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Selecting Acrylic Type Coagents for Hose and Belt Applications

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ABSTRACT

Hose and belt applications have traditionally been cured with sulfur-accelerator cure systems. In recent years, automotive hose and belt specifications have changed, requiring longer product life in terms of wear and heat aging. Sulfur cure systems suffer from embrittlement due to poor heat age resistance. Efforts have gone forth to develop improved cure systems. Peroxide-coagent cure systems do provide the improvement needed in heat aging while maintaining the desirable sulfur cure properties of good dynamic properties, tensile strength and wear. In addition, by selecting the right coagent, excellent adhesive properties can be achieved between rubber and reinforcement with-out the use of external bonding agents. A review of these coagents appropriate for peroxide cured hoses and belts is presented in this paper.

INTRODUCTION

Previous papers [1] [2] [3] [4] have discussed the need to select among the many coagents available for the coagent best able to satisfy the multiple properties needed in end use applications. This involves compromise and sometimes a decision to move from one cure system to another such as "sulfur/accelerator" to peroxide/coagent[4]. Notice the term "peroxide/coagent" in contrast to peroxide alone. In virtually every cure application a coagent should be used with a peroxide similar to the accelerators used with sulfur[4].

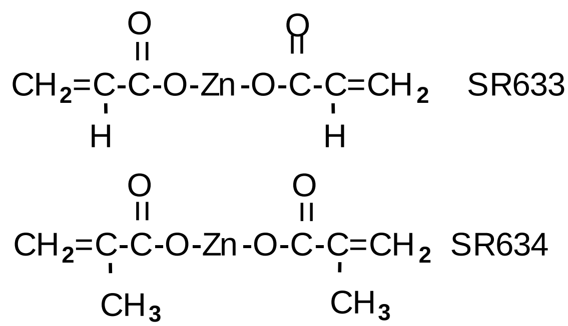
An examination of a typical reference manual on belting and hoses such as the Vanderbilt Handbook lists several formulations with various cure systems. These include neoprene with oxide cure (v-belt), SBR with sulfur cure (friction belt), NR with sulfur cure (conveyor belt), and EPDM with peroxide/coagent (high temperature transmission belt) and NR with sulfur cure. The cure systems are generally sulfur/accelerator systems.

Hose formulations continue in this trend, generally listing sulfur accelerators for NBR and hypalon unless chlorobutyl or neoprene are specified.

Opportunities to develop new elastomer systems for belts have come forth recently with the discovery that a particular peroxide/coagent cure system (zinc di(meth)acrylate) can duplicate and surpass the properties of the sulfur/accelerator system. This has started a new trend in the belting industry using new elastomers, which are price-effective[5]. The coagent system is shown below.

Figure 1

Coagents (Cure System)



SR633 + ZDA **SR634 = ZDMA**

While the same peroxide/coagent system (SR633/SR634) can be employed for hose production, there has been concern over the leaching out of the zinc ion, especially in radiator hoses. This has not been established with actual testing data and the use of SR633 in radiator hoses remains an open issue. Of course, the use of SR633 in other hydraulic type hoses is viable, especially when considering the good adhesive properties toward steel and fabric reinforcement.

EXPERIMENTAL

A masterbatch containing 100 phr Nordel 1040, 100 phr N762 carbon black, 50 phr Sunpar 2280, 5 phr zinc oxide and 1 phr stearic acid was used in all experiments related to EPDM rubbers. Nordel 1040 was obtained from the DuPont Company.

The scorch-retarded salts of acrylic and methacrylic acid were supplied by the Cray Valley Company.

FORMULATIONS

The rubbers were compounded according to the formulations given in Table 1 using a laboratory six-inch two-roll mill. The masterbatches described above were masticated on a two-roll mill until a flux was created at the nip of the rollers. At this point, the Naugard Q, dicumyl peroxide and coagent were slowly added to the flux roll. The band was then sheeted and folded and then rebanded for mixing. This process was repeated many times to ensure thorough mixing. The coagent concentration was varied from 0 to 15 phr, unless otherwise noted. The compounded rubbers were then cured in the plaque mold for twenty minutes at 160°C. The remaining formulations were compounded in a similar manner to the masterbatches with the dicumyl peroxide being added last.

