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# Effects of Ozone and UV on Tire Cord Adhesion

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## Synopsis

Ozone exposure of resorcinol-formaldehyde-latex (RFL) dipped tire cords reduces adhesion because ozone attacks the double bonds in the butadiene component of the rubber latex in RFL and impairs its cocuring with the solid rubber compound. This mechanism also explains: (a) the ineffectiveness of chemical antiozonants or chloroprene latex as RFL additives, (b) the increased ozone sensitivity of RFL adhesion with progressive curing of RFL dip, and (c) the insensitivity to ozone of adhesion with RF-EPDM adhesives. A major reduction in the rate of adhesion loss in either ozone (50 pphm, 50% RH) or UV (carbon arc, 4 hr) was demonstrated when small amounts of waxes (3% solids basis) were added to the RFL dip. The waxes protect the RFL adhesive by blooming to the surface of the adhesive treated cord.

## INTRODUCTION

Factors influencing the adhesion of tire cords to rubber compounds are documented in a recent review article[1] on developments with tire cords and cord-to-rubber bonding. Variables in tire cord adhesion investigated to date concern tire yarn substrates, adhesive systems, bonding methods, and rubber compounds. An important criterion for untreated or adhesive-treated tire cords is the sensitivity of adhesion to environmental exposure during their storage and/or processing. Particularly of interest are the effects of ozone and UV radiation. Considerable work has been reported in the literature on the effects of relatively long exposures of UV radiation on physical properties and morphology of polyamide and polyester yarns, including a recent paper[2] on UV degradation of high-performance synthetic fibers derived from aromatic polymers. The only published work on the effect of UV exposure of untreated tire cords on adhesion is a patent[3] dealing specifically with bonding of UV-treated gray polyester cords and adhesion-promoting rubber compounds. Information on the effect of ozone or UV exposure of adhesive-dipped tire cords on adhesion is also scarce. Patent literature[4,5] documents the adhesion loss of resorcinol–formaldehyde–latex (RFL) adhesive treated tire cords after storage under atmospheric conditions for extended periods. Addition of wax to the RFL adhesives was shown to minimize this adhesion loss. However, in either work, there was no information about the concentration or type of the specific agent ($O_3$, UV, etc.) causing adhesion loss during ambient exposure.

In recent work, Wenghoefer[6] found that the adhesion of nylon, polyester, and Kevlar aramid tire cords was substantially reduced when the RFL-treated cords were exposed to ozone or UV. Adhesion loss was at the interface of the rubber and the RFL adhesive, as shown by scanning electron microscope examination[6] of peeled cord/rubber samples. The reference work also discussed the surface changes of RFL dip films exposed to UV or ozone. The work described in this paper was aimed at understanding the effects of ozone and UV exposure of gray and RFL adhesive-treated gray cords on their adhesion to rubber compounds.

## EXPERIMENTAL

Gray and adhesive-treated tire cords of nylon 66 (T-728 1260/1/2), Dacron polyester (Types T-68 and D-503 1000/1/3), and Kevlar aramid (1500/1/3) tire yarns were exposed to ozone (50 pphm, 50% R.H., 100°F, 0–8 hr) in the Atlas Weather-Ometer 600 RI and to UV radiation (carbon arc) in the Atlas Fade-Ometer Type FD-AR (145°F, 0–20 hr). Cord skeins were exposed to ozone, whereas UV samples were wound on cardboard, mounted in the Fade-Ometer, and exposed on both sides. A standard RFL dip, D5A[7] (F/R, mole = 0.5, rubber/RF resin = 5.9, 20% solids), was used for nylon cords. The polyester cord was treated with a blocked isocyanate plus epoxy subcoat (D-417)[8] and the D5A topcoat and Kevlar with an epoxy subcoat and the D5A topcoat modified with carbon black. Rubber stocks used with nylon and Kevlar cords were based on a 75/25 blend of natural rubber and *cis*-polyisoprene (Natsyn 400) and contained 35 phr GPF carbon black. The vulcanization accelerator was a mixture of 90% 2-(morpholinothio)benzothiazole and benzothiazole disulfide (MBTS). A 50/50 NR/SBR stock containing 35 phr HAF black and 1.2 phr MBTS was used with polyester. In previous work,[9] lowering the NR level and eliminating the amine-producing sulfenamide accelerators reduced the sensitivity of polyester cord adhesion to the synergistic action of water and amines present in rubber stocks.

