Novel Adhesion Promoter for Various Elastomer/Substrate Combinations

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Abstract

Rubber adhesion to various substrates, such as metal, glass and textiles, can be achieved in a number of ways. The Hallbond Adhesion Promoter System (APS) is unique in that adhesion can be accomplished either through additions to the rubber compound or by applying a form of the Hallbond APS to the substrate. The Hallbond APS is a one-component system that can be mixed in or applied by conventional methods.

A variety of adhesion applications and elastomer substrate combinations are discussed in the paper. Low surface energy polymers, such as Ethylene propylene diene monomer (EPDM) and Natural Rubber (NR) are highlighted.

The APS improves rubber-to-metal adhesion and rubber-to-metal and rubber-to-synthetic fibers such as polyester, nylon and aramid. The APS provides equal or better adhesion as compared to standard adhesion systems. Improvements of 20 percent to 200 percent in adhesion force are achieved with many of the elastomer/substrate combinations.

Introduction

Rubber articles, such as powertrain belts, hoses, tires, etc., are reinforced with various metals and textiles to improve their strength, dimensional stability and long-term durability. Adhesion to these substrates is a critical property, especially considering the use of many reinforced rubber products in automobiles and machinery.

Despite the various adhesive systems that have been developed over the years, there is a continuing need for commercially available, cost-effective additives that improve the adhesion of rubber to various reinforcements and substrates. Achieving good adhesion of rubber to various substrates is quite complex and not always fully understood. Various treatments of textiles and metals must be done to enhance adhesion to rubber. Many additives have been developed for internal use in the rubber to enhance adhesion. All these steps are labor-intensive and require extensive processing expense and, in many cases, are subject to environmental and health regulations.

In this study, a novel adhesion promoter is introduced that can be used in many applications requiring rubber adhesion. Hallbond APS is not a product but a system that can be adjusted depending on the application or performance needs. Three different forms of the Hallbond APS are discussed in this study:

- **Hallbond APS-D** – 72 percent active on a calcium silicate carrier
- **Hallbond APS-S** – Solution grade
- **Hallbond APS-E** – Emulsion grade

Another form, a polymer masterbatch, has been developed but is not presented in this paper. The APS system will promote adhesion between rubber and reinforcements and is activated during the vulcanization process. The application of the Hallbond APS in various elastomer/substrate combinations is discussed.

Experimental

Experimental investigations for rubber-to-textile cord adhesion were performed using a proprietary EPDM compound. The polyester cords used were treated with resorcinol-formaldehyde (RFL), and the control was treated with an additional adhesive to enhance bonding to the rubber compound. The adhesion test and results for this part of the study was performed by Mark IV Corporation, Springfield, MO.

A standard natural rubber compound used for brass-coated steel wire cord adhesion was tested, and its composition is provided in the Results and Discussion section. The rubber compound used for yarn adhesion was based upon a peroxide-cured Chlorinated Polyethylene (CPE), and its composition is proprietary.

The rubber-to-metal adhesion work was done using a proprietary EPDM and natural rubber compounds. The recipe for natural rubber is: 100.0 – SMR-L, 5.0 Kadox 930, 2.00 Stearic Acid, 35.0 – N-330, 7.0 Hallbond APS-D, 2.25 – Sulfur, and 0.70 Santocure TBSI. The control compounds did not contain adhesion promoter. The metals used were bar stock quality, cleaned with solvent and not treated with primers or adhesives.

Test Methods

Compounds for performance testing were mixed in a BR Banbury, except for curatives, which were added on a two-roll mill. Test specimens for compound performance properties were molded as follows: press temperature – 149°C, press time – 1.25 x t'c(90) min and at 5.75 MPa on the sheet surface. Specimens for original properties, low-temperature testing, air oven aging and immersions were die cut from molded sheets.