MEASUREMENT

Physical tests were conducted for all molded compounds after molding and again after heat aging at 100°C for 70 hours. Tensile strength, modulus and elongation were determined according to ASTM method D-412 using a Thwing Albert model 1451-42 tensile tester at a crosshead speed of 20 in./min.

Shore A hardness tests were determined for samples after molding using a hand-held Shore A durometer.

Cure characteristics, which include scorch time, cure rate and torque values were measured over a twenty minute period at 160°C using a Tech Pro oscillating-disk rheometer according to ASTM method D-1084.

Tear strength was determined according to ASTM method D-624 using a die C specimen. Hot tear was determined by pre-heating the die C specimen for 10 minutes at 150°C; then determine tear strength by D-624.

Compression set was determined by compressing a one-inch diameter specimen built up with four plies to 50% original thickness for 22 hours at 100°C. The specimen was then removed and the permanent set measured as a percentage of original thickness (ASTM D-395).

Rubber-to-metal adhesion was determined by tensile testing a rubber specimen cured between two metal coupons. (The metal coupons were methanol washed and dried before curing). The tensile test was run at 1.0 IPM crosshead speed, and the force in pounds to break the lap joint in shear was measured. The rubber specimen, approximately 0.030 inch in thickness, was cured at 160°C-166°C for 30 minutes between two 1x3x0.030 inch metal coupons overlapped 1.0 inch in a plaque mold under 30,000 PSI pressure.

Adhesion peel tests were run by curing a ¼ inch thick rubber specimen against a metal coupon and then tensile testing at 180° with a 1.0 IPM crosshead speed. The rubber specimen was hand-pressed against the metal coupon.

DISCUSSION

Hose and Belts

Both hose and belt applications require several common properties as listed in Table 1. Scorch safety, needed for both applications, is provided with the patented retarder system. This retarder system provides extra scorch time without the loss of cured properties.

Hose applications uniquely require good compression set, no leaching of additives and good mandrel release, while belts require good flex and low Tan d to minimize heat build-up and low noise. For a radiator hose, it is difficult, if not impossible, to use a coagent promoting good adhesion to reinforcement and at the same time expect good release from the mandrel. EPDM has become the preferred elastomer for radiator hose combining good temperature, ozone, and chemical resistance(1). For V belts, low cost EPDM is replacing more expensive elastomers through the use of a unique peroxide/coagent system.

Due to conflicting property requirements, different coagents must be used in radiator hoses vs. belts.

EPDM Belts

The use of EPDM in V belts has been limited because of poor dynamic and fatique properties.

EPDM cured with peroxide and non-metallic (meth)acrylate coagents results in poor belt properties, especially the dynamic and fatique properties.

The dynamic and fatique properties can be greatly enhanced, however, with the use of a metallic (meth)acrylate such as zinc diacrylate (SR633) or zinc dimethacrylate (SR634). Table 2 shows the properties obtained with a sulfur/accelerator vs. peroxide/ SR633 and peroxide/SR634 in an EPDM cure. This data was generated by ARDL[a] in Akron, Ohio. The three systems were cured to approximately the same crosslink density.

Table 1: Radiator Hose Requirements vs. Belt Requirements Common Properties

Common Properties

Hose	**Belt**
Good heat age	Good heat age
Adhesion to reinforcement (interply)	Adhesion to reinforcement (interply)
Modulus	Modulus (tensile)
Tear resistance	Tear resistance
Processing, scorch	Processing, scorch

Unique Properties

Compression set	Good flex resistance
Non-leaching	Good Dynamic properties (tooth stiffness)
Non-sticking (mandrel)	Low noise (storage modulus)

