

Effects of Atmospheric Pollutants at High Temperature on the Adhesion of RFL-Coated Tire Cords to Rubber

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Synopsis

The examination of treating oven pollutant effects on the adhesion of RFL-coated polyester and nylon tire cord to rubber was conducted using a hot strip adhesion test. Ozone, ultraviolet light, and ozone-ultraviolet light were examined at 140°F. Nitrogen oxides, sulfur dioxide, and air were tested at 320°F. Ozone and ozone-UV (singlet molecular oxygen) systems were many orders of magnitude greater degradants than the other pollutants known to exist in the ovens. The remaining pollutants tested were ranked in order of degradation effect with $\text{NO}_2 > \text{NO} \gg \text{SO}_2 \approx \text{air} \approx \text{heat alone}$. The mechanism for adhesion loss involves addition to the olefinic double bonds to reduce unsaturation sites for cure.

INTRODUCTION

The adhesion of tire cords to rubber compounds is influenced by tire yarn substrates, adhesive systems, and rubber compounds.¹ Resorcinol-formaldehyde latex (RFL)-treated tire cords have shown a sensitivity to environmental exposure. Recent publications have discussed the effects of ozone and ultraviolet light on tire cord adhesion.^{2,3}

Atmospheric conditions, whether at room temperature or in high-temperature ovens, do not consist of pure environments. Direct-fired treating and drying ovens generate mixtures of nitrogen oxides and sulfur oxides by burning fuels with bound nitrogen^{4,5} and sulfur.⁶ Natural environments contain these pollutants as well as mixtures of other contaminants which can undergo equilibrium reactions.⁷⁻¹³ These natural environments can vary seasonally and locally. For example, Los Angeles smog contains high levels of ozone while sulfur dioxide is prevalent in the air of eastern cities.⁷

High temperature can further complicate the parameters for adhesion loss by overcure. The work described in this paper was directed to the establishment of the effects at elevated temperatures of ozone, UV light, nitrogen oxides, sulfur dioxide, and air on the adhesion of RFL adhesive-treated nylon and polyester cords to rubber compounds.

EXPERIMENTAL

Pollutant Gases

Nitrogen dioxide, nitric oxide, and sulfur dioxide were obtained at the listed ppm level in air or nitrogen from Airco Industrial Gases.

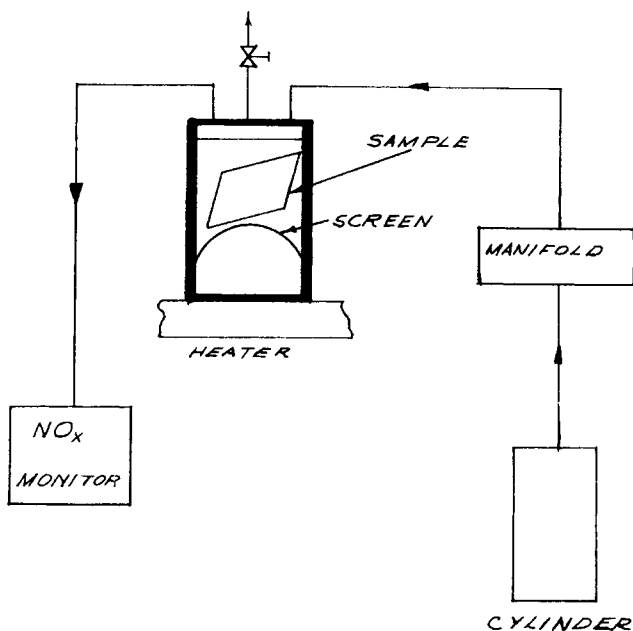


Fig. 1. Schematic diagram of glass chamber for 320°F studies.

Compressed air, oxygen, nitrogen, and argon were purchased from commercial distributors.

Ozone was generated by the passing of air over an electron discharge monitor.

Fibers

Nylon 6,6 (du Pont T-728) and polyester (du Pont T-503 Dacron) were twisted to tire cord constructions (T-728: 840/1/2, 13 × 13 tpi; T-503: 1000/1/3, 9.2 × 9.2 tpi). An open fabric was woven from the fiber (nylon, 20 epi; polyester, 25 epi).