Cord-to-rubber adhesion was determined by the single cord pull-through test, the H-pull test (ASTM D-2138) using a $^1/_4$ in. × $^1/_4$ in. H-block, and the 2-ply strap peel adhesion test (ASTM D-2630) with the cord spacings (ends/in.) of 44, 36, and 28 for nylon, polyester, and Kevlar, respectively. Both the peel strengths (pounds/in.) and appearance ratings were recorded. These subjective ratings cover a range of 1 to 5, with 1 signifying clean cord/rubber separation and 5 indicating complete rubber tear between plies. The adhesion samples were cured at 160°C for 20 min.

## RFL ADDITIVES OR MODIFICATIONS

Since the adhesion breakdown is at the RFL/rubber interface, stable aqueous dispersions of protective agents (antiozonants and UV screeners) were added to the RFL dip to see if adhesion degradation due to ozone or UV could be minimized or eliminated. In addition, the styrene–butadiene–vinylpyridine (Gen-Tac) latex in RFL was partially replaced by neoprene latex to see if the inherent ozone cracking resistance of this elastomer can be beneficial. In these and the subsequent experiments, ozone exposure was maintained at 50 pphm, 50% R.H., and 100°F. Under these conditions, moisture itself caused negligible degradation of adhesion, as shown by the blank test run with air at 50% R.H. and 100°F instead of ozone (Table I). The chemical antiozonants actually lowered the adhesion of ozone-exposed cords, suggesting interference with RFL/rubber bonding by the interaction of ozone, antiozonant, and the RFL system. None of the UV screeners (Table II) minimized the adhesion loss of cords exposed to UV for 4 hr.

TABLE I
Antiozonants and Neoprene Latex in RFL Dip

| Additives to RFL Dip | 2-Ply adhesion,[a] lb (appearance) | | | |
|---|---|---|---|---|
| | Unexposed | 3 hr Ozone[b] | 8 hr Ozone[b] | 3 hr Air[c] |
| None | 46 (4.8) | 33 (2.8) | 28 (2.3) | 47 (4.7) |
| Antiozonants[d] | 46 (4.5) | 20–26 (2–2.3) | 17–21 (1.5–1.8) | |
| Neoprene latex[e] | 47 (4.8) | 32 (2.7) | 29 (2) | 44 (4.5) |

[a] D-503 Dacron polyester fiber, D-417/D5A dipped.

[b] 50 pphm, 50% R.H., 100°F.

[c] Blank experiment without ozone in apparatus (50% R.H., 100°F).

[d] 3% Based on RFL (D5A) dip solids of the paraphenylenediamine derivatives: ● N,N'-bis(1-ethyl-3-methylpentyl) (UOP 88) ● N-isopropyl-N'-phenyl (Flexzone 3C) and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline (Santoflex AW).

[e] 50% Neoprene latex 750 and 50% Gen-Tac vinylpyridine latex.

TABLE II
UV Absorbers in RFL Dip

| UV Absorbers[b] | H-Pull,[a] 24°C, lb | | |
|---|---|---|---|
| | Unexposed | 2 hr UV | 4 hr UV |
| None | 50[c] | 23 | 10 |
| Solids[d] | 47–52[c] | 18–26 | 10–16 |
| Liquid[e] | 44[c] | 39 | 14 |

[a] D-503 Dacron polyester fiber, D-417/D5A dipped.

[b] 3% Based on RFL (D5A) solids.

[c] Cord filament breaks.

[d] 2-Hydroxy-4-methoxy and 2-hydroxy-4-*n*-octoxybenzophenones (Cyasorb UV 9 and UV 531), 2(2'-hydroxy-5'-methylphenyl) and substituted 2,2'-Hydroxyphenylbenzotriazoles (Tinuvin P and 328).

[e] Substituted acrylonitrile (Uvinul N-539).

A substituted acrylonitrile, which is a liquid at room temperature, offered some protection in cords exposed for 2 hr.

