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Evaluation of Low Hazardous Air Pollutant Thermoset Adhesives for the Application of Rubber-to-Metal Bonding on Army Tank Pads and Road Wheels

by Ryan D. Robinson, Faye R. Toulan, Christopher B. Stabler, David Flanagan, Henry Feuer, Paul Touchet, and John J. La Scala

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NOTICES

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14. ABSTRACT

The Environmental Protection Agency is in the process of mandating Defense Land Systems and Miscellaneous Equipment and National Emission Standards for Hazardous Air Pollutants that will affect Army surface coating operations. Bonding unvulcanized rubber to a metal substrate in the production and replacement of tank treads, track pad, track shoes, and road wheels uses thermoset adhesives and primers with a high hazardous air pollutant (HAP) content. This research focused on two alternative options to reduce HAP emissions while maintaining performance properties: the replacement of HAP-containing thinners used with rubber-to-metal thermoset adhesives or the use of an entirely new low-HAP adhesive system. Thinner miscibility in the baseline adhesives was conducted to identify acetone, methyl ethyl ketone, and naphtholite 66/3 as compatible non-HAP thinners. Peel adhesion testing was conducted to compare the adhesion strength of each adhesive, both neat and diluted in the test series on each of the rubber compounds used in tank pads, track shoes, and road wheels. The results indicated that a number of the low-HAP adhesives and primer combinations outperformed the baseline HAP-containing materials, including Thixon 532-EF adhesive with naphtholite 66/3 thinning solvent and Megum 3911 primer. This could result in HAP reductions of 10 tons/yr for the rubber-to-metal bonding operation at Red River Army Depot alone.

15. SUBJECT TERMS

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1. Introduction

The Environmental Protection Agency (EPA) is in the process of mandating Defense Land Systems and Miscellaneous Equipment (DLSME) and National Emission Standards for Hazardous Air Pollutants (NESHAP) that will affect Army surface coating operations (*1*). The materials used for coatings operations at many Army installations were surveyed, and it was found that the Army used numerous adhesives and sealants among other coating materials that contain significant amounts of hazardous air pollutants (HAPs). The Army has determined that it is more cost-effective to reduce or eliminate HAP emissions from coatings operations rather than using emissions control devices to capture and treat them (*1*). Therefore, the goal of the Sustainable Painting Operations for the Total Army (SPOTA) program is to significantly reduce the amount of HAP emissions produced in coatings operations, including adhesive and sealant application and removal. Army adhesives and sealants account for 10% of the Army's surface and coating materials and 5% of total HAP emissions (*1*).

Rubber-to-metal bonding (RTMB) currently uses thermoset adhesives and primers with a high HAP content. The adhesives studied were designed for bonding unvulcanized rubber to a metal substrate in the production and replacement of tank treads, track pad, track shoes, and road wheels. The adhesive Chemlok[*] 252X is currently used by the Army and was included in this research as a baseline for comparison. The amount of Chemlok 205 (baseline) primer used at Red River Army Depot (RRAD) was 7357 lb/yr, which contains 5518 lb/yr of HAPs. The primer is currently thinned with the exempt solvent methyl ethyl ketone (MEK). RRAD used Chemlok 252X adhesive at a rate of 9636 lb/yr, resulting in 14,615 lb/yr of HAP emissions when thinned with toluene.

Numerous rubber compounds are used for rubber-to-metal bonding operations of Army tank pads, track shoes, and road wheels. These include compression ground side rubber for integral pad track and injection road wheel compound for Armored Recovery Vehicle M88 tanks (*2, 3*), track injection compound designated for replaceable track pads and track shoe backing rubber (*2*), road wheel compound approved for Bradley M2 tanks, armored M113 personnel carriers, and Abrams M1 tanks (*3*), and an improved injection compound for Abrams M1 wheels (figures 1 and 2). Thus, any alternative adhesive must perform relatively well on a variety of rubber compounds.

[*] Chemlok is a registered trademark of LORD Corp.

Figure 1. Bradley fighting vehicle (left) and Abrams M1 tank (right).

Figure 2. Bradley fighting vehicle tank tread (left) and road wheel (right).

This research focused on two alternative options to reduce HAP emissions while maintaining performance properties: the replacement of HAP-containing thinners used with rubber-to-metal thermoset adhesives or the use of an entirely new low-HAP adhesive system. A thinner is a volatile liquid added to a coating to reduce viscosity while not materially affecting the product. Adhesive thinning is performed for brush or spray application in order to give the product the requisite solids per gallon for proper coverage (*4*). The Chemlok 6254-LH and Chemlok 6411-LH adhesives were suggested by the manufacturer (LORD) as commercial low-HAP alternatives for Chemlok 252X (baseline). In addition, low-HAP primers were identified as potential replacements for the existing high-HAP primers. Chemlok 205-LH was identified as an alternative to Chemlok 205, and Megum* 3911 was identified as an alternative to Thixon P-11.

The research began with a large list of HAP-free thinner candidates and a battery of tests, which were intended to narrow down the candidates to a single low-HAP alternative. Thinner miscibility in the baseline adhesives was the first evaluation conducted. Baseline adhesives, both neat and with various thinners, were tested to determine drying time. Nonvolatile content of the test series adhesives were determined to verify the compositional data provided by the manufacturers. Thermogravimetric analysis (TGA) of adhesives, both neat and with various thinners, was used to compare the pigment-to-binder (P/B) ratios. Differential Scanning

*Megum is a trademark of the Dow Chemical Company.

Calorimetry (DSC) of adhesives, both neat and with various thinners, was used to compare the temperature at which vulcanization occurs. Rheological studies of the adhesives, both neat and with thinners, were used to compare the viscosity. Peel adhesion testing was conducted to compare the adhesion strength of each adhesive, both neat and diluted, in the test series on each rubber compound used in tank pads, track shoes, and road wheels.

2. Experimental Method

2.1 Materials

The rubber-to-metal bonding adhesives used in this study were also paired with a manufacturer-recommended metal primer to promote better adhesion. The primers also contained HAPs and volatile organic compound (VOC) solvents. This study was focused on reducing the HAPs and VOCs in only the adhesives; however, a low-HAP primer (Chemlok 205-LH) was used with the low-HAP adhesives Chemlok 6254-LH and Chemlok 6411-LH (experimental name Chemlok E1005396) (*5*). The primers were used in the neat (undiluted) form during the course of this research.

2.1.1 Unvulcanized Rubber Compounds

Five different unvulcanized rubber compounds used by RRAD were selected for testing. Rubber no. 0064 is a “compression compound, ground side rubber for integral pad track approved for Armored Recovery Vehicle M88” (*2*). Rubber no. 0135 is a track injection compound designated for replaceable track pads and track shoe backing rubber (*2*). Rubber no. 0149 is an injection road wheel compound approved for Bradley M2 tanks, armored M113 personnel carriers, and Abrams M1 tanks (*3*). Rubber no. 0235 is an injection road wheel compound approved for Armored Recovery Vehicle M88 tanks (*2*). Rubber no. 5618 is an improved injection compound for Abrams M1 wheels (experimental) that has been shown to have improved durability relative to the previous rubber compound (no. 0149). Rubber compound nos. 0064, 0135, 0149, 0235, and 5618 were provided to the U.S. Army Research Laboratory by RRAD. The rubber compounds come as solid clay-like materials. They were stored in a refrigerator at 42 °F prior to rheology and molding operations.

