Durable Color Matching Coatings for Vehicle Tires

Ashley Mullins[1], Bryan E. Koene[1], Miranda Thornton[1], Matthew Newsome[1], Carol Kaplan[1], Michael Brown[1], Daniel M. De Bonis[2]

[1]Luna Innovations, 3155 State Street, Blacksburg, VA 24060; mullinsa@lunainc.com

[2] Army Research Lab Weapons and Materials Research Directorate

ABSTRACT

Luna has developed a durable elastomeric coating for tires that can be color-matched to Chemical Agent Resistant Coating (CARC) paint systems currently used on Army vehicles. Technology such as camouflage coatings on military tactical vehicles significantly reduces detection by enemy combatants. Black tires and tracks, however, are in direct contrast to the vehicle and surroundings and constitute a large portion of the vehicle profile. Due to the complex chemistry of tires, traditional, paints or coatings do not have the durability for long term adhesion to tire rubber. Commercial coatings, when applied to tires, fail either through delamination and/or severe color change. As a result Luna has developed coatings matched to all CARC colors and spectral profiles with demonstrated durability on tire rubber. Luna's coating can be easily applied in a timely manner to combat vehicle tires by covalently bonding directly to styrene-butadiene (SBR) and other types of rubber. Luna's rubber coating has many desirable attributes:

- Strong adhesion to the tire rubber, resulting in excellent durability through adverse environmental conditions (fatigue, fluid exposure, abrasion, and aging)
- Easy application using brush, spray and aerosol methods (spray can).
- Rapid application and ambient temperature cure to limit equipment downtime
- Demonstrated through extensive performance testing related to adhesion, wear, environmental durability, and fatigue.
- Maintains excellent physical properties with full pigment loading
- Proven to not degrade rubber properties after accelerated aging with coupon level and full tire endurance testing

Keywords: camouflage, rubber coating, tires

1. INTRODUCTION

Rubber compound and fillers are the two basic ingredients in the formulations for tire sidewalls and treads. Natural rubber (polyisoprene) is the traditional elastomer due to its good resilience, abrasion and thermal resistance, low friction coefficient, superior tear strength and flexibility at low temperatures, but has poor resistance to oils and environmental factors. Natural rubber is easily blended with many synthetic polymers and is typically combined with styrene-butadiene (SBR) for tire applications. SBR's typical composition is 75% butadiene and 25% styrene and exhibits excellent abrasion, crack and aging resistance, while the drawbacks are low tear strength, poor tack, and low resilience. For many purposes, SBR directly replaces natural rubber, as in MIL-STD-45301 for tread elastomer. Cis-1, 4-polybutadiene rubber (PBR) is compounded with SBR, comprising 16.8% and 39% of the formulation, respectively. 70% of all PBR produced is used in tire manufacturing. PBR is highly elastic and has a high degree of resistance to dynamic stress over a large thermal range. The combination of SBR and PBR improves abrasion, crack resistance, and reduces heat build-up under dynamic load.

Carbon black and silica are common fillers in tire rubber formulations. A curing package of sulfur, vulcanizing accelerators, and activators are combined with the rubber, oils, anti-oxidants and anti-ozonites for compounding. A high pressure and temperature cure follows the tire build to complete the tire assembly. The carbon black comprises 35% of the rubber compound in MIL-STD-45301, creating the black color. A durable, coating must be applied with the appropriate thickness to mask the black color, but not interfere with the tire function, and must maintain durability by covalently bonding to the rubber.

In order to provide a durable color matched coating for vehicle tires, our team has developed a toughened coating that is closely matched in mechanical properties (modulus, elongation, hardness) to tire rubber. The coating is based on a two component urea/urethane copolymer resin and must be applied in combination with a rubber-specific adhesion promoter. The combination of the adhesion promoter with urea/urethane coating chemistry provides a highly durable, covalently bonded finish to rubber substrates. The coating provides the same flexibility as tire rubber with excellent adhesion, impact resistance, durability, abrasion resistance, ozone resistance, and UV resistance.