Small concentrations (3–6% solids basis) of a paraffin wax–microcrystalline wax blend (J-1440) added as an aqueous dispersion to the RFL dip significantly improved the adhesion of polyester and nylon-dipped cords after exposure to ozone or UV (Figs. 1 and 2). In earlier work,[4,5] wax additives in RFL had been effective in minimizing adhesion (H-pull) loss of cords stored or exposed to the ambient atmosphere for several days. The ozone and UV concentrations were unknown and may have varied considerably during the relatively long exposures. The waxes apparently bloom to the surface of the dipped cord and provide physical protection analogous to their role in promoting ozone crack resistance in rubber stocks. Other similar commercial waxes (e.g., Heliozone Special, Vultex 8) equaled the protection level offered by the J-1440 wax tested initially. The combination of wax and chemical antiozonants or UV screeners did not enhance the adhesion protection given by wax alone, in contrast to the well-known synergistic effects of antiozonants and waxes in protecting against ozone cracking of rubber stocks.

Modifications of the RFL network by changes in R/F mole ratio (0.5–1.35) and rubber/resin weight ratio (2.2–5.9) failed to produce any significant change in the sensitivity of adhesion to ozone or UV. The addition of carbon black to

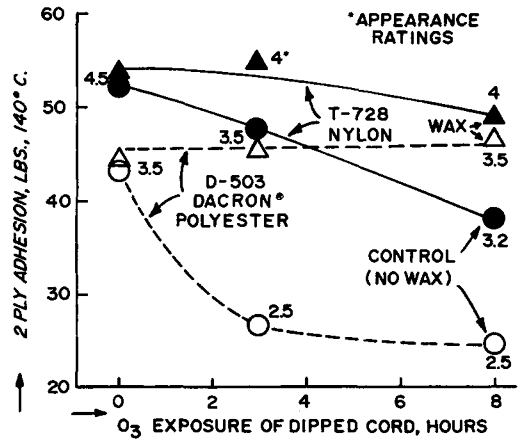

Fig. 1. Effect of wax (J-1440) in RFL on adhesion of ozone-exposed cords.

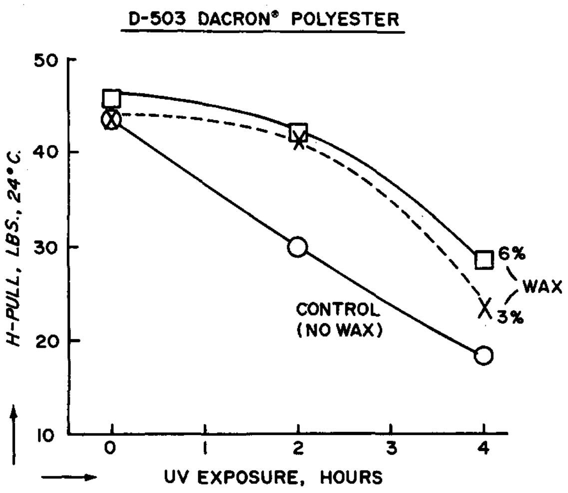

Fig. 2. Effect of wax (J-1440) in RFL on adhesion of UV-exposed cords.

RFL gave some improvement (~10 pounds) in the adhesion (hot 2-ply) of nylon and polyester cords exposed to ozone for 3 hr but no improvement after 8 hr.

## RFL/RUBBER ADHESION LOSS

### Cocuring of RFL and Rubber

Since the adhesion breakdown of ozone- and UV-exposed cords occurs between the RFL adhesive and rubber, a suggested mechanism for adhesion loss is the gradual elimination of curing sites in the unsaturated elastomer (butadiene) of the latex so the RFL network in the surface layers of the adhesive cannot cocure with the elastomer in the rubber compound. This concept was supported by work in which the RFL dip was cured to varying degrees (20 to 120 sec/425°F) on nylon and polyester cords. As the dip was cured longer, the adhesion of ozone (Figs. 3 and 4)- and UV (Fig. 5)-exposed cords worsened. Progressive curing of the RFL adhesive reduces the unsaturated sites available for cocuring with rub-

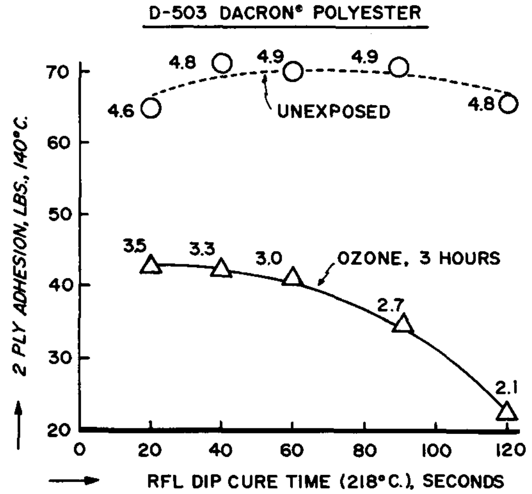

Fig. 3. RFL cure vs. adhesion unexposed and ozone-exposed polyester cords.

