JOURNAL OF APPLIED POLYMER SCIENCE VOL. 15, PP. 267-276 (1971)

Factors in Rubber Compounds Affecting the Adhesion of Polyester Tire Cords

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Synopsis

Several factors in rubber stocks were demonstrated to be important in the adhesion of polyester tire cords to rubber compounds. The retained adhesion of polyester tire cords, determined after heat-aging laboratory cord–rubber samples at elevated temperatures, was improved by (a) eliminating the sources of amines in the elastomers and compounding ingredients, (b) reducing the moisture content of the stocks, (c) increasing the overall water vapor permeability (WVP) of the cord–rubber composite, and (d) lowering the modulus of the stock. Sulfenamide cure accelerators and water were found to be synergistic in reducing the retained adhesion of polyester cord after in-rubber aging at high temperatures. The harmful effects of amines released from sulfenamides during curing and heat aging were eliminated by compounding the stocks with accelerators that do not form amines. Aliphatic diamines present as nonrubber components in natural rubber (NR) were shown to be detrimental to adhesion. Since synthetic polyisoprene rubber (IR) does not contain any nonrubber components, IR stocks containing the nonamine accelerator benzothiazyl disulfide (MBTS) showed excellent retained adhesion to polyester cords. A recently developed nonamine-type accelerator gave adhesion essentially equal to MBTS but showed excellent scorch safety and high stock modulus typical of sulfenamides. The retained adhesion in IR stocks after heat aging was less dependent on moisture level and stock modulus than in NR stocks. Finally, examples of practical rubber compounds giving improved retained adhesion to polyester tire yarns are given.

INTRODUCTION

The excellent initial adhesion of polyester cords to rubber, achieved with effective adhesive systems, is known to deteriorate with heat aging of cord–rubber specimens. The work described in this paper was aimed at clearly establishing the factors in rubber stock composition and physical properties influencing this adhesion retention. An understanding of these factors is essential to the development of stocks with improved adhesion to polyester cords.

EXPERIMENTAL

Tire cords made from Dacron* polyester fiber and treated with du Pont's two-step D417/D5A adhesive (blocked isocyanate + epoxy-resorcinol–

* Registered trade name of E. I. du Pont de Nemours & Co.

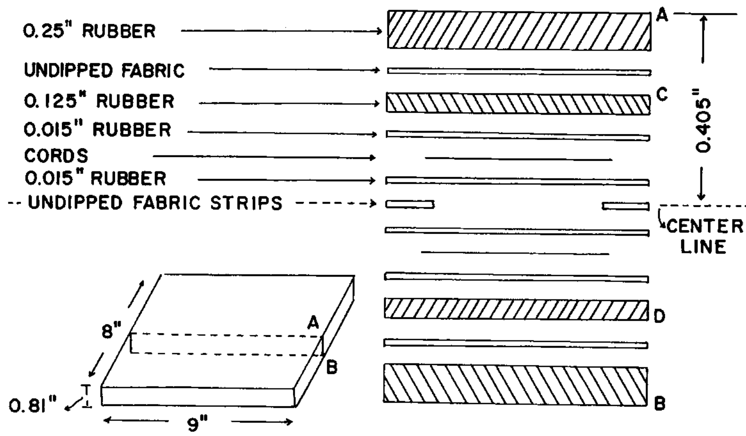


Fig. 1. 2-Ply cord–rubber adhesion samples (pads).

formaldehyde latex)[1] were used to make up 2-ply cord–rubber adhesion samples (pads) which were constructed with 0.25 in.-thick rubber on either side of the plies (Fig. 1) to simulate the tread rubber in a tire and also to accentuate the effect of rubber chemicals on cord–rubber adhesion. The plies consisted of 36 ends/in. of 1000/1/3 cords. While the entire pad (AB) was heat aged, only the inner 2-ply sample (CD) about $^3/_8$ in. thick was used for peel tests on the Instron at $2^1/_2$ in/min and 180° angle.