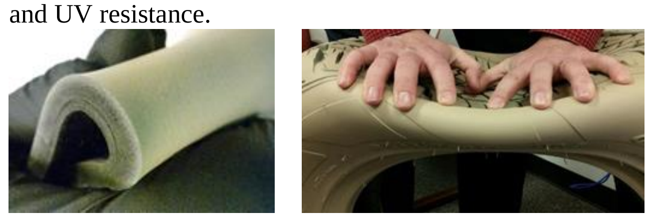

Figure 1. Left – Coated rubber substrate after flexing; Right – Sidewall compression of coated tire.

The thin (<4 mil), rapid-cure, dual coat system has been applied to both new and used tires as well as previously painted tires using common application techniques such as spray cans, brush, or high volume, low pressure (HVLP) spray systems. Seven colors have been developed, all color-matched to common CARC colors. The coating does not alter the properties of target substrates, but enhances camouflage ability, improves ozone and UV resistance, resists mechanical abrasion and impact damage, and resists weathering degradation of the rubber substrate.

Figure 2. Left to right: Foliage Green 504, Green 383, Green 808, Woodland Desert Sage, Tan 686A, Brown 383, Black.

2. EXPERIMENTAL PROCEDURE

The tough coating is solventborne polymeric coating that forms a chemical bond to styrene/butadiene based rubber. The coating is a simple, pigmented, two component system that cures in less than 24 hours under ambient conditions. The coating covalently bonds with rubber, imparting long-term durability and environmental protection properties. The isocyanate functionality provides a mechanism for superior adhesion to all types of rubber surfaces. The organic portion imparts flexibility and durability to match the strain of the rubber. Key attributes of the durable rubber coating are shown in Table 1.

Table 1. Key Attributes of the durable rubber coating.

Color matched with low gloss	Different colored coatings exhibit on average ΔE* < 4.0 110° with spectral gloss < 18 (60°)
Excellent adhesion to rubber	No loss of adhesion[1] (5B) after DeMattia fatigue testing[2]; Coating proven to outlast test rubber after DeMattia fatigue testing
Flexibility, abrasion resistance	Closely matched to the flexibility of rubber with coating elongation[3] of 500% and passes 1/8" mandrel bend tests without altering hardness of rubber substrate
Excellent durability without altering rubber properties	Does not alter rubber properties as determined through hardness, tensile, fatigue, and tire endurance testing (FMVSS No.139) on both used and new tires
Ease of Application	Easily applied, with minimal EHS concerns, using common application techniques – brush, HVLP, 2k spray cans – fast curing
Environmental Durability	Coating shows excellent resistance to degradation resulting from accelerated outdoor weathering[4] and ozone exposures[5]
Facile formulation	The solvent borne coating is readily prepared from commercial precursors. All materials are TSCA listed.

The coating formulations were applied by spray or brush onto selected substrates – new tires, used tires, and commercially available SBR (McMaster-Carr).

Figure 3. Left – HVLP application; Right spray can application.

Coated substrates were air cured at ambient temperature or force cured at 60°C for 60 minutes. Coating thickness was measured at 0.002-0.005" depending on substrate and application method. At least three specimens were used for each test and the data was averaged. Testing procedures are discussed below in the results section.

3. RESULTS

3.1 Color Matching and Gloss

The color matching properties and spectral gloss (60°) were measured using standard color chips and a BYK-Gardner 6807 color-guide 45/0 Spectrophotometer on coated rubber substrates according to ASTM E308[6]. Results are shown in Table 2. Samples were applied using either HVLP processes or 2k Spray Max cans. All colors are color matched with ΔE* values < 4.0 and average gloss numbers < 18. The color matching process for Tan 686A is shown in Figure 4.

