatically, even after three weeks in the oven.

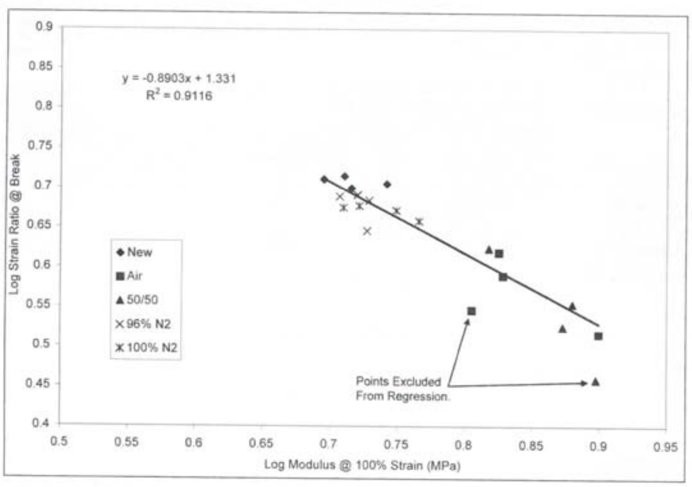


Fig. 4. Normalized strain at break vs. time for tires oven aged at 60°C with air, 50/50 N_2/O_2, 96 percent nitrogen and 100 percent nitrogen as the inflation media. Again, tires inflated with more than 95 percent nitrogen do not appear to change very much from the new tires. The exception is the data for tires at 12 weeks inflated with 96 percent nitrogen. The beginning of oxidative degradation can be seen. Nitrogen-inflated tires, however, degrade far slower than tires inflated with the oxygenated media.

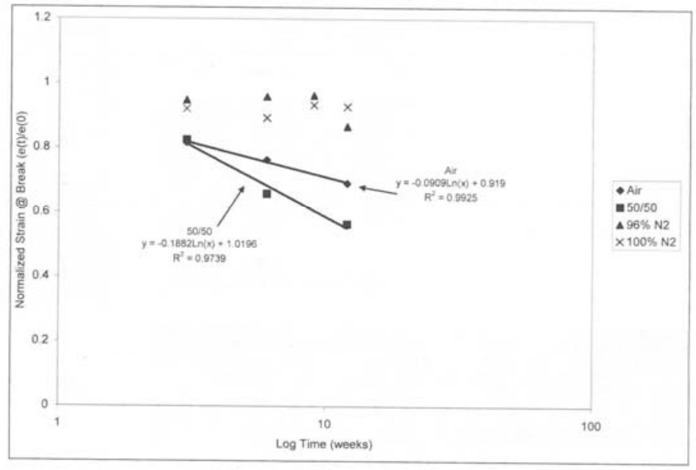


Fig. 5. Normalized peel strength vs. time for tires oven aged at 60°C with air, 50/50 N_2/O_2, 96 percent nitrogen and 100 percent nitrogen as the inflation media. The results show that tires inflated with more than 95 percent nitrogen degrade at a much slower rate than tires inflated with air or 50/50 N_2/O_2.

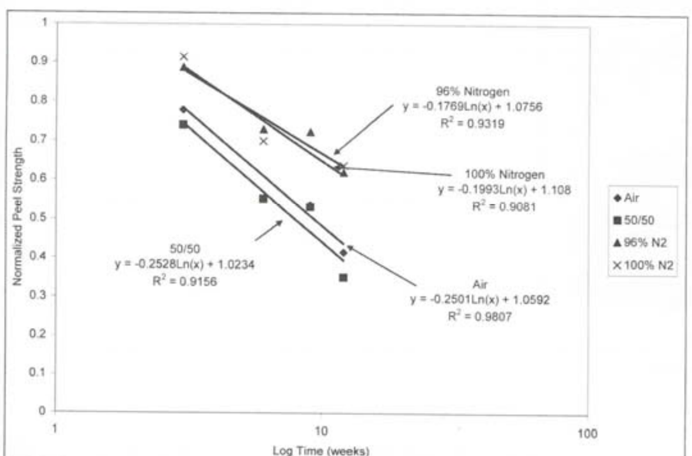
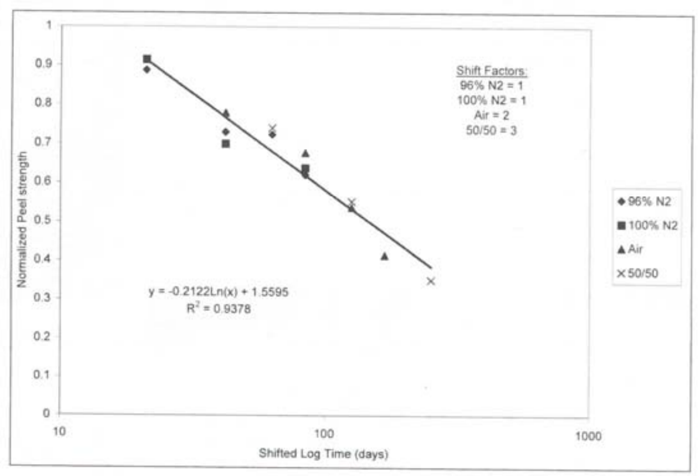