Mooney Viscometer	ASTM D1646-94, Monsanto Viscometer, large rotor, 1 min preheat
Oscillating Disc Rheometer	ASTM D2084-93, TechPro RheoTech Rheometer, round die, 3" arc, 30 s. Preheat. MH at central point of torque rise, rate – one lb., 2.5 cm/5 min
Original Properties	
Tensile, Elongation, Modulus	ASTM D412-92, Method A, Die C crosshead speed 51.0 cm/min
Hardness	ASTM D2240-91 1s reading
Specific Gravity	ASTM D792-91

Yarn Testing	ASTM D4393-85 HALLSTAR Modified, Crosshead speed 5 cm/min.
Metal Bonding	ASTM D429, Crosshead speed 5 cm/min
Wire Cord Adhesion	ASTM D2229-93, Crosshead speed 5 cm/min

The yarns used in this study were provided by Beaver Manufacturing and are Twaron 1008, Beaverloc 102, Acordis, 140, Powerloc, Acordis 161 and Beaverloc 108.

Results and Discussion

Polyester Cord Adhesion

The conventional practice has been to prepare the fiber by pretreatment with a combination of a hexamethoxymelamine or hexamethylenetetramine and phenol-formaldehyde condensation product, wherein the phenol is almost always resorcinol. By a mechanism not completely understood, the resin reacts with the fiber and the rubber, affecting a firm, reinforcing bond.

Especially suitable adhesion promoters for polyesters are also those that are applied in multi-stage processes, for instance, a blocked isocyanate being applied in combination with polyepoxide and the material then being treated using customary RFL resins (RFL dip). Combinations of RFL dips with other adhesion-promoting substances, that is, a reaction product of triallyl cyanurate, resorcinol and formaldehyde or p-chlorophenol, resorcinol and formaldehyde, are also used.

The effect is resin formation *in-situ* during vulcanization of the rubber, creating a bond between polymeric cords and the rubber. The Hallbond system is particularly useful with polyester cord, where adhesive pretreatment has been adequate but very costly.

The initial compounds were mixed into an existing EPDM recipe and tested for adhesion to polyester cord. The following variables were tested:

Variable	1	2	3
	Melamine A*	**Hallbond APS-D***	**Control – Current EPDM Formula**

***Melamine A** - Melamine-formaldehyde resin with 27 percent calcium silicate;
Hallbond APS-D – 72 percent active with 27 percent calcium silicate carrier.

The control compound was bonded with the polyester cord pretreated with a melamine-formaldehyde resin and dipped into an additional adhesive compound. The polyester cord used in compounds 1 and 2 was treated with melamine formaldehyde resin but not with an adhesive. Compound 1 contains just the melamine resin and provides basically equal adhesion to the control compound. Compound 2 containing Hallbond APS-D shows an unexpected increase in adhesion. The adhesive force for compound 2 is increased at least 100 percent compared to the control and Melamine A compound. The adhesion results of the room temperature and heat aging are listed in Table I.

TABLE I

Compound Variable	Adhesion-Newtons-Force	
	Room Temperature	257°C
Melamine A	95.94	15.92
Hallbond APS-D	212.17	63.21
Control	98.79	21.71

These results indicate that APS-D provides a significant increase in adhesive force between EPDM and the polyester cord compared to the control compound and the compound containing only resin. This unique adhesive additive approach allows for removal of the additional step of dipping the polyester cord into a bonding adhesive. It is theorized that the surface-active properties of Hallbond APS-D allow for penetration and wetting of the surface of the polyester fiber. The reacting components of this system will react with the rubber during vulcanization.

Wire Cord Adhesion

An increased need in the industry for wire cord reinforcing of rubber to survive high dynamic stress, such as flexing, to avoid tire belt separation has brought about a continuing search for other and better methods of achieving high adhesive strength.

Tires typically have a construction such that a carcass, edge portions of a belt, an under-belt pad and the like are intricately combined with each other in its shoulder portion. Because the under-belt pad is repeatedly subjected to load during running, heat builds up, causing internal rubber destruction in the under-belt pad and adhesion failures between the rubber components and between a rubber portion and the cords (steel cords) in the carcass. This causes separation of the belt edge portions and ply separation in the carcass, resulting in the breakdown of the tire. One conventional approach to this problem is that the under-belt pad is formed of a rubber compound that contains a reduced amount of carbon black for suppression of heat build-up.

However, the rubber compound for the under-belt pad is softened by the reduction of the carbon black content. This results in adhesion failure and internal rubber destruction in the under-belt pad due to the heat build-up. The recent performance improvement of automobiles requires that tires have a higher durability under higher speed running and heavy loads.