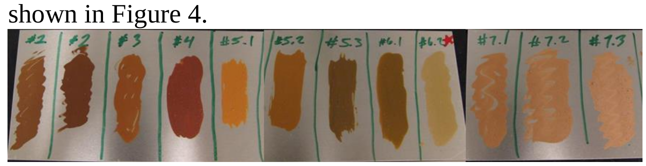

Figure 4. Color matching paint formulations utilizing various loadings of pigment (e.g. yellow oxide, red oxide, and black) to obtain a base paint formulation.

Table 2. Color matching and gloss data after cure.

Color Type	ΔE*	ΔG (60°)
Foliage Green 504	1.8	2.0
Green 383	4.0	2.8
Green 808	2.6	7.6
Woodland Desert Sage	3.0	9.9
Tan 686A	1.0	4.6
Brown 383	2.4	16.7
Black	3.6	6.9

3.2 Adhesion and Flexibility

Coating adhesion to rubber was assessed using the cross-hatch adhesion test outlined in ASTM D3359[1] and the best formulations were down selected for further examination by tensile and fatigue testing (ASTM D412)[3], color matching cross-hatch adhesion (ASTM D3359)[1], hardness (ASTM D2240)[7], and flexibility (ASTM D522)[8]. Results for the rubber coating are shown in Table 3. All samples passed 1/8 inch mandrel bend tests as tested according to ASTM D522.[8]. Examples of test specimens are shown in Figure 5.

Table 3. Adhesion, Hardness, Tensile Strength (psi) and % Elongation.

Type	Adhesion	Hardness (Shore A)	Tensile Strength (psi)	Elongation
Control	-	68	691 ± 1	240 ± 10
Coated	5B	67	680 ± 40	250 ± 10

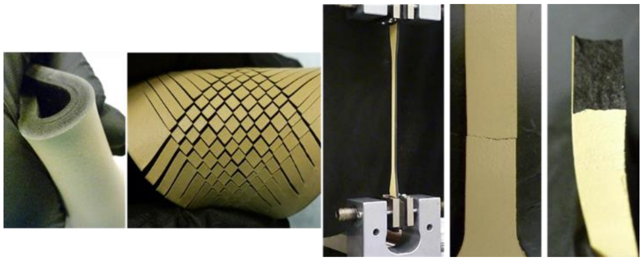

Figure 5. Left to right: Flexibility demonstration, flexibility/adhesion after cross-hatch adhesion testing, sample in tension with no visible cracking of coating at approximately 300% elongation, cross-section of dog bone specimen after rubber failure at 300% elongation.

3.3 Durability Assessment

A test method was developed by Luna[9] to simulate the wear generated in a blowing sand environment similar to desert driving conditions. Sand is pressurized at the top of the hopper using air pressure at 35 psi. This generates blowing sand at the bottom of the collection port at speeds ranging from 30 – 40 mph. Both Luna rubber coating and CARC samples were exposed to 1 liter of sand blowing through the test apparatus five times. Tristimulus color was measured before and after exposure to sand according to ASTM E308[6] and is shown in Figure 6.