2.1.2 Adhesives

LORD Chemlok 252X (baseline) is a general-purpose cover coat adhesive that will bond vulcanized or unvulcanized rubber compounds to metals (*6*). Application can be brush, dip, or spray. The composition of Chemlok 252X adhesive is a mixture of polymers, organic compounds, and mineral fillers dissolved or dispersed in an organic solvent system. The carrier solvents are xylene (65%) and ethyl benzene (15%), both of which are HAPs (*7*).

LORD Chemlok 6254-LH (alternative) is a low-HAP cover coat adhesive that will bond a variety of vulcanized and unvulcanized rubber compounds to metal (*8*). Application can be brush, dip, or spray. The composition of Chemlok 6254-LH adhesive is a mixture of polymers, organic compounds, and mineral fillers dissolved or dispersed in an organic solvent system. The carrier solvents are non-HAP n-butyl propionate (35%), a proprietary solvent (30%), and xylene (15%) (*9*).

LORD Chemlok 6411-LH (alternative) is a low-HAP cover coat adhesive that will bond a variety of rubber compounds to metal during vulcanization (*10*). This is an experimental adhesive suggested by the manufacturer as a low-HAP alternative. Application can be brush, dip, or spray. The composition of Chemlok 6411-LH adhesive is a mixture of polymers, organic compounds, and mineral fillers dissolved or dispersed in an organic solvent system. The carrier solvents are non-HAP n-butyl propionate (40%), a proprietary solvent (15%), non-HAP dimethyl carbonate (15%), xylene (10%), and ethyl benzene (5%) (*5*).

Rohm and Haas Thixon* 532-EF (baseline) is a vulcanizing adhesive used for bonding most elastomers to various metals. Application can be brush, dip, or spray (*11*). The carrier solvents are toluene (50%–52%), xylene (21%–23%), and ethyl benzene (1%–3%), which are HAPs (*12*).

Table 1 lists the HAP and VOC content, density, and solids content of these adhesives acquired from the manufacturers' technical data sheets (TDSs) and material safety data sheets (MSDSs). The alternative adhesives have considerably reduced HAP and VOC contents. However, the solids content and density are similar and thus should not affect film thicknesses or weight of the parts.

Table 1. Physical properties of test series adhesive and primers (*5–20*).

Product Type	**Product Name**	**Baseline/Alternative**	**HAP (wt. %)**	**VOC (g/L)**	**Density (lb/gal)**	**Solids (wt. %)**
Primer	Chemlok 205	Baseline	~75	702	7.9	22–26
Primer	Thixon P-11	Alt-baseline	72–78	703	7.8	22–26
Primer	Chemlok 205-LH	Alt-low HAP	~11	713	7.7	22–27
Primer	Megum 3911	Alt-low HAP	~12	~588	~7.9	23–25
Adhesive	Chemlok 252 X	Baseline	80–85	747	8.1	22–24
Adhesive	Thixon 532-EF	Alt-baseline	73–80	743	8.2	25
Adhesive	Chemlok 6254-LH	Alt-low HAP	20–25	688	7.8	23–26
Adhesive	Chemlok 6411-LH	Alt-low HAP	~15	697	8.2	~25

2.1.3 Primers

LORD Chemlok 205 (baseline) adhesive primer is designed for use under Chemlok cover coat adhesives to bond a wide variety of vulcanized and unvulcanized rubber compounds to metals and other rigid substrates (*14*). Application can be brush, dip, or spray. The carrier solvents are HAPs: methyl isobutyl ketone (MIBK) (60%), xylene (10%), ethyl benzene (5%), and non-HAP MEK (5%) (*13*).

*Thixon is a trademark of the Rohm and Haas Company.

LORD Chemlok 205LH (alternative) primer is a low-HAP primer for use under Chemlok cover coat adhesives to bond a wide variety of vulcanized and unvulcanized rubber compounds to metals and other rigid substrates (*18*). Application can be brush, dip, or spray. The carrier solvents are non-HAPs: methyl-n-propyl ketone (MPK) (65%), n-butyl propionate (10%), and HAP MIBK (10%) (*17*).

Rohm and Haas Thixon P-11 (baseline) is a vulcanizing cover coat adhesive primer used with Thixon adhesives for bonding most elastomers to various substrates (*16*). Application can be brush, dip, or spray. The carrier solvents are HAPs MIBK (57%–59%) and xylene (10%–13%) (*15*).

Rohm and Haas Megum 3911 (alternative) is a low-HAP general-purpose primer for adhering hot and cold rolled steel, stainless steel alloys, brass aluminum, and zinc-plated metals during vulcanization (*19*). This product is approved for use with Thixon 532-EF adhesive. Application can be brush, dip, or spray. The carrier solvents are non-HAPs butyl propionate (14%–16%), MPK (48%–50%), and HAP MIBK (8%–10%) (*20*).

Table 1 lists the HAP and VOC content, density, and solids content of these primers acquired from the TDSs and MSDSs. The alternative primers have considerably reduced HAP and VOC contents. However, the solids content and density are similar and thus should not affect film thicknesses or weight of the parts.

2.2 Solvent Miscibility

Thixon 532-EF and Chemlok 252X use toluene and/or xylene as the main carrier solvents (*7, 12*). Therefore, a compatible thinner to be used with the adhesives must be miscible in toluene and xylene. Figure 1 (*21*) contains a solvent miscibility chart that was used to down-select the alternative thinner candidates.

Solvent miscibility was determined by preparing dilutions in 20-ml vials using the manufacturer-recommended baseline adhesive and thinner as well as the alternative thinners from figure 3. As described on the TDS, a mixture for spray application of Chemlok 252X was prepared using adhesive (60 weight-percent [wt. %]) and thinner (40 wt. %) (*6*). A mixture for spray application of Thixon 532-EF was prepared using adhesive (75 wt. %) and thinner (25 wt. %) (*11*). The Chemlok 252X was mixed by hand using a metal spatula, but the Thixon 532-EF required more thorough mixing and was mixed on a paint shaker for 30 min before combining with a thinner. There were 10–15 g of solution in each 20-ml vial. The vials were sealed and vigorously shaken while observing miscibility. The thinners that were miscible were subjected to further testing, while the thinners that were visibly immiscible were eliminated. All dilutions containing HAP-free thinners were compared to the baseline (Chemlok 252X and Thixon 532-EF) thinned with toluene and xylene.