Initial and heat-aged (325°F/24 hr) adhesions were measured at 285°F after conditioning the sample in the Instron oven for at least 10 min. Both the peel strengths (lb/in.) and appearance ratings of the pulled samples 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 cord plies. The rubber stocks contained 35 phr of high abrasion furnace (HAF) black and other conventional compounding ingredients; viz., plasticizer, antioxidant, sulfur, ZnO, stearic acid, and accelerator.

RESULTS

Sulfenamide Accelerators and Water

The individual and the combined influences of water and accelerators liberating amines were established by laboratory pad adhesion tests with dry (desiccated) and conditioned ($\sim$0.2% H_2O) rubber stocks containing sulfenamide or disulfide-type accelerators. The sulfenamide accelerator used was 2-(morpholinothio)benzothiazole, which liberates the amine morpholine during rubber cure. The disulfide accelerator used was benzothiazyl disulfide (MBTS). For the most effective drying action, layers of stock containing 24 phr CaO (32 phr 75/25 CaO/oil dispersion) were used for the outer 250-mil layers of the pad on either side of the plies. Note

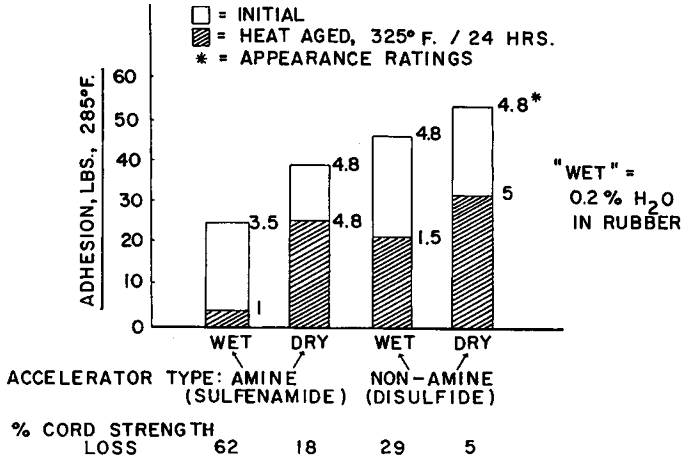


Fig. 2. Effect of H_2O and amine on adhesion and cord strength (50/50 NR/SBR stock).

that desiccant was not used in the stock adjacent to the cord plies. Retained adhesion was highest in the absence of amines (sulfenamide) *and* water but lowest in the presence of both (Fig. 2). Adhesion and break strength of the polyester cord followed the sequence.

dry nonamine > dry amine > wet nonamine ≫ wet amine.

The combined effect of sulfenamide and water was larger than the arithmetic sum of the individual effects, illustrating their synergistic influence on retained adhesion (Table I). Note the outstanding levels of adhesion and

TABLE I

Relative Effects of Amine and H_2O on Retained Adhesion[a]

Effects	Reduction in retained adhesion lb	(appearance)
H_2O	10	(3.5)
Amine (dry)	6	(0.3)
Sum	16	(3.8)
H_2O + amine	28	(4)

[a] 50/50 NR/SBR stock.

cord strength retained when moisture *and* sulfenamide were both absent. In this case, the heat-aged samples showed almost complete rubber tear.

Rubber Stock Modulus

Rubber stock modulus was suspected as being a factor in polyester adhesion since stocks showing good retained adhesion had relatively low levels of modulus at 300% extension. The effect of rubber stock modulus on retained adhesion was investigated with 50/50 NR/SBR (MBTS) stocks in which the modulus was varied by changes in accelerator and carbon black levels. In these stocks, the retained adhesion of the polyester cords increased with decreasing stock modulus (Fig. 3), suggesting that

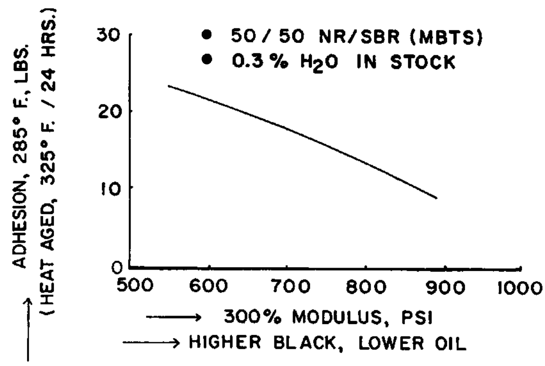


Fig. 3. Adhesion vs. stock modulus.

the reduced stress concentration between the cord layers in stocks of low modulus may have benefited the peel strength of the composite.