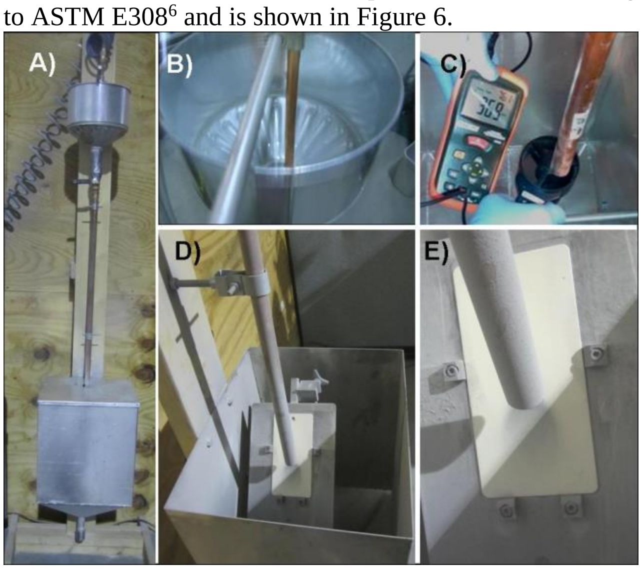

Figure 6. Blowing Sand Testing: A) Full assembly with pressurized hopper; B) Hopper to hold sand to accelerate the sand through copper pipe; C) Airflow meter measuring 37mph exit velocity; D) Sample panel orientation in metal box at tube outlet E) Close up of panel in process of blowing sand abrasion.

Neither coating shows noticeable wear or loss of adhesion. The CARC coated samples crack when placed in the test fixture.

Table 4. Color change after falling sand test.

Specimen Type	Color Before Falling Sand (ΔE^*)	Color After Falling Sand (ΔE^*)
CARC	2.06	2.41
Luna Sample A	2.03	8.52
Luna Sample B	2.06	11.14

Lab scale durability tests were conducted according to ASTM D430 – Standard Test Methods for Rubber Deterioration – Dynamic Fatigue. A custom fatigue test fixture similar to the DeMattia test fixture outlined in ASTM D430 (extension strain) was fabricated. The modified DeMattia fatigue test method is an extremely aggressive test and a good indicator of coating adhesion to rubber, as well as coating flexibility and durability. Samples coated with the Luna rubber coating and CARC were tested. The tests were conducted using 0.25" thick straight bar specimens with a 0.5" gage width, at 1 Hz and 120% elongation. Both aged and non-aged uncoated samples were evaluated. Luna found that aging does slightly reduce the number of cycles required to take the rubber to failure. Uncoated, non-aged samples fail on average after 27,000 cycles while uncoated aged samples fail after 23,000 cycles. Unlike CARC, the Luna rubber coating does not show any cracks or failure modes prior to rubber failure.

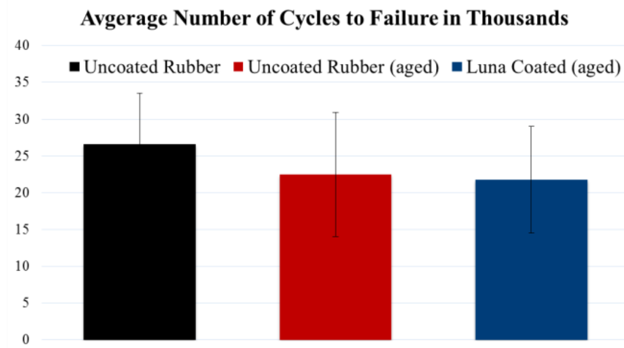

Figure 7. ASTM D430 DeMattia fatigue testing to failure - Comparison of Luna rubber coating to uncoated rubber.

Figure 8. Flexibility/elongation of coated rubber substrates when tested in fatigue according to ASTM D430. Top – CARC coated rubber after 1 cycle at 120% elongation; Bottom – Luna coated rubber after 10000 cycles at 120% elongation.

Full scale tire endurance tests were conducted according to U.S. Department of Transportation and National Highway Traffic Safety Administration FMVSS No.139 testing standard. Test were conducted at Smithers Rapra in Akron, OH. The test tire was applied to an approved test rim and inflated to a predetermined pressure based on the tire type. Tires were purposely inflated to the lowest allowable pressure and preconditioned at 100 ºF for three hours prior to test. Tires were placed on the test rig and tested at 100 ºF under increasing load. Tests were conducted at 74.6 mph for all load increments and without pressure adjustment or other interruptions for the first 35.5 hours. Total initial test time was 35.5 hours. After the initial 35.5 hours, if the tires had not failed or if no damage was detected, load was increased incrementally until tire failure. Results are summarized in Table 5. Images before and after testing can be seen in Figure 9. Test results indicate that Luna's rubber coating does not negatively impact tire endurance performance.