Table 2: Properties of Sulfur/Accelerator vs Peroxide/SR633

	Peroxide	**SR633**	**SR634**	**Sulfur**
Hardness, Shore A		57	53	62
Tensile Strength, psi	530	1340	1180	1240
Elongation, %	1050	455	710	515
$Modulus_{100}$ psi	80	260	160	260
Tear, Trouser, PLI	-	129	135	38
Compression Set, %	32	30	50	72
DeMattia flex, cycles	0.11/>1MM	0.23/>1MM	0.13/>1MM	0.5/5M
Monsanto flex, cycles	-	>1MM	>1MM	600M - >1MM
Tan	0.45	0.3	0.3	0.3
E^*_{120}/E^*_{25}	0.5	0.8	0.7	0.9
Heat Age Prop. 150°C/70 hr				
Tensile strength, psi	-10%	-9%	+9%	+5%
Elongation, %	-15%	-13%	-20%	-62%
$Modulus_{100}$ psi	0	+16%	+7%	+63%
Hardness, Shore A	0	0	+5%	+9%

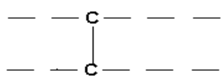
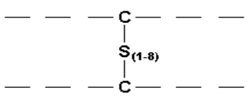
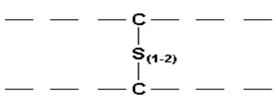
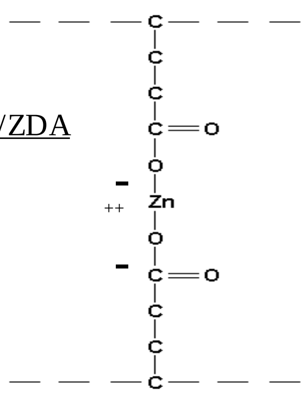
The comparison between the sulfur/accelerator cured system properties and the peroxide/SR633 and SR634 properties cure systems give superior properties! These properties include:

1. Higher Tensile Strength
2. Lower Compression Set
3. Better de Mattia flex
4. Better Monsanto flex
5. Better Tear
6. Better Heat Age Properties
7. Equivalent Elongation
8. Tan δ Equivalent

The listed properties, especially good heat age properties and flexibility, combine to produce superior belt performance (longer life) over sulfur cured systems.

Possible reasons for the above performance benefits SR633 over sulfur cured systems and peroxide alone may be related to the structure of the networks as shown below:

Figure 2

Cure Network		Bond Strength Kcal/mol	Heat Age	de Mattia	Tan δ	E^*_{120}/E^*_{25}
Peroxide		84	Excellent	Good	0.45	0.5
Sulfur		49	Poor	Good	0.3	0.9
EV		66	Good	Poor	-	-
Peroxide/ZDA		68	Good	Good	0.3	0.8

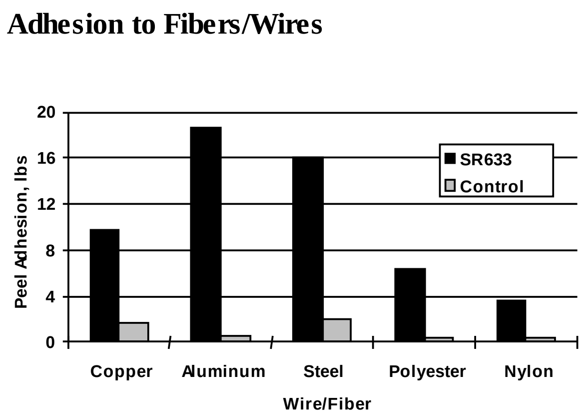
In the case of the peroxide covalent bond, the bond is strong but short and non-flexible resulting in good heat age and good de Mattia flex, but poor dynamic properties.

The sulfur network is longer and flexible but the bond strength between sulfur atoms is weak, giving poor heat age properties and good de Mattia flex. Reducing the number of sulfur atoms in the network to the EV system improves heat age perfomance but makes the network brittle and non-flexible like the peroxide system resulting in poor de Mattia flex.