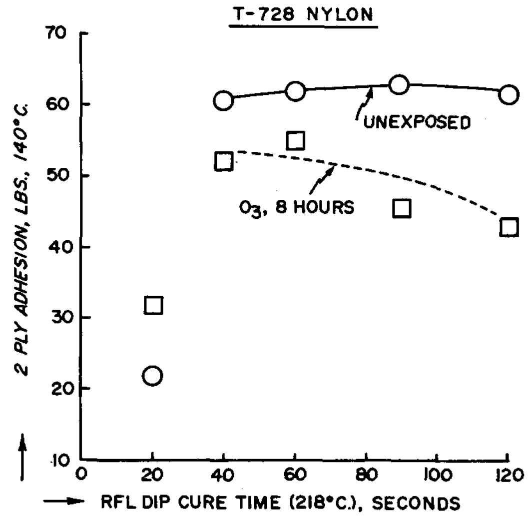

Fig. 4. RFL cure vs. adhesion unexposed and ozone-exposed nylon cords.

ber by two mechanisms. Phenolic compounds react with unsaturated olefins by chromane formation,[10] where the double bond is actually eliminated or phenolic "crosslinks" between olefinic chains are formed adjacent to the double bond, hindering and deactivating it. Consequently, ozone or UV effects become critical in the more extensively cured RFL systems which have already been depleted of available bonding sites for curing to rubber. Previous work[11] showed that even the initial adhesion of nylon cords is weakened by overcuring (>450°F/80 sec) the RFL dip on the cord. The maximum dip curing (425°F/120 sec) used in the present work was not severe enough to decrease the adhesion of unexposed cords.

The nylon cords given the shortest cure (20 sec) showed poor adhesion, which actually improved after ozone treatment (Fig. 4). This increased adhesion is due to thermal effects during ozone treatment (100°F, 3–8 hr), as shown by data on

TABLE III
Ozone and Heat Effects on Undercured RFL Adhesive

| Dipped cord treatment | 2-Ply adhesion, 140°C, lb (appearance) | |
|---|---|---|
| | 20 sec RFL cure[c] | 60 sec RFL cure[c] |
| None (unexposed) | 22 (2) | 62 (4.9) |
| Ozone, 8 hr | 32 (2.8) | 55 (4) |
| Heat,[b] 8 hr | 39 (3.2) | 66 (4.7) |

[a] T-728 Nylon cords, D5A dip.

[b] Exposed in ozone chamber (100°F, 50% R.H.) without ozone.

[c] At 425°F.

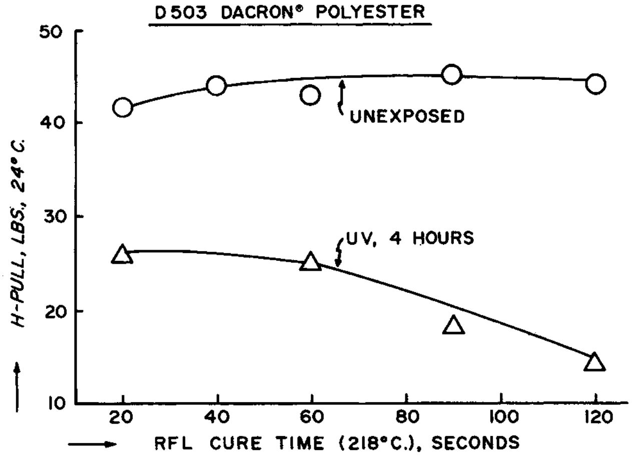

Fig. 5. RFL cure vs. adhesion unexposed and UV-exposed polyester cords.

cords exposed in the ozone chamber without ozone (Table III). Heat treatment of the RFL can improve the RF/nylon bonding[11] and also the cohesive strength of the undercured RFL adhesive. Apparently, the magnitude of heat treatment (100°F, 3–8 hr) in the ozone chamber was not adequate to raise the adhesion level of the undercured (20 sec/425°F) cords to that attained at optimum curing (>40 sec/425°F).