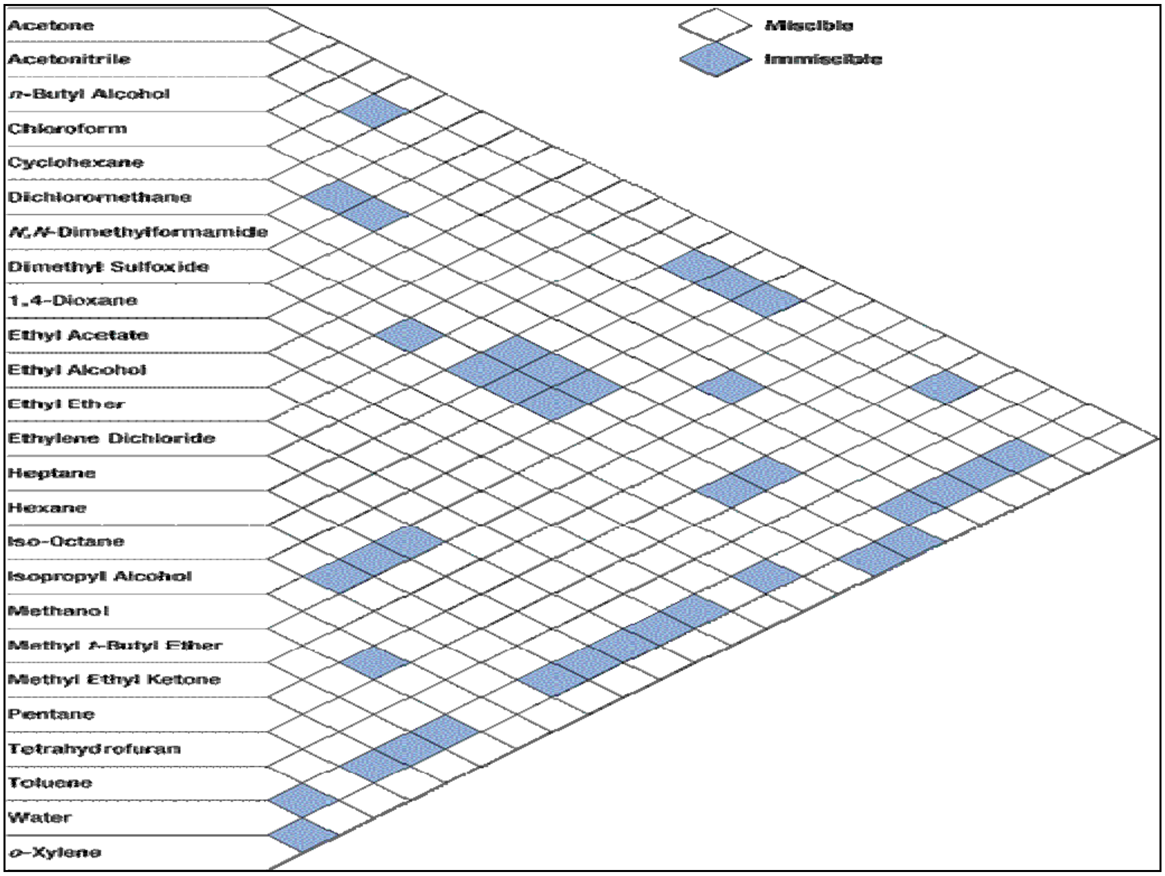

Figure 3. Solvent miscibility chart (*21*).

2.3 Dry Time

To verify that the alternative thinner candidates would dry at least as quickly as the baseline thinned adhesives, ASTM 1640 03 (*22*) was used as a guideline to test the drying time of each mixture. The adhesive was applied with a Bird applicator to a uniform thickness of 4 mil. The tackiness of the samples was then assessed periodically with a wooden dowel using an industry standard “touch test” as a function of time until the sample was no longer tacky (wet). The time required for the sample to become tack-free (dry) was recorded as a range rather than a single value. In particular, the product is dry to the touch or tack-free when the product did not transfer to the dowel and film was not deformed.

2.4 Nonvolatile Content

To determine the percent of nonvolatile solids in the neat adhesives, ~2 g of each sample was placed in a tared aluminum weighing pan. These pans were then placed in a fume hood overnight to allow most of the solvent to evaporate. The samples were then placed in an oven set at 150 °F (66 °C) for 24 h. The samples were reweighed and compared to the previous weight measurements. The oven drying process was repeated in 24-h increments until the sample reached a constant weight, ±0.0005 g.

2.5 Thermogravimetric Analysis (TGA)

TGA was conducted on the samples of dried formulation solids using a TA Instruments TGA 2950. Wet formulation samples were dried in an oven until the sample weight remained constant. A 5- to 10-mg sample of dried adhesive was placed on a tared platinum sample holder suspended on a weight-sensing wire hook. The samples were heated in air up to 800 °C at 10 °C/min. The TGA instrument measured the sample mass as a function of temperature throughout the experiment. Three samples of each formulation were tested to achieve a good measure of percent error.

2.6 Differential Scanning Calorimetry (DSC)

DSC data was collected from 5- to 10-mg dried samples of Chemlok 252X thinned with toluene (baseline adhesive solution), Chemlok 252X thinned with acetone (alternative adhesive/thinner solution), and Chemlok 6254-LH thinned with a 50/50 solvent blend of n-butyl propionate and Varnish Makers and Painters (VM&P) naphtha (low-HAP adhesive solution). This test series was performed to measure the extent of cure the adhesive experienced when exposed to a similar temperature used during the rubber vulcanization process. Thus, these DSC studies allowed us to determine whether different curing conditions are necessary for alternative adhesives/thinners. The TA Instruments Q1000 DSC was set to ramp the temperature at 10 °C/min, from room temperature to 250 °C and an isothermal hold at 250 °C for 5 min. Then a temperature ramp of 10 °C/min down to 50 °C, an isothermal hold for 5 min, and a final temperature ramp back down from 10 °C/min to 50 °C. The temperature of 50 °C was chosen as the end point value because no changes in the adhesive happened near or below this temperature.

2.7 Rheology

Rheological studies were performed on all test specimens to determine viscosity (Pa·s) and shear stress (Pa) at a particular shear rate (1/s). A similar rheological profile to the baseline may equate to consistent application properties. Significantly different viscosities would affect the ability to spray the adhesive at the depot and would not be desired. Studies were conducted using an AR 2000 Rheometer from TA Instruments with the AR 550/1000 Concentric Cylinder System with Peltier temperature control. This type of geometry allows for a very accurate measurement of low-viscosity liquids and prevents sample drying through volatile loss during testing. The water jacket around the cup allows for temperature control during the test. A temperature of 20 °C was maintained by the water jacket around the cylindrical cup. Samples were pipetted (~7 ml) into the cylindrical cup, and the rotor was slowly lowered into the sample with a gap of 500 µm between the bottom of the rotor and the inside bottom of the cup.

Viscosity for each sample was evaluated using a steady-state flow procedure. The shear rate (1/s) was increased in a logarithmic progression from 10 to 1000 s^{-1}, taking five points per decade to determine whether the adhesive solutions are shear thinning. Then the shear rate was decreased logarithmically from 1000 to 10 s^{-1}, taking three points per decade to determine if the sample displayed any thixotropic properties. Thixotropy is the characteristic of time-dependent viscosity, also known as recovery time for shear-thinning materials.

2.8 Peel Adhesion Strength (ASTM D 429 03)

2.8.1 Substrate Preparation

Steel panels were cut to a dimension of 4 × 8 × 0.0625 in and grit blasted on one side with aluminum oxide no. 60 blast media to create a rough surface for bonding. An acetone rinse was used to remove any debris or residues from machining and grit blasting.

2.8.2 Adhesive/Thinner Preparation

Appropriate metal primers were selected for each adhesive based on the manufacturers' recommendation. The baseline adhesives Chemlok 252X and Thixon 532-EF are currently in use and were included in this experiment for comparison. The baseline thinner (toluene) was chosen from the manufacturer's recommendation listed on the TDS. Table 2 contains the adhesive/thinner combinations used in this test series. Instructions given by the adhesive manufacturer were used to determine the percentage by weight of toluene (baseline thinner) to mix with Chemlok 252X (baseline adhesive 60/40) and Thixon 532-EF (baseline adhesive 75/25). The 50/50 blend of n-butyl propionate and VM&P naphtha (non-HAP solvent blend 20%) was the manufacturer-recommended thinner for Chemlok 6254-LH (low-HAP adhesive 80/20). This solvent blend was composed of two non-HAP solvents, therefore Chemlok 6254-LH remains classified as a low-HAP adhesive. Chemlok 6411-LH (low-HAP adhesive 75/25) was thinned with t-butyl acetate (25%), also a non-HAP/non-VOC solvent per the manufacturer's TDS. The percentage by weight of acetone and MEK (alternative non-HAP thinners) used with Chemlok 252X (baseline adhesive 60/40) and Thixon 532-EF (baseline adhesive 75/25) was determined by the TDS-suggested toluene level. The amount of non-HAP solvent used to replace toluene was kept at a ratio of 1:1 by weight to compare compatibility, application, and performance properties with the baseline adhesive. For the purposes of this research, the primers were used neat and brushed onto the metal substrate. However, RRAD does dilute the primer with MEK (exempt solvent) for spray application.