Fig. 6. A graph of the normalized peel data whereby the data for tires inflated with air or 50/50 N_2/O_2 are shifted along the x-axis to line up with data from tires inflated with more than 95 percent nitrogen. The data shifts overlap and appear to have an excellent fit to a logarithmic regression. This fact suggests that the change in the peel strength for nitrogen inflated tires is caused by oxidation in the skim rubber, not by changes in the crosslink distribution.



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constructed formula. It appears that the skim and wedge compounds for this tire construction are the same. It is also important to realize that the formula represents the rubber as tested, not necessarily as formulated.

Results and discussion

As stated in the introduction, the wedge rubber is one of the most important components of the tire construction related to durability. One of the more useful ways to analyze the change in properties of the wedge rubber is to utilize the data analysis method of Ahagon and co-workers, which correlates the strain ratio at break with the modulus at 100-percent strain.[8,9,10]

This approach is particularly useful in distinguishing between different aging mechanisms. By plotting the log of the strain ratio at break vs. the log of the modulus at 100-percent strain, a straight line with a slope of -0.75 is indicative of the aerobic aging of rubber. This approach was arrived at by taking one compound with different levels of sulfur and measuring the stress-strain data. The same compound (at one level of sulfur) was then oxidatively aged and it was shown that the stress-strain data behaved identically to the compounds with increased sulfur. Thus, the mechanism of oxidative aging was inferred to consist of increased crosslink formation. High temperature aerobic (defined as Type III aging) or possibly anaerobic aging (defined as Type II aging) of the rubber results in data deviating from the straight line.

It is important to realize that the slope of -0.75 is an empirically derived number and more than likely dependent on the aging characteristics of the individual compound being studied. Careful reading of the referenced studies does not yield a "first principles" reason for the slope to be any particular value. **Fig. 2** is a representation of how data for the various aging types would look in graphic form. Aerobically aging NR typically stress hardens, leading to lower elongation, which yields a prediction of a negative slope, given the data treatment shown.

Fig. 3 shows the results for the tires in the present study plotted in the manner described above. The nitrogen concentrations in the tire cavity at the beginning of oven aging for the four filling gas conditions were (in ascending order): 56 percent (the 50/50 N_2/O_2 inflation blend with 1 atmosphere of air present), 78 percent (air inflation), 96 percent (99.9 percent nitrogen with 1 atmosphere of air present), and 99.9 percent (99.9 percent nitrogen with the 1 atmosphere of air purged). The tires were aged at 60°C for three to 12 weeks. As can be seen in **Fig. 3**, the wedge rubber of the tires containing more than 95 percent nitrogen experienced almost no change in stress-strain

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properties, even after 12 weeks in the oven, while tires filled with air or 50/50 N_2/O_2 experienced a substantial change after only three weeks of oven aging. The changes seen in the data for tires inflated with more than 95 percent nitrogen are consistent with completion of curing of the new tire, not oxidative aging. The excluded points on the graph are for tires with air and the 50/50 N_2/O_2 mixture at 12 weeks in the oven. The mechanism of aging has been affected by loss of oxygen due to permeability over that time and the oxidation of the wedge rubber has become limited by diffusion.

An additional method used to analyze the data was to plot the normalized strain ratio at break vs. residence time in the ovens at 60°C (**Fig. 4**). Normalized strain ratio at break is determined by dividing the strain at break of a tire aged in the oven for time t ($e_{(t)}$) and dividing it by the strain at break for a new, unaged tire ($e_{(0)}$). The results in **Fig. 4** show that for tires inflated with more than 95 percent nitrogen there is an initial drop in strain at break. The reason for that again could be that new tires generally are undercured and the continuation of cure was completed during the first three weeks in the oven.

After the first three weeks, the results are unchanged for the durations tested, except for the point at 12 weeks oven duration and 96 percent nitrogen concentration. It may be that the oxygen concentration present in the tire took that long to reach the wedge in concentrations large enough to affect the strain at break properties. Again, tires filled with air or 50/50 N_2/O_2 experienced a substantial change after only three weeks of oven aging and continued that trend out to 12 weeks.