## Chemical Antiozonants

The failure of chemical antiozonants in RFL to improve the adhesion of ozone-exposed dipped cords is not surprising, based on the mechanisms of antiozonant action in rubber compounds. Antiozonants do not prevent the ozone attack on olefinic double bonds, but react with ozonides[12] and other products of interaction of ozone and double bonds. Consequently, adding antiozonants to the RFL dips exposed to ozone cannot prevent depletion of double bonds of the latex elastomer needed for providing sites for cocuring RFL with the rubber compound.

The failure of neoprene latex additive to reduce adhesion loss can be explained from Gilbert's work[13] on the mechanism of ozone cracking resistance of polychloroprene. He found that neoprene absorbs ozone just as rapidly as natural rubber or SBR but that the liquid reaction products formed in the ozone–polychloroprene–water reaction spread rapidly on the polar polychloroprene

TABLE IV
Adhesion of RF/EPDM-Dipped Cords

| Dipped cord | Exposure | 2-Ply Adhesion,[a] 24°C, lb |
|---|---|---|
| T-728 Nylon | none | 43 (3.5) |
| | $O_3$, 8 hr, 50 pphm | 43 (3.5) |
| D-503 Dacron[b] | none | 48 (2.5) |
| Polyester | UV, 4 hr | 47 (2.5) |

[a] In a sulfur-cured Nordel EPDM carcass-type stock.
[b] D-417//RF/EPDM.

surface,[12] providing resistance to ozone cracking. Since the double bonds in chloroprene are easily attacked by ozone, the addition of neoprene to RFL cannot provide the unsaturation needed for cocuring of ozone treated RFL to rubber.

## EPDM Latex in RFL

Since EPDM elastomers have outstanding resistance to ozone attack due to their saturated backbone, adhesives containing an EPDM type latex (in place of styrene–butadiene–vinylpyridine latex) should not be susceptible to ozone attack. Polyester and nylon tire cords treated with RFL dip made with Nordel EPDM latex did not lose adhesion when exposed to ozone or UV and tested in an EPDM rubber stock (Table IV). Apparently, ozone did not destroy the side chain unsaturation in the EPDM of the latex sufficiently to impair its cocuring with the EPDM elastomer compound.

## RFL Film Properties

Since the elastomeric adhesive film on tire cords is relatively thin ($\sim 5 \times 10^{-3}$ cm), reduction in mechanical (cohesive) properties of the RFL dip film by ozone attack could be a factor in the adhesion loss of cords. The depth of ozone attack on unstrained elastomers has been estimated in literature by Gilbert[13] from ozone absorption measurement and by Andries and Diem[14] from ATR spectroscopy. Based on Gilbert's data, the ozone absorption depth under the most severe exposure conditions (100 pphm, 100% R.H., 3.5 hr) is about $2 \times 10^{-5}$ cm, which is a negligible proportion (0.4%) of the dip film thickness on cord. Similarly, the depth of ozone attack (10 pphm, 24 hr) estimated from ATR work was very small ($2 \times 10^{-8}$ cm). Consequently, ozone attack should have negligible effect on the bulk properties of the RFL dip film.

## UV Effects

UV effects are complicated[15] by the presence of oxygen (air) in the system which introduces photo-oxidation in addition to purely photochemical reactions (isomerization, chain scission). Oxygen absorption is autocatalytic at low light-energy levels. An additional factor is the ozone generated during UV irradiation in air, although this was probably insignificant in the present work since air was constantly swept through the Fade-Ometer. Our data on the effects of UV on the adhesion of dips cured to varying degrees suggest that UV irradiation destroys active sites involved in cocuring of RFL with rubber. It is interesting that UV absorbers (benzophenone derivatives), which did not minimize the adhesion loss of UV exposed RFL to rubber, have also been found ineffective in improving the discoloration and crazing characteristics of elastomers.[16]

## CORDS EXPOSED BEFORE BONDING TO RUBBER

The work discussed so far dealt with adhesion degradation of RFL-dipped cords exposed to ozone or UV radiation. Another objective of our work was to establish if adhesion loss occurred when the substrates themselves (yarns or gray cords) are exposed to these elements and then bonded to rubber either after adhesive treatment or directly when adhesion-promoting ingredients (HRH) are present in the stock. Nylon, polyester, and Kevlar aramid cords showed no adhesion loss when they were exposed to ozone/UV and then adhesive treated (Table V). Also, exposed nylon cord and an experimental nylon monofil (P-20, developed by du Pont for tire reinforcement) retained excellent adhesion when bonded directly to the HRH stock containing a methylene donor, a methylene acceptor, and silica. Since monofils do not need hot-stretching treatments that are essential for stabilizing twisted cord structures, the undipped monofil/HRH system is interesting.