The two-dip adhesive system¹⁴ developed by Shoaf¹⁵ was applied to the polyester. Nylon was coated with an RFL system of similar formulation to the dip described in the literature.¹ The coated fabric was dried and cured at temperatures and times previously reported.^{1,2}

Testing Chambers for Pollutant Effects

A pollution chamber was designed and constructed for the experimental work at 320°F (Fig. 1). A 1000-ml resin reaction kettle fitted with a heating mantle was used as the chamber. A wire screen was inserted in the chamber to a height of 3 in. from the bottom. The screen acted as a stand to hold fabric during testing and to prevent fabric charring from contact on the bottom glass surface. When two fabric samples were tested simultaneously, the fabric was enclosed in a wire tube. An inlet tube in the cover of the vessel was connected via a glass manifold to the cylinders containing the pollutant gases. An exit tube to the flowmeter and the Aero Chem Research Laboratories' Model AA-5 Chemiluminescence instrument for NO-NO_x monitoring was attached to the cover plate. A second

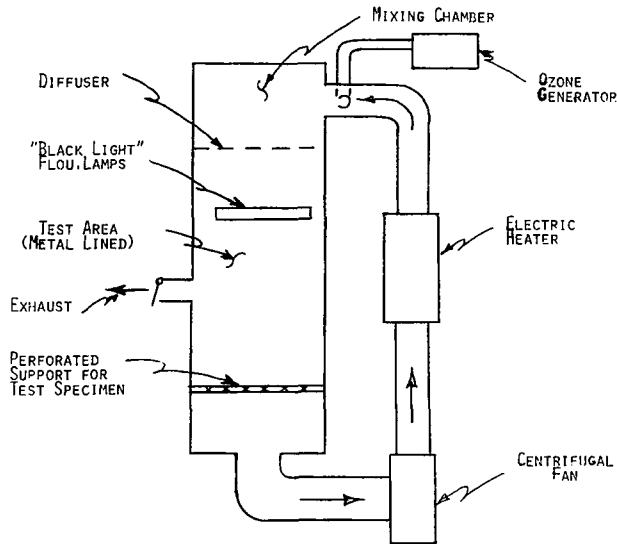


Fig. 2. Schematic diagram of aluminum lined chamber.

exit line for maintaining a positive pressure was also connected to the cover plate. When testing, the chamber was preheated and then purged with the test gas for 15 min. Fabric samples were placed in the vessel and the gas flow continued throughout the test.

The ozone, UV, and ozone-UV work was conducted in an aluminum-lined chamber diagrammed in Figure 2. The temperature inside the chamber was increased to 140°F (the maximum limit of the chamber) for all tests.

Adhesion Testing

Cord-to-rubber adhesion was determined by the strip peel test.¹⁶ A typical rubber formulation would be a 35/45/20 blend of natural rubber, styrene-bu-

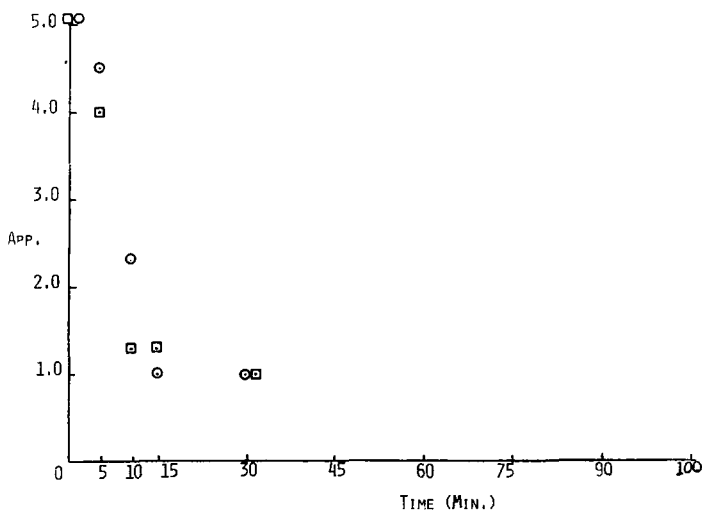


Fig. 3. Effect of ozone at 140°F on adhesion: (O) polyester; (□) nylon.

TABLE I
Effect of Heat on Adhesion

	Polyester, lb/app. ^a		Nylon, lb/app.	
	Air	Argon	Air	Argon
Atmosphere:	Air	Argon	Air	Argon
Temp., °F:	140	320	140	320
<u>Time, min</u>				
0	39/5.0	39/5.0	37/5.0	37/5.0
5	41/4.9	34/5.0	36/4.6	33/4.8
10	37/4.8		31/4.5	
15	33/4.8		30/4.7	
20	25/3.8		27/4.8	
25	30/4.5		27/4.7	
30	26/4.3	34/5.0	23/4.7	38/4.9
60		35/5.0		33/4.9

^a Pounds pull/adhesion appearance ratings for strip adhesion pads.

tadiene rubber, and *cis*-butadiene rubber carcass stock. The assembly was cured in a press for 6 min at 360°F platen temperature and 200 psi pressure. Adhesion was tested at 250°F in an Instron at 5 in./min.