Water Vapor Permeability

Since the presence of moisture was shown to be detrimental to polyester adhesion on heat aging, it was postulated that increasing the water vapor permeability of cord–rubber systems would improve the adhesion by enhancing the diffusion of water away from the cord–rubber interface.

This effect of water vapor permeability (*WVP*) on adhesion was investigated by experiments in which stocks of different *WVP*s were combined in the inner and outer layers of the pads to give a range of overall *WVP*s across the pad. This overall *WVP* (P_M) can be calculated[2] by knowing the permeabilities P_1 and P_2 of the outer and inner stocks and their respective thicknesses A_1 and A_2:

outer layer	inner layer	A	B	
← 0.375 in. → (A_1)	← 0.015 in → (A_2)			A = cord B = center line

$$\frac{1}{P_M} = \frac{1}{A_1 + A_2}\left[\frac{A_1}{P_1} + \frac{A_2}{P_2}\right] \tag{1}$$

Note from eq. (1) that the relatively thick outer layer (A_1 = 0.375 in.) controls the overall permeability (P_M) of the structure. For the sake of convenience, *WVP* indices rather than absolute *WVP* values were used. The outer stocks used and their *WVP* indices are given by the following:

Outer Stock	*WVP* Index
75/25 *cis*-BR/NR	14
50/50 NR/SBR	5.8
70/30 Chlorobutyl/NR	1

Actual *WVP*s were determined on 0.015-in.-thick cured stocks by a procedure similar to the ASTM 96-66 method, using water in the cup and maintaining 5% R.H. and 100°F outside the cup. Each of two inner stocks (50/50 NR/SBR, 75/25 BR/NR) were used in combination with each of the above three outer stocks. All stocks contained MBTS accelerator. For a given inner stock, retained polyester cord adhesion (lb and appearance) was increased by using outer stocks of higher *WVP* (Fig. 4). This effect of *WVP* was completely absent for nylon tire cord treated with the same adhesive (D417/D5A).

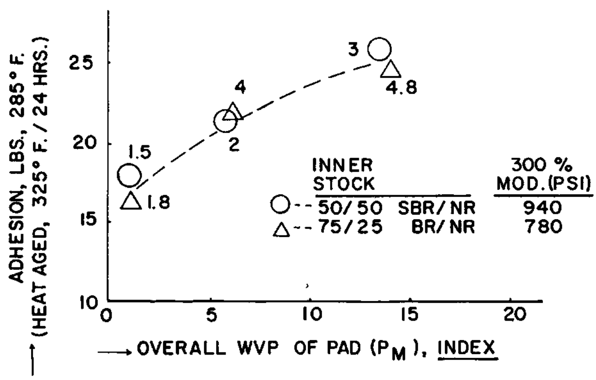


Fig. 4. Retained adhesion vs. *WVP* of pad.

Since stocks containing large amounts of *cis*-BR were used to attain high *WVP* of cord–rubber systems, additional work was undertaken to establish whether the chemistry or molecular structure per se of polybutadiene had any bearing on the excellent retained adhesion in these stocks. Emulsion- and solution-polymerized polybutadienes covering a wide range of *cis*-1,4 (14–97%) and vinyl-1,2 (3–17%) contents were used in establishing the effect of BR structure on adhesion. In the solution polymers, the catalyst system regulates the ratio of *cis*, *trans*, and vinyl contents of the polybutadiene. Commercially produced solution BRs range in *cis* content from 38% to 97%. Information on the chemical composition of the elastomers is shown in Table II, which also contains data on *WVP* and modulus of 75/25 BR/NR stocks chosen for the present investigation in preference to the very poorly processable 100% BR stocks. All the stocks contained the same compounding ingredients. *WVP* value of each stock is the average for two samples determined from the linear slope of water vapor loss-versus-time plots over a period of eight days. The BR stocks do not all have the same modulus level, so retained adhesion was plotted against *WVP*/

TABLE II
Polybutadiene Elastomers[a]