One conclusion that is inescapable from this initial work is that the oxidation of the steel belt rubber truly is driven from the contained air pressure inside a normal passenger or light truck tire. Granted, the rate of degradation would be much higher if no halobutyl innerliner was present, but the presence of innerliner and antioxidant packages only slows the rate of degradation, not eliminating it.

Peel strengths of the steel belt composites also were evaluated. The peel strength is a measure of the force required to separate the two steel belts and is a simple way to measure tearing energy.[11] **Fig. 5** shows the results of the normalized peel strength vs. log time. Normalized peel strength is determined by dividing the peel strength of a tire aged in the oven for time t ($p_{(t)}$) and dividing it by the peel strength for a new, unaged tire ($p_{(0)}$).

As opposed to the results for the strain at break of material obtained from the wedge region of the tire, the peel strength of rubber from the much thinner skim region does degrade with time for all inflation media used in the study. The results in **Fig. 5** also show, however, that the tires inflated with more than 95 percent nitrogen degrade at a much slower pace than tires inflated with air or 50/50 N_2O_2. The fact that tires inflated with either 96 percent or 99.9 percent nitrogen degrade almost identically leads one to believe that ei-

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ther oxygen is reaching the belt skim rubber from the outside of the tire or that the change in peel strength is due to a change in the crosslink density distribution not detected in the wedge material properties. Both mechanisms are being investigated and will be reported in future work. Oxygen uptake measurements are being taken on the skim stock to determine whether oxygen is reaching the area from another source and crosslink distribution measurements are being made to determine if any sulfur rearrangements have occurred.

The data shown in **Fig. 5**, however, all appear to be changing according to the same mechanism. If that is true, then one should be able to shift the data according to a time-pressure superposition method to determine the acceleration of the degradation mechanism present. Ferry has shown that ultimate properties can be analyzed using reduced variables and shifted with respect to temperature or pressure.[12] In this case, the partial pressure of oxygen is different between the four conditions analyzed.

Fig. 6 is a graph of the normalized peel data whereby the data for tires inflated with air or 50/50 N_2/O_2 are shifted along the x-axis to line up with data from tires inflated with more than 95 percent nitrogen. The data shifts overlap and appear to have an excellent fit to a logarithmic regression. This fact suggests that the change in the peel strength for nitrogen-inflated tires is caused by oxidation in the skim rubber, not by changes in the crosslink distribution.

One could infer from the shift factor between air and nitrogen inflation that tires inflated with nitrogen would take twice as long to deteriorate as air-inflated tires would. While this may be true at 60°C, the magnitude of improvement may be lessened if the data were shifted down to temperatures that tires operate at normally. The discrepancy would be caused by possible diffusion limited oxidation effects at 60°C vs. ambient temperature. The concentration of oxygen diffusing into the tire may be sufficiently low enough in the oven so that it never reaches the wedge and only small amounts reach the skim because at elevated temperatures the oxygen reactivity is increased. At ambient temperature, however, more oxygen may reach the

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skim and perhaps even reach the wedge. This is not to say that tire oxidation is not driven by the inside air pressure, just that in the absence of inside air pressure, oxidation in the wedge and skim regions may occur from outside air and the rate could be higher than what is reported at 60°C. Nonetheless, it is perhaps a fair assumption to say that there would be some improvement in tire durability if nitrogen was used as the inflation media, but it is too soon to speculate as to how much of an improvement it would be.

Conclusions

The overall conclusion of the study is: When N_2 is used as the inflation media, the change in rubber properties is slowed down significantly or even halted. From a practical standpoint it is important to note that the presence of 1 atmosphere of air in the 96 percent nitrogen-inflated tires did not significantly affect the results, as compared to the 99.9 percent nitrogen-inflated tire. This is important for the average consumer because the need to purge existing tires completely of air before filling with nitrogen may not be necessary.

Another conclusion is that the oxidation of the steel belt rubber truly is driven from the contained air pressure inside a normal passenger or light truck tire. The skim region may be oxidized slightly from outside the tire when filled with nitrogen, but the rate of degradation is significantly lower than when the tire is filled with air. The wedge rubber, on the other hand, is in a sufficiently thick part of the tire, and is not nearly as susceptible to oxidation from the outside. The converse of this conclusion, therefore, is that oxidative aging can be accelerated by the use of oxygen enriched filling gases in the tire cavity without changing the mechanism of degradation in the tire's internal components.

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Table I. Chemical reconstruction of the wedge rubber compound found in the tires used in this 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
Dioctyl Adipate	1.0	1.0		1.0
Hydrocarbon Oil	5.4	5.4		5.5
Cobalt Napthenate	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*	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

* Formulation may contain processing aids, waxes, etc.