Table 2. Adhesive/thinner combinations in test series.

Adhesive Type	Adhesive Name	Thinner Name	Dilution (wt. %)	Thinner Type
Baseline	Chemlok 252X	Toluene	60/40	HAP
Baseline	Chemlok 252X	Acetone	60/40	Non-HAP
Baseline	Chemlok 252X	MEK	6040	Non-HAP
Baseline	Thixon 532-EF	Toluene	75/25	HAP
Baseline	Thixon 532-EF	Acetone	75/25	Non-HAP
Baseline	Thixon 532-EF	MEK	75/25	Non-HAP
Low HAP	Chemlok 6411-LH	T-butyl acetate	75/25	Non-HAP
Low HAP	Chemlok 6254-LH	n-butyl propionate and naphtha VM&P (50/50 blend)	80/20	Non-HAP

2.8.3 Primer and Adhesive Application

For the purposes of this research, the primer was not thinned before application. The TDS specifies that the primer may be used thinned or full strength (*14, 16, 18*). Primer was applied to the grit-blasted surface of the 4- × 8-in steel panel using a brush until a uniform film was achieved. After allowing the primer to dry for ~24 h at room temperature, the corresponding adhesive was applied with a brush over the primed surface until a uniform film was achieved. Two to three coats of adhesive, applied at 10-min intervals, were required to achieve a uniform film. The time interval between primer and adhesive application was kept constant at 24 h for the purpose of this research. Adhesives used were either unaltered (neat) or thinned with various solvents (table 2). The adhesive film was allowed to dry for 24 h at room temperature. Long layover times between adhesive application and bonding (e.g., 30 days) usually have no adverse effect on the bond, provided the coated parts are covered to prevent contamination. Release tape was applied to one end of the panel, providing an unbonded area of the rubber strip ~2 in long.

This application method was used successfully for all adhesives in the test series except for Chemlok 6411-LH. A uniform film could not be achieved for Chemlok 6411-LH. Figure 4 (left) shows the inconsistent film of Chemlok 6411-LH adhesive over Chemlok 205-LH primer. The manufacturer was contacted to determine the reason for this performance issue. A special application process for this adhesive was required due to resolvation of the primer. Panels were prepared by the manufacturer because of this unusual application method. The panels were preheated to ~150 °F and then sprayed with Chemlok 205-LH primer. This process was repeated with the application of the adhesive. Figure 4 (right) shows that a uniform film was achieved by preheating the panels during application of the Chemlok 6411-LH adhesive.

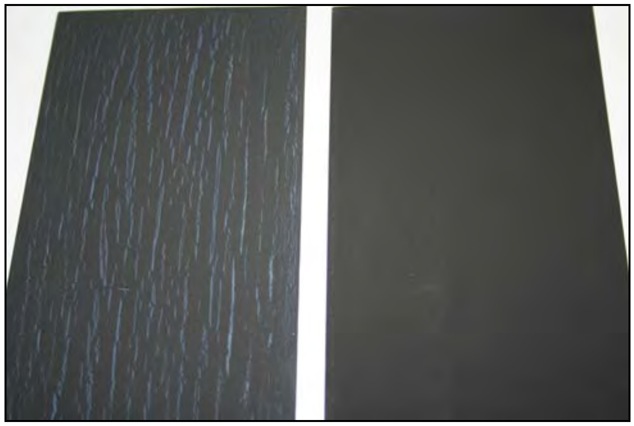

Figure 4. Chemlok 6411-LH adhesive applied at room temp (left) and panel preheated to 150 °F (right).

Although the adhesives were applied by brush, verification that the low-HAP thinned adhesives could also be sprayed onto panels and achieve a similar uniform coat as the baseline adhesive was conducted. The same steel panels (4 × 8 in) used for sample preparation were primed by brush application and allowed to dry for 24 h. The adhesive was then sprayed onto individual panels.

2.8.4 Rubber Compound Preparation for Vulcanization

Rubber formulation nos. 0064, 0135, 0149, 0235, and 5618 were provided by RRAD as samples of unvulcanized rubber commonly bonded to metal in the production of Army tank pads and road wheels. Prior to vulcanization, the rubber compounds are similar in appearance and texture to vulcanized rubber. However, vulcanized material is less tacky and has superior mechanical properties. Vulcanization is an irreversible chemical change (e.g., cross-linking) in which a rubber compound has an increase in elasticity, strength, stability, and chemical resistance over a greater range of temperatures (*23*). Molding/vulcanization parameters (temperature, pressure, and cure time) were experimentally determined through a combination of expertise and rheological testing conducted on each of the five rubber compounds. Each rubber compound was placed in a Flexsys Rheometer MDR 2000E with temperatures ranging between 220 and 320 °F. Pressure was applied to simulate common vulcanizing conditions, and the sample was oscillated to measure the torque generated while the rubber vulcanized vs. time. The rheology graphs produced showed a plateau of the torque when the rubber was vulcanized (figure 5). The time necessary for vulcanization to occur was determined from the plateau portion of the graph in figure 5. A supplementary 5 min was added to the molding time to accommodate the thickness of the mold (0.25 in). The initial temperature and pressure for the rheological tests were chosen based on common vulcanizing temperatures (240–320 °F) and then adjusted from the slope of the curves produced.

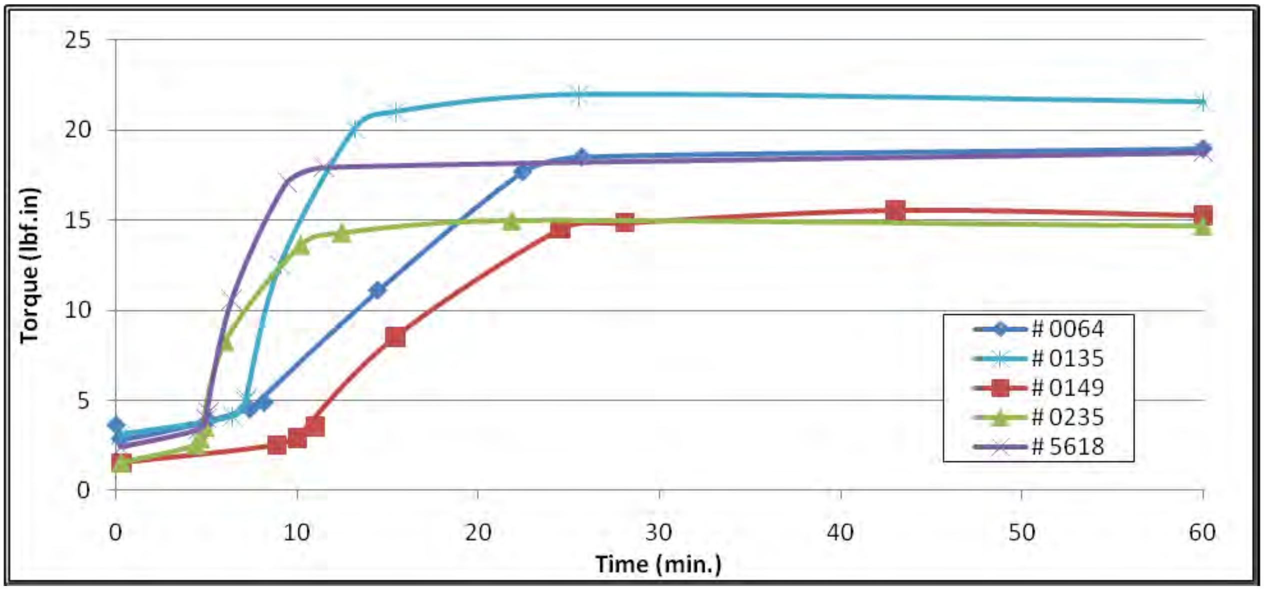

Figure 5. Rubber rheology curves performed at various temperatures.