BR type	E or S	*cis*-1,4, %[b]	Vinyl-1,2, %[b]	Stock properties WVP	300% mod, psi
1203	E	94.5	4.5	112	860
Cisdene	S	92	—	111	757
220	S	96.5	2.5	109	863
Diene 35 NF	S	43	8	96	953
Diene 55 NF	S	38	9	80	1126
8407[c]	E	14	17	68	638
5001[d]	E	—	—	77	885
8110[e]	E	—	—	60	1133

[a] All stocks contain MBTS accelerator and the same compounding ingredients. E = Emulsion; S = solution polymerization; *WVP* = water vapor permeability, in g/100 sq meters per hr; 15 mil stock.
[b] Analytical data, refs. 3, 4, and 5.
[c] 37.5 phr oil extended.
[d] Hot polymerized.
[e] SBR, 5% styrene.

modulus since previous work had shown adhesion to decrease with increasing modulus. Such a plot (Fig. 5) indicates that retained adhesion shows a linear trend with *WVP* after approximately normalizing for stock modulus. Even the approximately linear correlation is remarkable considering the fact that the elastomers included emulsion (hot and cold polymerized) or solution BR and SBR polymers and oil-extended elastomers.

Since the experimentally determined *WVP*s of identically compounded BR/NR stocks cover a significant range (68–112 *WVP* units), the structure of the polybutadiene component was suspected of having a direct bearing on *WVP*. Figure 6 shows that the *WVP* of the stocks increases with *cis*-1,4 content and decreases with vinyl-1,2 content. The inverse correlation with

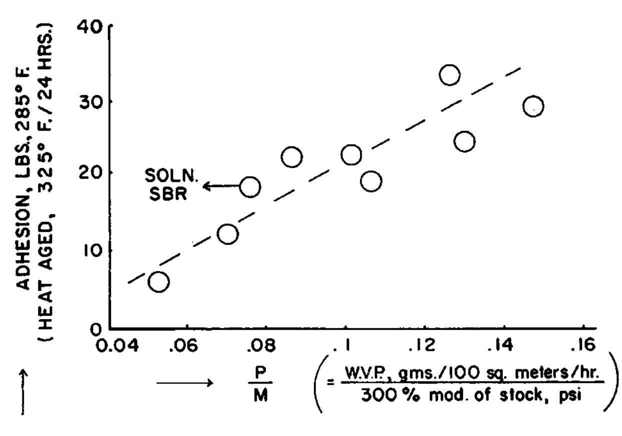


Fig. 5. Retained adhesion/*WVP*/modulus relationship in 75/25 BR/NR stocks.

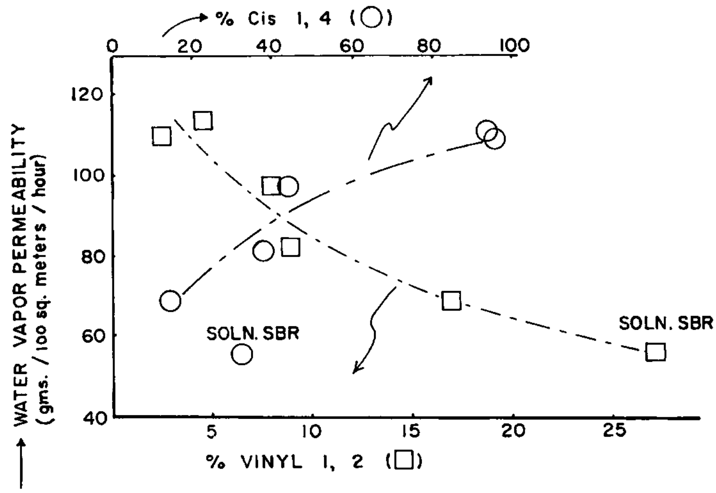
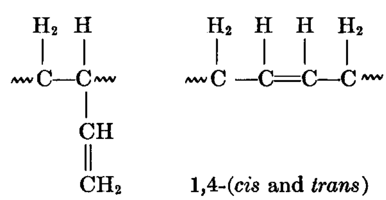


Fig. 6. *WVP* vs. molecular structure of BR in 75/25 BR/25 stocks.

vinyl content also includes the data for solution-polymerized SBR and is consistent with previous work[2] where *WVP* of elastomers was shown to be inversely proportional to a factor related to the nature and concentration of steric groups in the elastomer structure. The minor vinyl-1,2 component in BR can be considered as a "steric" group in the predominantly 1,4-backbone structure:



vinyl-1,2 1,4-(*cis* and *trans*)

Increasing the vinyl-1,2 content of BR enhances this steric factor and consequently decreases the *WVP* of the elastomer.