The peroxide/SR633 network is long and flexible and relatively strong. The metallic bond under stress can also undergo cleavage with subsequent reformation[6]. These properties of the eroxide/SR633 network help provide the combination of good heat aging, de Mattia flex, and dynamic properties.

EPDM Reinforcement Adhesion (Hose or Belt)
Belt performance and long belt life depend on the tensile properties of the belt reinforcement. If the adhesive bond between elastomer and reinforcement fails, then the strength of the belt is reduced with obvious belt failure. Unaged adhesive bonding to various reinforcements is shown for the coagent system in Fig. 3. Peel values were highest for steel; however cohesive failure was noted in each case.

Figure 3

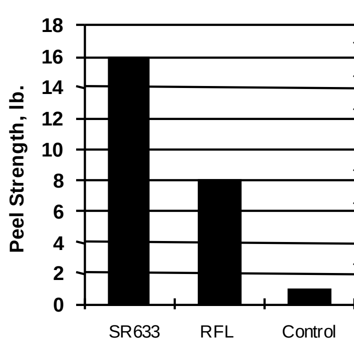


* Tee Pull Adhesion
10 phr SR633/EPDM

Figure 4 illustrates adhesion to a ½ inch wide strip of nylon/polyester warp fabric without treatment where the EPDM rubber containing 10 phr ZDA (**SR633**) and peroxide was cured at 160°C for 20 minutes against the fabric. A RFL[a] coated control was bonded with EPDM without **SR633.** The graph illustrates the ability of the coagent/peroxide cure system to bond to fabrics without the use of fabric treatment such as RFL.

Figure 4

Peel Adhesion
EPDM Bonded to Nylon/Polyester Warp Fabric



- Peroxide cured Nordel EPDM
- 10 phr SR633
- RFL treated is normal fabric from supplier
- Control is untreated fabric
- EPDM bonded to fabric during curing at 160C for 20 min.
- Peel test on 1/2 inch wide specimen at 1.0 in/min. Peel angle was 180 degrees

Bonding Elastomers to EPDM

The coagent/peroxide cure system is versatile and can bond to other elastomers not containing SR633. In the following table the elastomers listed contained only peroxide or ECHO in the case of CPE and were sandwiched between two EPDM layers containing 10 phr **SR633**. Steel coupons were positioned outside the sandwich and the entire system cured at 160°C for 30 minutes. High bond strength was achieved in each case along with cohesive failure. Special built-up layers for either belt or hose costruction should be possible using the peroxide/SR633 cure system.

Table 3

Rubber	Shear Adhesion, psi
EPDM	1240 C
NBR	870 C
CPE	1050 C
Natural Rubber	1240 C

Aged Adhesion Testing (Belts and Hoses)

The question now remains, how well does the adhesive bond of the peroxide/SR633 cure system hold up to heat and moisture? The table below illustrates the aged adhesion of EPDM containing 10 phr cured between two steel coupons and heat aged at 300°F for up to 165 hours.

Table 4

Hours @ 300°F	Lap Shear Adhesion, psi
0	1160 C
96	1204 C
165	1230 C

The ability of the adhesive bond to remain stable at high temperature is important for long belt and hose life.

Water Resistance

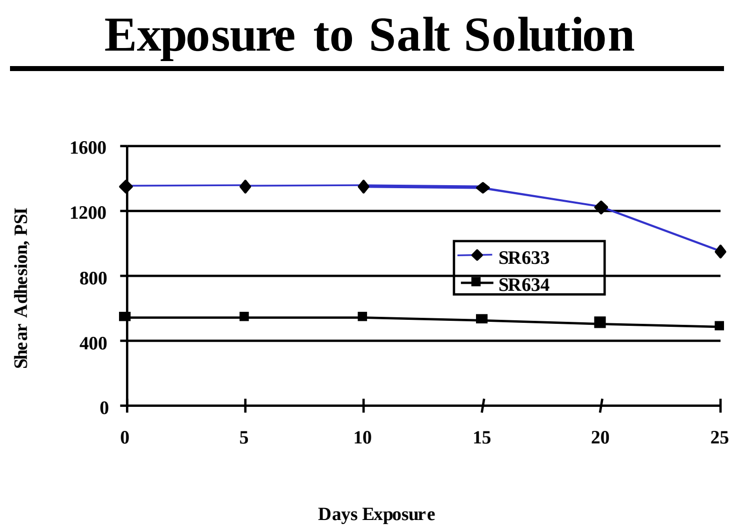
Coupons similar to those above were aged under 70°F water for the same time period. Again, no deterioration in properties were observed as shown in Table 5.