2.8.5 Peel Assembly

The process of preparing the rubber compounds for molding and vulcanization started with an unvulcanized sample of each rubber compound that was inserted into a two-roll mill (8 inches in diameter) for mixing. The sample was reinserted to the rollers several times to improve dispersion (*24*). This mixing on the rollers was repeated 7 to 10 times to produce a thoroughly blended sheet of rubber ~0.125 in thick, which was then cut into strips (*24*). The strips were placed in a preheated mold (1 × 6 × 0.25 in) and folded over to a slightly higher thickness of 0.25 in to ensure that the rubber completely filled the mold when under pressure. Once a steel panel (prepared with primer and adhesive) was placed over the rubber and the top half of the mold was put in place, the mold was inserted into a PHI 50-ton manual hydraulic press with electric heated platens. These platens pressed against the molds and generated the heat needed for bonding. The molding pressure was increased to the predetermined value in two increments. The value of the pressure was chosen based on the maximum attainable pressure by the hydraulic press (500 psi) and is typically used in rubber molding.

In the first step, the pressure was removed briefly to release any air pockets from the mold. Next, the pressure was returned and increased until the predetermined pressure was achieved. After the sample was in the hydraulic press for the predetermined amount of time, the mold was removed from the press and allowed to cool to room temperature on the bench. Table 3 contains the molding parameters used to vulcanize the five rubber compounds in this experiment. The heat and pressure from the vulcanizing process applied to the RTMB assembly allowed the adhesives to simultaneously thermoset while the rubber vulcanized. The thermosetting of the adhesive along with vulcanization of the rubber are necessary to provide the high degree of bonding and adhesion strength between the rubber and the adhesive.

Table 3. Molding parameters.

Rubber Compound No.	Time (min.)	Temp. (°F)	Pressure (psi)
0064	26	300	500
0135	28	300	500
0149	16	280	500
0235	13	280	500
5618	12	280	500

After thermosetting of the adhesive-coated panels to the rubber compound was completed, the panels were cleared of excess rubber around the bonded sample (1- × 6-in strip). The outer edges of the rubber substrate (at the rubber-to-metal interface) were scored to ensure that the rubber would peel evenly across the width of the 1-in strip, thus reducing the possibility of edge effects during testing. Edge effect in the context of this test method is defined as the error arising from inconsistencies of the sample bonding area at the rubber-to-metal interface. Controlling this variation allows a more meaningful comparison between sample test data sets.

2.8.6 Peel Test Method

RTMB adhesion strength was tested using ASTM D 429 03, *Standard Test Methods for Rubber Property – Adhesion to Rigid Substrates*, Method B-90° Stripping Test-Rubber Part Assembled to One Metal Plate. The method states the following (*25*):

> This test is intended for determining the adhesive strength of rubber-to-metal bonding agents. The results are obtained by measuring the force necessary to separate a rubber from a metal surface. The data obtained indicate the strength of adhesion along a line across the width of the rubber strip being separated from a metal plate at a 90° angle. The test provides valuable data for development and control of rubber compounds and test methods of bonding, and it also serves as a screening test for the evaluation of various bonding agents or techniques, or both.

ASTM D 429 03 was used as a guideline for this test method to determine the peel strengths of vulcanized rubber-to-metal bonding. Peel strength is the average load per unit width of bond line required to progressively separate a flexible member from a rigid member or another flexible member (*25*).

Testing was conducted on an Instron model 1123, a power-driven machine that was capable of uniform expansion between the grips. The metal panel was placed onto the horizontal fixture,and the released portion of the rubber substrate (~2 in long), or tab, was inserted into the top hydraulic grip of the Instron machine for a 90° peel adhesion test (figure 6).

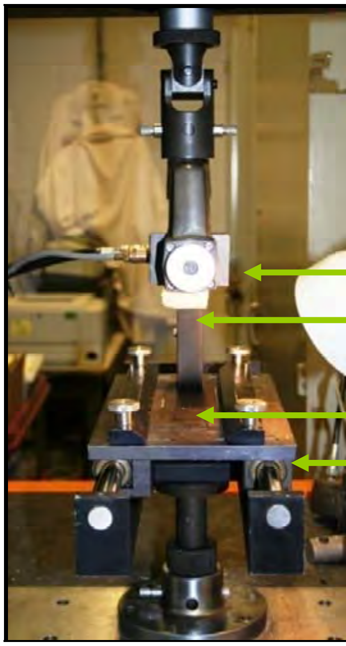

Figure 6. The 90° peel adhesion test setup.

A hydraulic clamp is required for use as a grip because as the rubber is pulled, it elongates and thins. The hydraulic clamp provides constant pressure to keep the rubber substrate in the grip. The bottom grip of the Instron was a table mounted on linear bearings (figure 6). The linear bearings of the table allowed forward movement, while the rubber strip was peeled from the metal panel and remained perpendicular to the panel. It was important to keep the peel at an angle of 90° because the loading data collected would have been inconsistent if the angle of peel changed. Clamps on the table affixed the steel panel of the RTMB assembly in the bottom Instron grip (figure 6). Test specimens consisted of 1-in-wide × 6-in-long × 0.25-in-thick rubber strips adhered to a steel panel 4 in wide × 8 in long × 0.0625 in thick. An area of ~1 × 4 in of the rubber strip was bonded to the steel panel. The head of the machine was set to travel at a rate of 2 ± 0.2 in/min. The test machine digitally measured the load applied and the extension to the rubber strip during the 90° peel.

3. Results and Discussion

3.1 Solvent Miscibility

According to the solvent miscibility chart (figure 3) (*21*), toluene and xylene are miscible with non-HAP methyl acetate, MEK, acetone, heptanone, tert-butyl acetate, tetrahydrofuran (THF), isopropyl alcohol (IPA), and ethanol. Water, the ideal solvent in terms of environmental regulations, is not miscible and thus was eliminated from further study. In addition to the designation of HAP-free, methyl acetate, acetone, and tert-butyl acetate are also VOC exempt (meaning that each is a volatile organic compound but was given a regulatory exemption by the EPA).

Vials of the mixtures were prepared for verification of miscibility with Chemlok 252X. Miscible samples of adhesive and thinner were homogenous mixtures (figure 7, left). The samples containing IPA and ethanol failed the miscibility test. The adhesive in these samples solidified, and the solution turned an amber color after sitting on the bench overnight (figure 7, right). IPA and ethanol were eliminated from the study after immiscibility with Chemlok 252X was determined. Heptanone and THF formed a white precipitate in the bottom of the vials within 24 h after preparation and thus were eliminated from the study. According to visual inspection and physical resistance when mixing the diluted samples, methyl acetate, MEK, and acetone had a similar viscosity to the control dilutions with toluene and xylene. Heptanone, tert-butyl acetate, THF, and Oxsol 100 had slightly higher viscosities, as compared to the controls.