Thus, experiments with layered pads and with pads containing BR elastomers covering a wide range of *WVP*s and structural parameters show that retained adhesion increases with increasing permeability of rubber stock adjacent to the cords. While stocks containing high proportions of *cis*-BR give good adhesion retention, such stocks are impractical for tires since they are very difficult to process in commercial rubber-making equipment.

Natural Versus Synthetic Polyisoprene

Natural rubber is known[6] to contain about 6% by weight of nonrubber ingredients including fatty acids, sterols, esters, amines, and proteins. Since synthetic polyisoprene rubber (IR) does not contain any nonrubber components, a simple way to determine if the nonrubber ingredients, especially amines, in NR affect adhesion was to compare IR stocks with NR stocks. When compounded to the same modulus level with the same compounding ingredients, a 100% IR stock showed excellent retained adhesion in contrast to the lower adhesion level of a 100% NR stock (Table III). Similarly, in more practical stocks containing 25% SBR, IR/SBR combinations gave better adhesion than NR/SBR stocks (Table III).

TABLE III
IR Versus NR Stocks[a]

Elastomer[b]	MBTS, phr	Black, phr	Oil,[c] phr	300% mod., psi	Adh., 285°F, lb (app.) (H.A., 325°F/24 hrs)	M.S.,[d] min
100% IR	1.5	40 HAF	5	870	24(2)	9
100% NR	1	35 HAF	9.3	848	4(1)	9
IR/SBR (75/25)	1	40 HAF	9.3	830	29(2.5)	11
IR/SBR (75/25)	1	40 HAF	5	1043	19(1.5)	10
NR/SBR (75/25)	1	35 HAF	9.3	975	6(1)	12
NR/SBR (50/50)	1	35 HAF	9.3	880	9(1)	13

[a] MBTS accelerator, 0.3% H_2O.
[b] Other ingredients (phr): 3 ZnO, 1 stearic acid, 1 antioxidant, and 3.13 20% oiled insoluble sulfur.
[c] Naphthenic-type plasticizer.
[d] Mooney scorch; 5-pt. rise, 270°F.

NR Diamines

The consistently low retained adhesion of polyester cords after heat aging in nonamine (MBTS) accelerated stocks containing relatively large proportions of NR suggested that some ingredient in NR may be harmful to adhesion retention. Aliphatic diamines (NH_2—$(CH_2)_n$-NH_2) are believed to result from the bacterial decomposition and putrefaction of proteins which constitute nearly half of the 6% nonrubber ingredients in natural rubber. The excellent retained adhesion of polyester cord in an MBTS-

TABLE IV
Effect of NR Diamines on Polyester Adhesion

Diamine[a]	300% modulus, psi	Mooney scorch, min[b]	Retained adh., lb (app)
None	500	11	26(4.8)
—$(CH_2)_4$—	705	6	15(1.5)
—$(CH_2)_5$—	630	6	21(1.8)

[a] NR diamines, NH_2-$(CH_2)_n$-NH_2, added to 100% IR stock at 0.1 phr level; MBTS accelerator.
[b] 270°F/5-pt. rise.

accelerated 100% IR stock was significantly reduced (Table IV) by adding very small amounts (0.1 phr) of 1,4-diaminobutane or 1,5-diaminopentane, both of which are[6] nonrubber constituents of NR. The effectiveness of such small concentrations of these NR diamines in reducing retained adhesion in IR stocks suggests that the variable adhesion of polyester tire cords seen frequently in stocks containing NR may be due to the fluctuations in diamine and water concentrations in different batches or grades of NR. The combined influence of amine and water is strongly dependent on their concentrations, as has been shown in the work with sulfenamide accelerators