Despite their good abrasion resistance, radial tires become unusable sooner than bias tires because of the belt separation that takes place while the tread still remains.

One way that this problem has been addressed is by improving the tread or steel cord-embedded rubber. An improved steel cord-embedding rubber is made of a rubber composition containing an adhesive such as a cobalt salt of an organic acid, hydroxybenzoic acid or resorcinol, which increases adhesion between rubber and the steel cord. These improvements, however, are not completely successful. Not only is it necessary that adhesion between rubber and metal (e.g., steel or polymeric cord) be high, but it is also necessary that any decrease in adhesion be as small as possible while tires are in use. In actuality, tires containing a steel cord-embedding rubber with good adhesion occasionally lose the initial adhesion to a great extent after use. The Hallbond APS is a one-component adhesion system that allows for removal of resorcinol from the wire cord-embedded compound. The use of resorcinol or RFL resins present both health and waste disposal issues. The Hallbond APS is evaluated as a replacement for both the resorcinol and the melamine resin. Table II lists the compounds used for the wire cord adhesion evaluation.

TABLE II

	1	**2**	**3**
SMR-L	100.00	→	→
N-326	60.00	→	→
Kadox 930	10.00	→	→
Cobalt Napthenate	2.00	→	→
Stearic Acid	1.20	→	→
Santoflex 13	1.00	→	→
PVI	0.20	→	→
Melamine A	11.20	-	-
Hallbond APS-D	-	11.20	-
Pennacolite	-	-	3.85
Resimene 3520	-	-	4.23
Sub Total	185.60	185.60	182.48
Mill Addition			
Sulfur	5.60	5.60	5.40
Vulkacit DZ	0.50	0.50	0.50
TOTAL	191.70	191.70	188.38

The original wire-cord adhesion results for all three compounds are judged to be acceptable, with excellent wire coverage. The heat aging results show that the Hallbond APS-D provided higher adhesion values, better wire coverage and less force change than the other two compounds. These results are shown in Table III.

TABLE III

Wire Cord Adhesion

Form of APS	**APS-D-dry**		
Polymer	**Natural Rubber (Sulfur cure)**		
Substrate	**Brass-coated Steel Wire Radial Grade**		
Adhesion (Newtons - force at 25°C)	**1**	**2**	**3**
Original Properties	**Melamine A**	**HALLBOND APS-D**	**Control**
Maximum Force - Newtons (avg.)			
Average	694	720	784
Coverage, %	98	99	100
Air Oven Aging: 48 h at 121°C			
Maximum Force - Newtons. (avg.)			
Average	327	547	470
Coverage, %	75	95	88
Force Change, %	-39	- 8.3	-30

The humidity aging results after seven, 14 and 21 days show that Hallbond APS-D provides the greatest adhesion with the least change from the original adhesion results.

Based on the heat and humidity aging adhesion, the Hallbond APS-D can improve wire-cord adhesion versus known systems. The data in Table IV indicate that improved adhesion can be obtained on brass-coated steel and other brass wire applications.

TABLE IV

Wire Cord Adhesion

Form of APS	**APS-D-dry**		
Polymer	**Natural Rubber (Sulfur cure)**		
Substrate	**Brass-Coated Steel Wire Radial Grade**		
Adhesion (Newtons - Force at 25°C)			
Humidity Aging: 7 d at 94°C	**Melamine A**	**Hallbond APS-D**	**Control**
Maximum Force - Newtons (avg.)			
Average	532	679	677
Coverage, %	98	99	100
Force Change, %	-30	-5.7	-14
Humidity Aging: 14 d at 94°C			
Maximum Force - Newtons (avg.)			
Average	422	661	550
Coverage, %	75	95	88
Force Change, %	-39	-8.3	-30
Humidity Aging: 21 d at 94°C			
Maximum Force - Newtons (avg.)			
Average	286	562	451
Coverage, %	75	88	87
Force Change, %	-59	-27	-43

The effect of the APS-D upon cure and physical properties is minimal as compared to the control and Melamine A compounds. Tensile strength and hardness values are increased slightly, indicating some reinforcement of the rubber. Rheometer and original physicals for the wire cord adhesion compounds are listed in Table V.