Table 5

Hours @ 70°F	Lap Shear Adhesion, psi
0	1160 C
96	1250 C
165	1145 C

Salt solution testing was conducted on both acrylate and methacrylate coagent/peroxide cure systems in EPDM as shown in Figure 5. Extending the testing time period did show drop off in adhesion for the SR633 system after 15 days, whereas the SR634 went to 25 days without loss of adhesion. The initial adhsion for the SR634 system was half the SR633 value to begin with. The SR634 system appears to be less sensitive to the water/salt solution system than the SR633, presumably due to the presence of the methyl group in the molecule.

Figure 5



de Mattia in Alternate Elastomers

The ability of the peroxide/SR633 cure system to enhance de Mattia performance was also demonstrated in a mixed cure system with BrIIR elastomer. Table 6 shows data for several cure systems which were cured to a constant modulus_{100} of 160-175 psi. The addition of SR633 to a sulfur cure and a mixed sulfur-peroxide cure improves de Mattia flex sinificantly. An additional control using sulfur and peroxide resulted in poor de Mattia flex. This test data helps generalize the ability of SR633 to form a flexible network and improve de Mattia flex.

Table 6

	Modulus_{100}, psi	**de Mattia cycles to 0.5"**
Sulfur	160	25M
Sulfur/SR633	170	140M
Sulfur/SR633/Peroxide	175	145M
Sulfur/Peroxide	160	35M

In a cooperative study with Bayer (Canada) a peoxide/coagent cure system was evaluated in HNBR as a replacement for sulfur thiuram cure for the automotive drive belt applicaton. The sulfur/thiuram cure suffered from poor retention of tensile and tear properties after hot air aging. A mixed carbon black/SR633 cure system was able to achieve the following:

1. Improved retention of properties after hot air aging

2. Ozone resistance was significantly improved

3. Tan d @11 Hertz was comparable to sulfur cure

4. Dynamic complex modulus (E*) with SR633 had lower temperature dependence

Conclusion

EPDM belts cured with peroxide and **SR633** or **SR634** offer an improved replacement for the traditional sulfur/accelerator cure. The sulfur dynamic properties are improved. The **SR633** and adhesive properties are improved. The **SR634** can be utilized in other elastomers such as bromobutyl and HNBR as well as neoprene, hypalon, etc.

References

1. Richard Costin and Walter Nagel,“Coagent Selection For Rubber Application” Paper 14, American Chemical Society, Pittsburgh, PA October 11, (1994).

2. Richard Costin and Walter Nagel, “Selecting The Optimum Coagent For Several Rubber Applications”, Paper 97, American Chemical Society, Cleveland, OH October 19, (1995).

3. Walter Nagel, “New Coagents for Improved EPDM Properties”, Paper 70, American Chemical Society, Louisville, Kentucky, October 8-11, (1996).

4. Richard Costin and Walter Nagel, “Coagent Selection For Peroxide-Cured Elastomers”, Paper 4, American Chemical Society, Indianapolis, Indiana, May 5-8, (1998).

5. G. Vroomen, J. Noodermeer, M. Wilms “Automotive Coolant Hose Technology Keltan® EPDM, Peroxide Curing”, Paper 42, American Chemical Society Rubber Show, September 29-October 2, (1998).

6. Walt Nagel, “Use of Metallic Coagents in Pumpable Sealants”Adhesive and Sealants Industry May 1997.