The separated surface was then examined to see how much of the cord had become visible due to stripping of the rubber from the cord. Appearance ratings were recorded according to the following scale: 5 = 100% rubber failure, no cord visible; 4 = 75% rubber failure, 25% cord visible; 3 = 50% rubber failure, 50% cord visible; 2 = 25% rubber failure, 75% cord visible; 1 = 0% rubber failure, 100% cord visible.

Thus, the highest value of the scale indicates that the adhesion bond was so strong that the failure occurred in the rubber stock; the lowest value of the scale indicates a weak adhesion bond, failure having occurred at the interface of the rubber stock and the cord rather than in the rubber stock itself.

RESULTS

The atmosphere of the processing ovens contains nitrogen oxides, ozone, and sulfur oxides among the potential pollutants. Initially, the effect of heat alone on the adhesion of polyester and nylon-treated fabrics was determined. The testing at 320°F was conducted in the modified glass resin kettle (Fig. 1) under an argon atmosphere. Using the aluminum-lined chamber of Figure 2 at 140°F,

TABLE II
Effect of Air on Adhesion^a

Time, min	Polyester, lb/app. ^b	Nylon, lb./app.
0	39/5.0	37/5.0
5	38/5.0	24/4.5
30	31/4.9	24/4.8
45	32/4.5	
60	28/3.8	22/4.5

^a Temperature = 320°F.

^b Pounds pull/adhesion appearance ratings for strip adhesion pads.

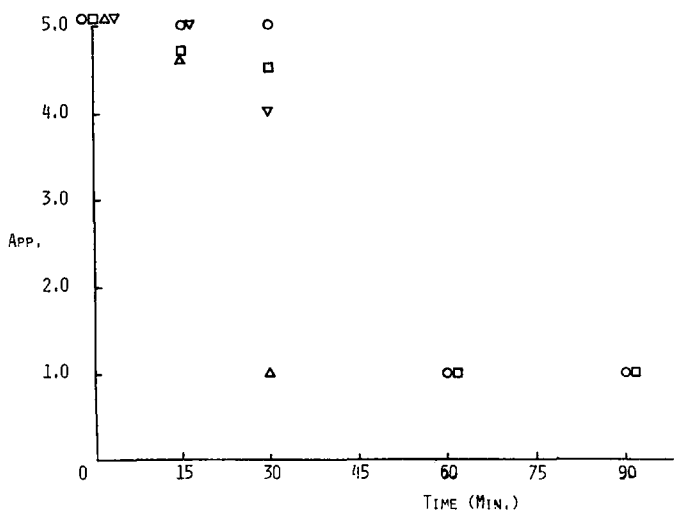


Fig. 4. Effect of ultraviolet light at 140°F on adhesion: (O) polyester with 2537-Å light; (■) nylon with 2537-Å light; (Δ) polyester with 3654-Å light; (▽) nylon with 3654-Å light.

the ambient air present in the chamber was not removed from the system. The results in Table I and Figure 3 show negligible loss in adhesion appearance through 1 hr of testing. However, pounds pull did decrease from overcure of the rubber.

Under a purge of compressed air, nylon retains adhesion through 1 hr of testing at 320°F (Table II, Fig. 4). Polyester, however, exhibited a slight drop in appearance (Table II, Fig. 4). However, pounds pull did decrease from overcure of the rubber.

Ozone, ultraviolet light, and the ozone-ultraviolet light combination was studied at 140°F in the chamber diagrammed in Figure 2. Ozone was employed