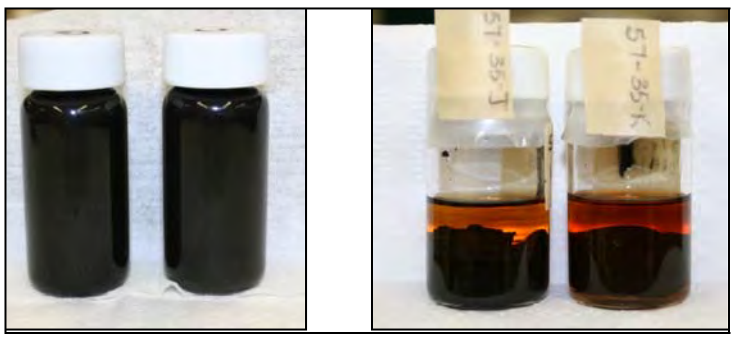

Figure 7. Miscible (left) and imiscible (right) samples.

Oxsol 100, a halogenated solvent, incurs a greater expense to the user than the other solvents used in this research. Therefore, Oxsol 100 was removed from further testing.

3.2 Dry Time

Dry time of the baseline adhesives was an important performance parameter to replicate with any alternative thinner chosen. A similar or shorter dry time would not require current depot operating procedures to be altered, whereas significantly longer dry times would require changes to procedures and would be considered unacceptable. Table 4 shows the vapor pressures of the solvents used in this study. Vapor pressures of various organic solvents were considered to determine how using a different thinner might change the dry time of the adhesive. Similar vapor pressures correlate to similar dry times. Heptanone and Oxsol* 100 (parachlorobenzotrifluoride [*26*]) are the only thinners in the test series that had a lower vapor pressure than the controls (*27*). Thus, all other alternative thinners in the test series were expected to produce adhesive mixtures that dried similarly to the baseline thinners.

*Oxsol is a registered trademark of Occidental Chemical Corp.

Table 4. Solvent vapor pressure (*27*).

Solvent	Vapor Pressure (kPa @ 25 °C)
Heptanone	0.49
Oxsol 100	0.71
Xylene	1.07
Special naphtholite 66/3	1.51 (@ 20 °C)
Toluene	3.79
Isopropyl alcohol (IPA)	6.10
Tert-butyl acetate	6.30
Ethanol	7.90
MEK	12.60
Tetrohydrofuran (THF)	21.60
Methyl acetate	28.80
Acetone	30.80

Dry times were determined for the neat adhesives and the adhesives thinned with toluene, xylene, methyl acetate, MEK, acetone, tert-butyl acetate, and naphtholite 66/3 (figure 8). Figure 9 compares both the neat and thinned with the down-selected solvent dry times of Chemlok 252X and Thixon 532-EF, Chemlok 6254-LH, and Chemlok 6411-LH. All of the Chemlok neat adhesives dried slower than the thinned adhesives. However, the Thixon neat adhesive dried faster than the Thixon diluted counterparts. The main carrier solvent in Chemlok 252X is xylene (65%), which has a vapor pressure of 1.07 kPa at 25 °C. The main carrier solvent in Thixon 532-EF is toluene (~60%), which has a vapor pressure of 3.79 kPa at 25 °C (table 4). The significantly lower vapor pressure of xylene could have contributed to the longer dry time of Chemlok 252X neat. The dilution ratio for Chemlok 252X is 60/40 by weight (table 2), which may account for the similarity in dry time of the xylene thinned sample compared to the neat sample. The rest of the Chemlok 252X series had a dry time between 12 and 18 min. The dilution ratio for Thixon 532-EF is 75/25 by weight. The thinned samples of Thixon 532-EF had a dry time between 18 and 23 min. The thinned Chemlok low-HAP adhesives (6254-LH and 6411-LH) with a dilution ratio of 80/20 by weight and 75/25 by weight, respectively, had a dry time between 20 and 23 min, which was similar to the Thixon series.

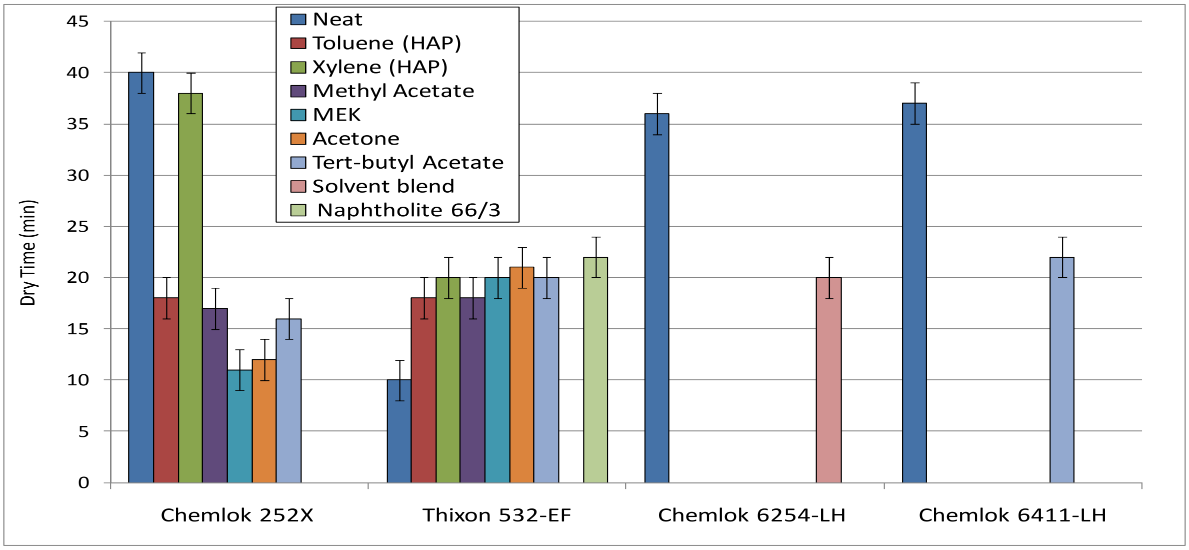

Figure 8. Dry times of adhesive dilutions.

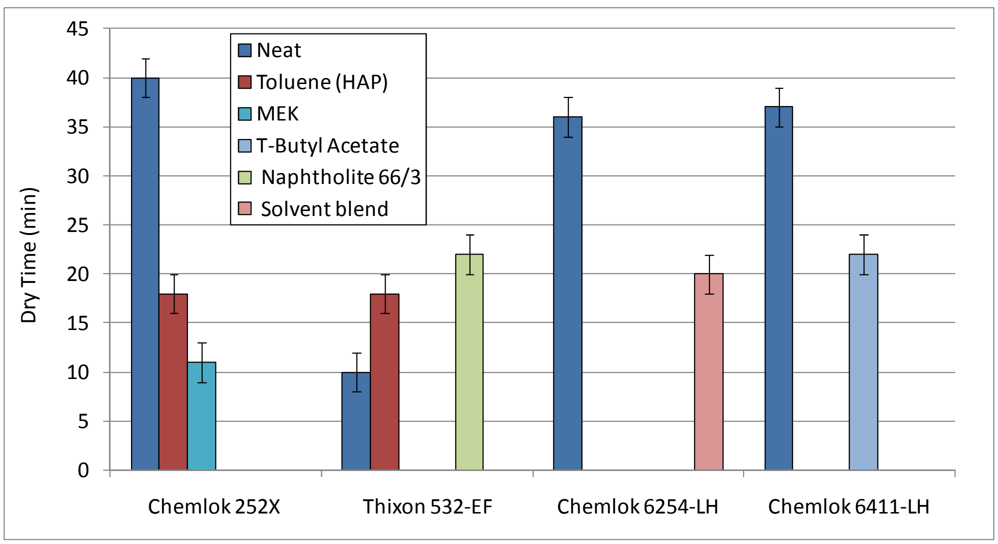

Figure 9. Dry time comparison of down-selected adhesive/thinner combinations.