TABLE V

Compound	1	2	3
	Melamine A	Hallbond APS-D	Control
Oscillating Disc Rheometer at 168°C(335°F)			
M_L	23.4	15.3	18.6
M_H	74.8	88.7	85.2
t_s2, min	1.6	1.6	1.4
t'c(90), min	4.9	12.5	5.8
1.25*t'c(90), min	6.2	15.6	7.2
Original Physical Properties			
Stress at 100% Elongation, MPa	6.6	7.4	
Stress at 200% Elongation, MPa	12.8	15.5	15.3
Stress at 300% Elongation, MPa	18.5	---	---
Tensile Ultimate, MPa	18.5	20.2	19.2
Elongation at Break, %	300	265	255
Hardness Duro A, pts.	79	82	80
Specific Gravity	1.213	1.193	1.198

Rubber-to-Textile Adhesion

Reinforcement of rubber is important in producing many goods, such as power transmission belts, hoses, gaskets, seals and air springs. Raw materials used for textile reinforcement include polyester, nylon, aramid, polyvinyl alcohol, glass and rayon. Modern high-performance yarns must satisfy the most stringent physical properties, defined tenacity, shrinkage resistance to temperature and chemicals, and optional adhesion to all rubber compounds.

Most chemical fibers show poor adhesion to most common rubber compounds. There are many pretreatments of fiber, such as epoxies or isocyanates. In addition, many fibers are impregnated with an RFL resin to enhance adhesion. Depending on the application or rubber compound used in the composite, further adhesive dip is used to create a strong bond.

In this study, Hallbond APS-D is evaluated two ways: the APS-D is evaluated as an internal adhesion promoter, and the APS-S and APS-E are evaluated as treatments for the yarns. The yarns used were as follows:

- **Aramid**
    - Twaron 1008 – untreated
    - Beaverloc 102 – treated

- **Nylon**
  - Acordis 140
  - Powerloc – treated
- **Polyester**
  - Acordis 161 – untreated
  - Beaverloc 108 – treated

The APS-D was mixed into a proprietary peroxide-cured CPE compound. The rubber/yarn composites were molded and then tested for adhesion. The results for aramid to the CPE compound are listed in Table VI.

TABLE VI

Aramid Yarn Adhesion

Form of APS:	**APS-D-dry**			
Polymer:	**CPE (Peroxide cure)**			
Substrate	**ARAMID**			
Adhesion (Newtons - Force at 25°C)	**3 PHR**	**6 PHR**	**10 PHR**	**Control**
Aramid - iso treated - Beaverloc 102-Twaron 1008 Aramid	36.5	43.6	41.4	29.5
Aramid untreated - Twaron 1008	18.2	28.4	21.35	24.5

Aramid fiber adhesion to various elastomers is, at best, marginal. The addition of APS-D has increased adhesion, and it would appear that six PPHR is an optimal amount to increase adhesion of the treated fiber. The untreated aramid shows no effect of the addition of APS-D, and thus would indicate that a pretreatment of some sort will be needed to optimize adhesion. The results for nylon adhesion are listed Table VII below.

TABLE VII

Nylon Yarn Adhesion

Form of APS	**APS-D-dry**			
Polymer	**CPE (Peroxide cure)**			
Substrate	**NYLON**			
Adhesion (Newtons - Force at 25°C)	**3 PHR**	**6 PHR**	**10 PHR**	**Control**
Untreated Nylon – Acordis 140	35.5	42.8	45.1	37.5
Iso-treated Nylon – Powerloc-Acordis 140	116.1	134.9	155.4	110.5

Rubber Failure →

The treated nylon has excellent adhesion to the CPE compound. In this case, the failure is cohesive. This phenomenon is indicative of a network being formed in the rubber compound. Further investigations into the mechanism of increased cohesive failure will be studied and reported in a future paper. The results for treated and untreated polyester are listed in Table VIII.