Synthetic fibers derived from aromatic polymers are known to be sensitive to light-induced degradation. Recent work[2] showed significant loss of mechanical properties of Nomex aramid fiber when exposed to UV radiation (xenon arc) for prolonged periods (150 hr). Photodegradation by chain scission was indicated. In view of this, the adhesion of Nomex and Kevlar aramid yarns was determined after a relatively long exposure (20 hr vs. 2–4 hr) to UV. Neither of the aramids showed adhesion loss (Table VI), indicating no problems of adhesion deterioration of yarns or gray fabric during extended exposure to UV in the environment.

TABLE V
Adhesion of Ozone- or UV-Exposed Gray Cords

| | | | 2-Ply adhesion, 140°C, lb (appearance) | | |
|---|---|---|---|---|---|
| Cord | Adhesive | Rubber stock[a] | Unexposed | 8 hr ozone[b] | 4 hr UV |
| D-503 Dacron Polyester | D-417/D5A | standard A | 54 (4.4) | 59 (4.4) | 60 (4.7) |
| T-728 Nylon | D5A | standard B | 46 (4.6) | 47 (4.6) | 48 (4.5) |
| T-728 Nylon | none | HRH | 53 (3.8) | 51 (3.8) | 54 (3.8) |
| P-20 Nylon monofil[c] | none | HRH | 56 (4) | 54 (4) | 51 (4) |
| Kevlar Aramid | IPD-22/D5C[d] | standard B | 43 (4) | 46 (4) | 42 (4) |

[a] Standard A: 50/50 NR/SBR, MBTS accelerator (low amine): standard B: 80/20 NR/IR, sulfenamide accelerator (high amine): HRH: 100% NR: HRH ingredients, phr, 3.5 Cohedur A, 2.5 resorcinol (added as 60% stearic acid dispersion), and 25 Hi-Sil 233 silica.

[b] 50 pphm, 50% R.H., 100°F.

[c] 3000 denier.

[d] IPD-22 = Epoxy resin, D5C = D5A dip with HAF black additive (12% solids basis).

TABLE VI
Adhesion of UV-Exposed Aramid Fibers

| | Adhesion, 140°C, lb (appearance) | | |
|---|---|---|---|
| Fiber[a] | Unexposed | 10 hr UV | 20 hr UV |
| Nomex | 35 (1.5) | 41 (2) | 38 (1.5) |
| Kevlar | 51 (4) | 49 (3.5) | 53 (4) |

[a] Gray cords exposed to UV and then treated with epoxy/RFL adhesive.

In fact, Nomex has consistently shown a slight improvement in adhesion. In summary, the exposure of a variety of tire yarn substrates to reasonably large dosages of ozone or UV did not impair their bonding to rubber.

## SUMMARY AND CONCLUSIONS

A major reduction in the rate of adhesion loss in either ozone (50 pphm, 50% R.H.) or UV was demonstrated when small amounts of waxes (3% solids basis) were added to the RFL dip. The waxes protect the RFL adhesive by blooming to the surface of the adhesive-treated cord. Antiozonants (alkyl para-phenylenediamines) or solid UV absorbers (benzophenones, benzotriazoles) were ineffective as RFL additives. The combination of wax and antiozonants did not enhance the adhesion protection given by wax alone.

Ozone exposure of RFL-dipped cords reduces adhesion because ozone attacks the double bonds in the butadiene component of the rubber latex in RFL and impairs its cocuring with the solid rubber compound. This mechanism also explains (a) the ineffectiveness of chemical antiozonants or chloroprene latex as RFL additives, (b) the increased ozone sensitivity of RFL adhesion with progressive curing of RFL dip, and (c) the insensitivity to ozone of adhesion with RF–EPDM adhesives. In contrast to the sensitivity of RFL-dipped cords to ozone or UV, gray cords of nylon, polyester, and Kevlar and nylon monofilaments that were first exposed to ozone or UV and then treated with adhesives showed no adhesion loss.

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