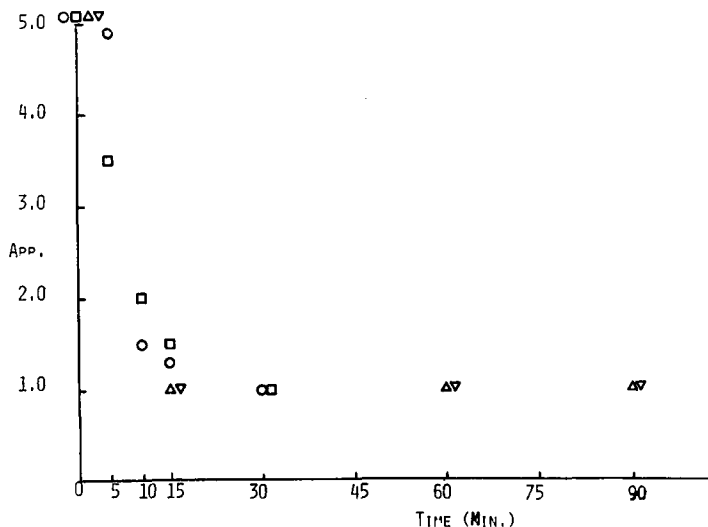


Fig. 5. Effect of ozone-ultraviolet light combination at 140°F on adhesion: (O) polyester with 2537-Å light; (□) nylon with 2537-Å light; (Δ) polyester with 3654-Å light; (▽) nylon with 3654-Å light.

TABLE III
Effect of Ozone, UV, and Ozone-UV on Adhesion^a

Atmosphere Ultraviolet:	Ozone —	Argon 2537 Å	Argon 3654 Å	Ozone 2537 Å	Ozone 3654 Å
Polyester, lb/app					
<u>Time, min</u>					
0	38/5.0	37/5.0	38/5.0	37/5.0	38/5.0
5	30/4.5			32/4.9	
10	27/2.3			28/1.5	
15	22/1.0	34/5.0	36/4.6	19/1.3	13/1.0
20	21/1.0			10/1.0	
25	20/1.0			9/1.0	
30	15/1.0	34/5.0	17/1.0	8/1.0	12/1.0
60		20/1.0	18/1.0		12/1.0
90		10/1.0	18/1.0		10/1.0
120		11/1.0	17/1.0		13/1.0
Nylon, lb/app.					
0	37/5.0	35/5.0	36/5.0	35/5.0	37/5.0
5	26/4.0			28/3.5	
10	18/1.0			24/1.5	
15	19/1.0	36/4.7	29/5.0	17/1.5	21/1.0
20	25/1.0			15/1.0	
25	20/1.0			15/1.0	
30	19/1.0	30/4.5	26/4.0	15/1.0	19/1.0
60		17/1.0	20/1.0		28/1.0
90		12/1.0	20/1.0		24/1.0
120		13/1.0	15/1.0		25/1.0

^a Temperature = 140°F in chamber.

at a 10 pphm (0.1 ppm) level (Table III, Fig. 5). Adhesion appearance loss had begun for nylon for the 5-min sample. Complete adhesion loss, represented as 1.0 appearance ratings for 100% visible cord, was found for the 10-min nylon test sample. For polyester, a slower rate of adhesion loss was found with 15 min of testing required for complete adhesion loss.

Two UV lamps, a short wavelength 2537-Å germicidal white light, and a long wavelength 3654-Å black light were employed in an inert atmosphere at 140°F. The results in Table III show a similar adhesion appearance degradation to that found with free ozone. The rate of degradation is slower than for ozone as represented by the 30- to 60-min exposure periods required to produce a 1.0 appearance rating compared to 5 to 10 min with ozone.

Finally, a combination of ozone with the UV light was tested (Table III). With the 2537-Å lamp, the initial ozone reading decreased from 10 pphm to 2 pphm, indicative of singlet molecular oxygen formation. With the 3654-Å lamp, the ozone reading did not decrease from 10 pphm. Adhesion loss for polyester and nylon was evident in the 5-min test samples, and 100% cord was visible after the 10-min tests.

Nitrogen dioxide and nitric oxide were tested in both nitrogen and air as carrier gases. These pollutants in the inert nitrogen atmosphere had little or no effect on adhesion appearance through 1-hr test samples (Table IV). At levels of 12 to 17 ppm of the nitrogen oxides in air and in a nitrogen-oxygen mixture, adhesion appearance loss for polyester was found in the 30- and 40-min test samples.

TABLE IV
Effect of Nitrogen Oxides on Adhesion^a

Time, min	Polyester, lb/app. ^b	Nylon, lb/app.
	A. 15 ppm NO ₂ in Nitrogen	
0	38/5.0	37/5.0
5	38/4.9	36/5.0
20	42/5.0	36/5.0
60		30/4.4
	B. 12 ppm NO ₂ in Air	
0	38/5.0	37/5.0
20	38/5.0	24/5.0
40	18/1.0	22/5.0
60	18/1.0	19/1.0
	C. 35 ppm NO in Nitrogen	
0	38/5.0	37/5.0
15	32/5.0	
30	31/5.0	
60	39/5.0	38/4.8
	D. 17.5 ppm NO in Nitrogen-Oxygen Blend (Equal Gas Volume Blend)	
0	38/5.0	37/5.0
15	36/5.0	
30	17/1.0	25/4.0
60	25/1.0	23/2.0

^a 320° F.