TABLE VIII

Polyester Yarn Adhesion

Form of APS	**APS-D-dry**			
Polymer	**CPE (Peroxide cure)**			
Substrate	**Polyester**			
Adhesion (Newtons - Force at 25°C)	**3 PHR**	**6 PHR**	**10 PHR**	**Control**
Untreated Polyester - Acordis 161	43.2	79.0	77.4	39.6
Iso-treated Polyester - Beaverloc 108-Acordis 161	150.3	134.7	144.6	136.2

Rubber Failure →

The untreated polyester yarn shows substantial increase in adhesion, and the six PHR level provides optimal adhesion, as was observed with nylon adhesion. The treated polyester has excellent adhesion to CPE and at all levels of APS, with cohesive failure on all compounds.

The APS-S and APS-E products were initially developed for use as yarn treatments and potentially as primer adhesives for rubber-to-metal bonding. Untreated aramid fiber was coated and dried and compared to iso-treated aramid. The adhesion results of this evaluation are listed in Table IX.

TABLE IX

Aramid yarn adhesion

Form of APS	**APS-S (Liquid-Solvent)** **APS-E (Liquid-Emulsion)**		
Polymer	**CPE (Peroxide cure)**		
Substrate	**Aramid**		
Adhesion (Newtons - Force at 25°C)	**APS-E**	**APS-S**	**Control**
Aramid – APS treated **- Beaverloc 102-Twaron 1008 Aramid**	34.2	41.8	23.1
Aramid iso treated **-Beaverloc 102 - Twaron 1008**			47.1

The APS-S and APS-E improved adhesion significantly over the untreated and treated Aramid fiber. These materials will also be investigated further for use as treatments for various yarn/rubber composites.

Rubber-to-Metal Adhesion

The use of adhesives to bond rubber to metal is well known. The processes of treating metal prior to bonding are extensive and costly. In this part of the study, Hallbond APS-D is evaluated at six PHR as an internal adhesion promoter in sulfur-cured NR and peroxide-cured EPDM. The APS-S was evaluated as an adhesive/primer on the metal and then bonded to the rubber compounds. The results of this study are listed in Table X below.

TABLE X

Rubber-to-metal adhesion

Form of APS:	**APS-D-Dry**
Polymers:	**Natural Rubber (Sulfur Cure)** **EPDM (Peroxide Cure)**
Substrate :	**Brass**

Adhesion (Newtons - Force at 25°C)	**Melamine A**	**APS-D**	**Control**
Natural Rubber (Sulfur Cure)			
Metal Adhesion – ASTM D429			
Adhesion Force	500	607	366
Failure Type	R	R	R
% Failure	100	100	100
EPDM (Peroxide Cure)			
Metal Adhesion – ASTM D429			
Adhesion Force	271	408	--
Failure Type	R	R	RM
% Failure	100	100	100

R = Rubber Failure, RM = Rubber-to-Metal Failure

All three compounds have excellent adhesion to brass, with the compound containing APS-D having the highest value. The failure mechanism is cohesive, and the results are indicative of a crosslinking network being developed in the rubber matrix.

The APS-D provided good adhesion of steel to EPDM, while the Melamine A provided some adhesion and the control completely failed. The APS-S, when applied to steel as an adhesive/primer, provides excellent adhesion and, again, the control shows no adhesion. Further investigation of Hallbond APS-S as an adhesive for rubber-to-metal bonding will be reported in the future. The steel adhesion data is reported in Table XI.

TABLE XI

Rubber-to-metal adhesion

Form of APS:	**APS-D-Dry** **APS-S-Liquid**
Polymer :	**EPDM (Peroxide Cure)**
Substrate:	**Steel**

Adhesion (Newtons - Force at 25°C)	**Melamine A**	**Hallbond APS-D**	**Control**
APS-D-Dry			
Metal Adhesion – ASTM D429	74.8	186.7	--
Adhesion Force	R	R	RM
Failure Type	100	100	100
% Failure			
APS-S	**APS-S**	**Control**	
Metal Adhesion – ASTM D429			
Adhesion Force	267.0	Fail	
Failure Type	R	RM	
% Failure	100	100	

R = Rubber Failure, RM = Rubber-to-Metal Failure

Summary

The Hallbond APS system can be used in a variety of rubber applications requiring adhesion to a reinforcement or substrate. The data shows excellent adhesion to polyester cord, brass-coated steel wire and a variety of yarns, such as polyester, aramid and nylon. The system can be supplied in many forms, which allows the product to be used as an internal adhesion promoter or applied on a substrate to create a strong bond.