Practical Rubber Compounds

Since the moisture content of rubber stocks used in practical applications, such as tires, fluctuates depending on ambient conditions during storage and processing, a practical stock for use with polyester cords should show minimum dependence of adhesion on moisture content. In this respect, IR stocks are very superior to NR stocks, as shown by adhesion data on MBTS accelerated stocks varying in moisture content from 0 to 1% (Table V). The lower sensitivity of IR compared to NR stocks is due to the fact that the former represents a completely amine-free system whereas the latter contains NR diamines. IR stocks are also less sensitive to stock modulus changes than NR stocks, as seen by comparing the IR data in Table III with NR data in Figure 1.

While the IR stocks containing the disulfide (MBTS) accelerator (Table III) gave excellent retained adhesion, these stocks did not match the high modulus (>1000 psi, 300% mod.) and long scorch time generally attained with tire carcass compounds containing the well-known sulfenamide-type cure accelerators. With IR or IR/SBR stocks, a nonamine-type accelerator (ECD-071) experimentally prepared by the Elastomer Chemicals Department of the du Pont Company not only showed excellent levels of adhesion retention similar to MBTS but also developed high modulus and long scorch time superior to MBTS and typical of sulfenamides (Table VI). The excellent retained adhesion with ECD-071 is attributed to the fact that this compound does not contain or liberate amines. N,N-Dicyclohexylbenzothiazolesulfenamide, which liberates the sterically hindered dicyclohexylamine, improved the retained adhesion under relatively mild heat-aging conditions (300°F/24 hr) but lost its advantage under severe condi-

TABLE V
Adhesion Versus % H_2O in Stock (IR Versus NR Stocks)[a]

Stock	Adhesion, 285°F, lb (app.) (H.A., 325°F/24 hrs)		
	0% H_2O	0.2% H_2O	1% H_2O
100% IR	33 (5)	33 (3.8)	24 (2.3)
NR/SBR (50/50)	32 (5)	22 (1.5)	6 (1)

[a] MBTS Accelerator.

TABLE VI
Nonamine Accelerators

Accelerator, phr[a]	Adhesion, 285°F, lb (app.) H.A., 300°F/24 hr	Adhesion, 285°F, lb (app.) 325°F/24 hr	Stock properties 300% mod.	Stock properties M.S., min[b]
	100% IR Stocks			
1.5 ECD-071 + 0.5 MBTS	25 (2.5)	25 (2.5)	1410	12.3
1.25 DCBS[c] + 0.25 MBTS	21 (1.5)	5 (1)	825	13.6
(1.5 MBTS		24 (2)	670	10)
(1.25 Sulfenamide A[d] + 0.25 MBTS	—	~0	1080	13)
	75/25 IR/SBR			
1.5 ECD-071 + 0.5 MBTS	—	27 (3)	1508	23
(1.5 MBTS		25 (2)	700	11)
	50/50 IR/SBR			
1.5 ECD-071 + 0.5 MBTS	—	28 (3)	1460	26

[a] Compounding ingredients: 35 HAF black and other ingredients shown at bottom of Table III.
[b] Mooney scorch, 270°F/5-pt. rise.
[c] N,N-Dicyclohexyl benzothiazolesulfenamide.
[d] Sulfenamide A = 2-(morpholinothio)benzothiazole.

tions (325°F/24 hr). Apparently, the dicyclohexylamine becomes progressively more active and hence detrimental to adhesion as the conditions of heat aging become severe. A sulfenamide accelerator containing an even more hindered component than dicyclohexylamine would be expected to give good adhesion retention to polyester cords under severe heat-aging conditions. Such compounds are not yet commercially available.

In summary, factors that are important in the adhesion of polyester tire cords to rubber have been established. Based on this knowledge, routes have been developed to formulate rubber compounds showing good physical properties and excellent adhesion to polyester cords after heat aging under severe conditions in the rubber stocks.

The help and cooperation of the Elastomer Chemicals Department of the du Pont Company, Wilmington, Delaware, in compounding and characterizing of rubber stocks is gratefully acknowledged.

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Received October 16, 1970