^b Pounds pull/adhesion appearance rating for strip adhesion pad.

Nylon, however, required 1 hr of exposure before essentially complete adhesion appearance loss occurred (Table IV).

A range of sulfur dioxide levels from 22 to 116 ppm in air was used in the chamber at 320°F. Essentially, no adhesion loss occurred for both polyester and nylon at all sulfur dioxide levels through 1 hr of exposure (Table V).

DISCUSSION

Ozone alone and in combination with ultraviolet light is the number-one degradant for adhesion at high temperatures. The ozone was found to be harmful at a level a hundred times lower than any other pollutant tested. It was even harmful at 180°F lower temperature than the other pollutants. Under these less stringent conditions, adhesion appearance loss with ozone was apparent after 5 to 10 min of exposure compared to a minimum of 30 min required for the other pollutants which were found to be harmful.

Ozone with 2537-Å ultraviolet light favors singlet oxygen formation.^{17,18} Both ozone and singlet molecular oxygen will initially add to the olefinic double bonds of rubber.¹⁹⁻²² Cleavage of the intermediate adducts to form the final reaction products then occurs.^{17,19,22} Thus, unsaturation sites needed for later cure reactions with the crosslinking agents of the rubber stock would be removed and adhesion loss would be caused.³

The slow adhesion degradation by ultraviolet light alone in an inert atmosphere is not completely understood. Wenghoefer² explained the phenomenon as a surface change, but no chemical explanation was given. Cyclization,²³ formation of vinylidene and vinyl groups,²³ and crosslinking^{24,25} reactions have been re-

TABLE V
Effect of Sulfur Dioxide in Air on Adhesion^a

Time, min	Polyester, lb/app. ^b	Nylon, lb/app.
	A. 22 ppm SO ₂	
0	39/5.0	36/5.0
5	37/4.9	34/5.0
20	33/4.9	34/5.0
60	32/4.9	34/4.9
	B. 40 ppm SO ₂ ^c	
0		36/5.0
15		33/5.0
30		33/5.0
60		33/5.0
	C. 80 ppm SO ₂ ^c	
0		36/5.0
15		34/5.0
30		29/5.0
60		28/5.0
	D. 116 ppm SO ₂	
0	39/5.0	36/5.0
15	36/5.0	34/5.0
30	37/5.0	35/5.0
60	34/4.5	32/5.0

^a 320° F.

^b Pounds pull/adhesion appearance rating for strip adhesion pad.

^c From oxygen blend with 116 ppm SO₂ in air sample.

ported for the reactions of *cis*- or *trans*-1,4-diene rubbers with ultraviolet light in the absence of air. Cyclization and crosslinking reactions, which would consume available unsaturation, may be responsible for the decrease in adhesion caused by UV radiation.

The remaining pollutants also cause a much slower adhesion degradation rate than ozone and are ranked NO₂ > NO >> SO₂ ≡ air ≡ heat. The test data showed some adhesion degradation at >10 ppm NO_x in air with 30 to 60 min of exposure at 320° F. Nitrogen dioxide is reported to add to olefinic double bonds²⁶ and reduce the unsaturation sites.

The adhesion of RFL-coated tire cords was found to be essentially unaffected by relatively high concentrations of sulfur dioxide. Even though reactions of sulfur dioxide with low molecular weight saturated organic molecules²⁶ and olefins²⁷ have been reported, the reaction rates with unsaturated rubbers would be expected to be slow at these sulfur dioxide concentrations. Therefore, the results obtained in this study are not surprising.

Results with heat and heat-air indicated that overcure in an inert atmosphere or air oxidation are not major contributors to adhesion appearance loss for RFL-based systems but do cause decreases in pounds pull.

In summary, the mechanism for adhesion loss is attack by the pollutant on the olefinic unsaturation in the adhesive surface layer. The differences in degree of adhesion appearance loss is related to their rates of reaction with these olefinic sites. The loss in unsaturation sites reduces the available double bonds for interfacial co-cure with the rubber stock.³ The new products from the reaction of the rubber of the RFL adhesive with the pollutants would be expected to

present a different cohesive energy density at the surface.²⁸ This would cause an incompatibility of the surface of the adhesive-coated tire cord with the surface of the rubber stock during curing reactions.²⁹

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