Table 5. FMVSS No.139 tire endurance test results from Smithers Rapra

Brand	Name	Tire Condition	Hrs. Run	Results / Failure Type
Spector	Advanta SUV	Used Coated	50.11	Sidewall Delamination
Master Craft	Courser STR	New Coated	71.55	Sidewall/Rim Cushion Cracking; Delamination
Master Craft	Courser STR	New Uncoated	70.78	Sidewall Rim Cushion Cracking

Figure 9. Left – Coated tire prior to endurance testing; Right – Same tire after endurance testing

Actual tire testing in a real life environment have been ongoing for approximately six months. The Luna coating has been demonstrated to survive six months of driving in actual conditions after approximately 5000 miles.

August 2016 October 2016 January 2017

Figure 10. Luna coated tires after six months of driving.

3.4 Ozone Resistance

Luna rubber coating was applied to sidewall rubber formulations and sent to Smithers Rapra for ozone exposure evaluation. A control (uncoated, untreated), samples with only adhesion promoter applied, and coated (with adhesion promoter) were tested according for resistance to ozone according to ASTM D1149. Samples were exposed at different conditions 72 hours at 40 °C and 50 pphm ozone and 72 hours at 40 °C and 100 pphm ozone. It is evident that the presence the Luna coating prevents ozone degradation of sidewall when compared to the control. It is anticipated that if all exposed areas (edges and back) of the sample were coated there would be no rubber degradation of the coated samples.

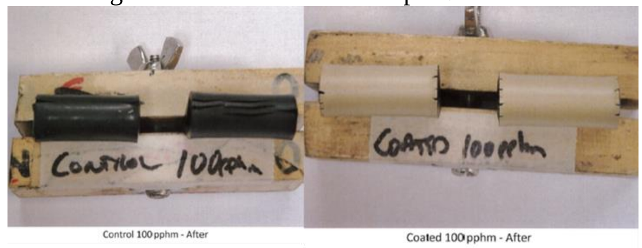

Figure 11. Ozone exposure of control and Luna coated rubber.

4. CONCLUSIONS

Coating rubber substrates, particularly tires, is difficult due to the complex, constantly changing chemistry of tires as they age. Commercial coatings usually fail quickly after coating through delamination or through rapid color change. The Luna rubber coating provides a color-fast, durable finish to tires. The incorporation of polyurethane-urea chemistry in the Luna coating imparts a highly flexible and durable coating system. The resulting coating has strong adhesion to the tire rubber and as result the coating maintains durability through adverse environmental conditions (fatigue, fluid exposure, abrasion, and aging). The coating is designed for ease of application using brush, spray and aerosol methods. The coating can be rapidly applied (both pretreatment and coating application) and cures quickly. The tough polyurethane-urea coatings excel in performance testing related to adhesion, wear, environmental durability, and fatigue.

5. ACKNOWLEDGEMENTS

This work was performed with the assistance of an Army SBIR Phase I (W911QX-14-C-0046) and Army SBIR Phase II (W911QX-16-C-0001).

[1] ASTM D3359; Standard Test Methods for Measuring Adhesion by Tape Test

[2] ASTM D430; Standard Test Methods for Rubber Deterioration – Dynamic Fatigue

[3] ASTM D412; Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers – Tension

[4] ASTM G90; Standard Practice for Performing Accelerated Outdoor Weathering

[5] ASTM D1149; Standard Test Methods for Rubber Deterioration – Cracking in an Ozone Controlled Environment

[6] ASTM E308; Standard Practice for Computing the Colors of Objects by Using the CIE System

[7] ASTM D2240; Standard Test Method for Rubber Property—Durometer Hardness

[8] ASTM D522; Standard Test Method for Pigment Content of Solvent Reducible Paints

[9] Abrasion Resistant Hydrophobic Coatings for Corrosion Protection, USAF Phase II, Contract # FA8501-08-C-0033