3.3 Nonvolatile Content

Nonvolatile content analysis allowed for verification of the values given by the manufacturers (*6*, *8*, *11*, *23*), and a comparison of the solids remaining after thinning would show whether the low-HAP thinned adhesive would be similar to the baseline (HAP-thinned adhesive). Similarity of dried adhesives may equate to similar performance qualities. For an alternative adhesive system, significantly different nonvolatile content may result in a change in depot operation procedures and would have to be noted. Figure 10 is an example of the dried adhesive in an aluminum pan that was used to calculate the nonvolatile content. The percent of nonvolatiles was calculated from the following equation:

$$\% \text{ solids} = \frac{(w_3 - w_1)}{(w_2 - w_1)} \times 100, \quad (1)$$

where

w_1 = weight of empty Al pan,

w_2 = weight of pan and wet sample, and

w_3 = weight of pan and dry sample.

Figure 10. Dried nonvolatile mass sample pan.

In table 5 the non-volatile mass of each neat adhesive was verified with the theoretical mass from the respective MSDS (*7, 9, 12*). The experimental results were very close to those of the theoretical results. In addition, nonvolatile mass was similar to the values for the baseline adhesives. Thus, the nonvolatile mass should not pose any processing issues for Army depot work.

Table 5. Theoretical vs. actual nonvolatile mass.

Adhesive Name	Theoretical Nonvolatile Mass (%)	Actual Nonvolatile Mass (%)
Chemlok 252X (baseline)	22–24	22
Thixon 532-EF (baseline)	25	26
Chemlok 6254-LH (alternative)	23–25	23
Chemlok 6411-LH (alternative)	22–24	22

3.4 Thermogravimetric Analysis (TGA)

Knowing the percentage of ash in the nonvolatile portion of the formulation can allow an estimation of the pigment-to-binder ratio. The percent mass remaining at the end of the TGA experiment is the residual inorganic ash content. The organic resin, which acts as the binder, is burned off during TGA, and the remaining ash comprises the pigments, extenders, and other fillers in the formula. P/B can be a useful parameter for formula comparison. Adhesive formulations with similar residual inorganic ash content compared to the baseline formulations would be expected to have similar characteristics when dried. For alternate thinners, significant differences would raise a warning flag regarding the use of that thinner. For a new adhesive system, significantly different P/B may result in a change in depot operation procedures and would have to be noted. In addition, significant mass loss at low temperatures (below 150 °C) would indicate entrapped solvent within the dried adhesive. Entrapped solvent would result in reduced adhesion strength and would not be acceptable for these applications.

The pans with dried adhesive that were used to measure the nonvolatile mass were used to run TGA. Figure 11 shows the TGA results of Thixon 532-EF neat and thinned with acetone, heptanone, MEK, methyl acetate, tert-butyl acetate, toluene (baseline thinner), and xylene (baseline thinner). Thixon 532-EF samples (thinned) plateaued at a maximum loss of mass percentage at 550–610 °C, with 4%–5% remaining. The mass percentage remaining was the inorganic pigment, which was used to calculate the mass percent binder (resin). Table 6 is the total calculated content of the formulation for neat adhesives in the test series. From the high-temperature plateaus on the TGA curves produced, Thixon 532-EF neat adhesives' P/B was similar to the thinned adhesives' P/B (figure 11). Therefore, the addition of the alternative thinners to the neat adhesive did not cause a fundamental change in the performance properties.

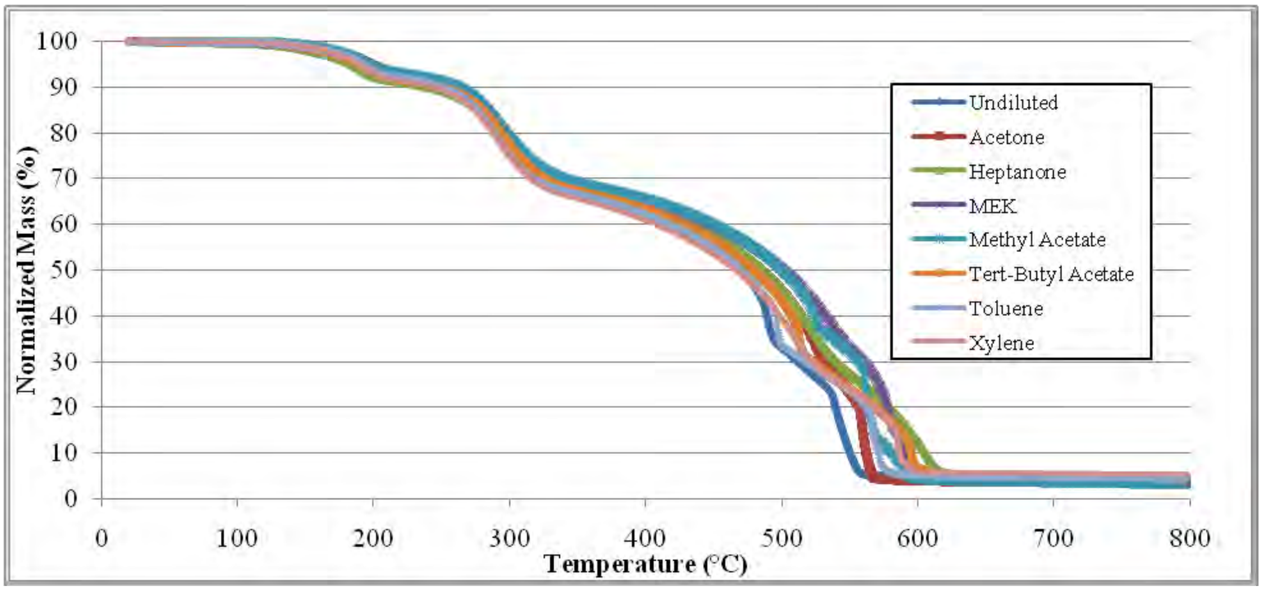

Figure 11. TGA results for Thixon 532-EF.

Table 6. Calculated composition of adhesive formulations.

Components	Chemlok 252X (% by wt.)	Thixon 532-EF (% by wt.)	Chemlok 6254LH (% by wt.)
Volatiles	77 ± 2	75 ± 2	76 ± 2
Resin	20 ± 2	23 ± 2	23 ± 2
Pigment	3 ± 1	2 ± 1	1 ± 1

Figure 12 shows the results of Chemlok 6254LH neat and thinned (50/50 solvent blend) compared to Chemlok 252X neat and Thixon 532-EF neat. The Chemlok 6254LH P/B ratio is very similar to the Thixon 532-EF, with 3%–5% mass percentage remaining. While Chemlok 252X appears to have significantly higher residual mass at higher temperature (pigment) relative to the other adhesives, this difference is magnified due to the scale of the TGA graph (i.e., 100% sample weight represents 23% of the total Chemlok 252X formula). After multiplying the residual weight (14%) on the TGA graph by the wt. % of solids in the formula, we determined the pigment content of the total formula (table 6) showing similar volatile and resin contents among the different adhesives. No adhesives or thinners showed low-decomposition temperatures. Thus, there is no entrapped solvent in any of these adhesives.

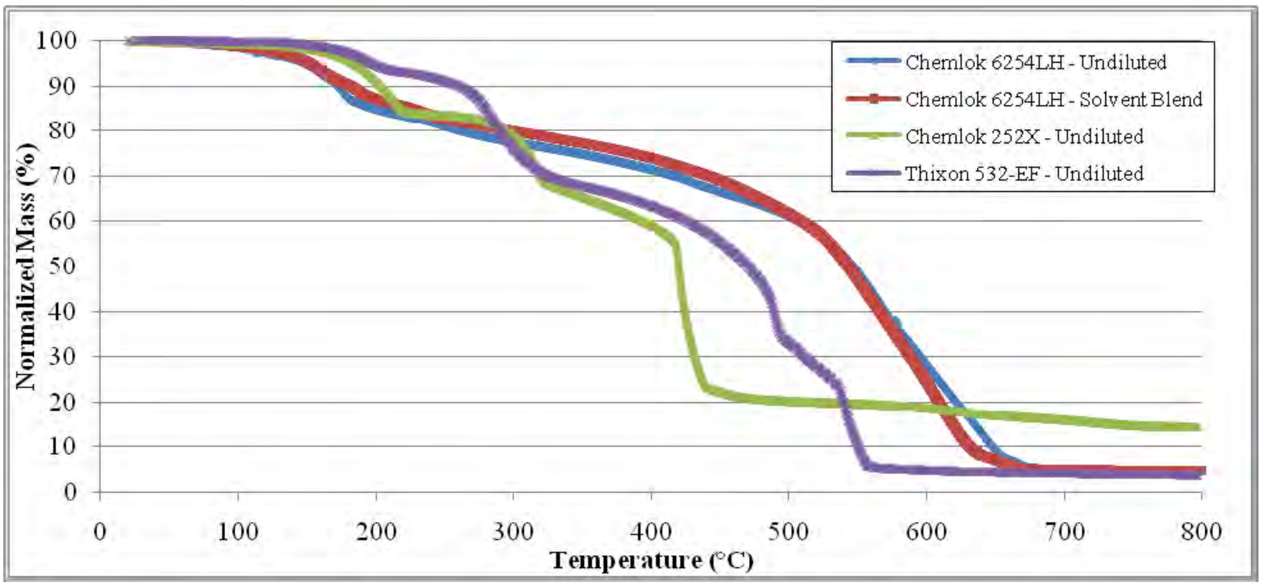

Figure 12. TGA results of various adhesives "dried."

3.5 Differential Scanning Calorimetry (DSC)

TA Instruments Data Analysis software can be used to calculate the integral of the peaks on the graphs produced from DSC. The integral of the exothermic peak was the heat of cure, or extent of cure. During the vulcanization process of the rubber substrate, the adhesives experience temperatures up to 149 °C (300 °F). The DSC experiments were ramped to 250 °C, past the established temperature for vulcanization (table 3), to observe any further curing and gauge the extent of total cure. According to the graphs in figure 13, the cure of each adhesive occurred at a higher temperature than was determined for the vulcanization process. Chemlok 252X with a toluene thinner (baseline adhesive solution) had an exothermic peak value at 203 °C (397.4 °F). Chemlok 252X thinned with acetone (low-HAP adhesive solution) had an exothermic peak value at 203 °C (397.4 °F). Chemlok 6254LH with the 50/50 solvent blend (low-HAP adhesive solution) had an exothermic peak value at 194 °C (381.2 °F). The cure (thermosetting) of the

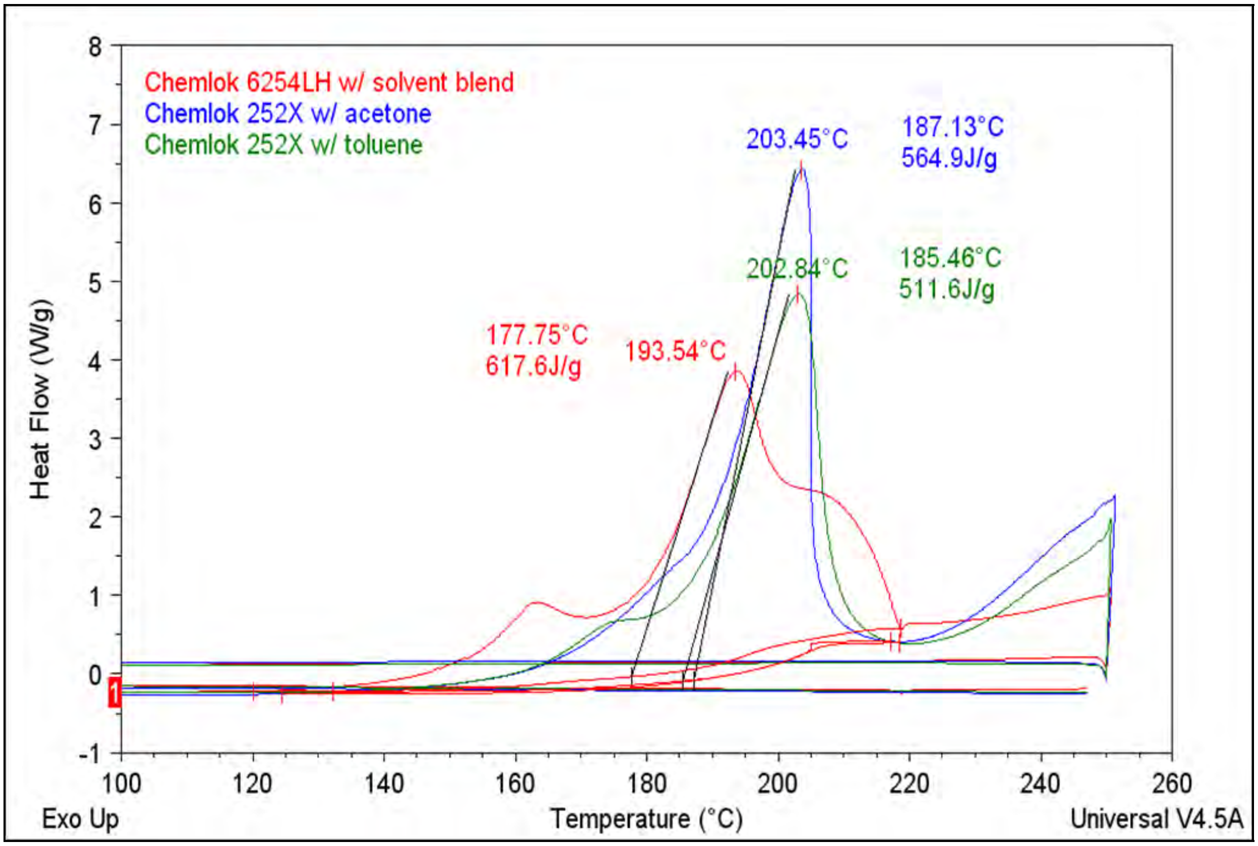

Figure 13. DSC results for baseline and alternative adhesive mixtures.

adhesives occurred at a lower temperature than measured by the DSC due to the pressure applied (500 psi) during the vulcanization process. Therefore, the extent of cure cannot be accurately quantified with the DSC data gathered by the current available means, and the data collected can be used only to qualitatively compare the low-HAP to baseline adhesive solutions. Nonetheless, the results indicate that the particular thinner has no effect on the cure temperature, and Chemlok 6254-LH has a similar, although slightly lower, cure temperature than the baseline Chemlok 252X.

3.6 Rheology

These samples were expected to act as Newtonian fluids having the same viscosity regardless of shear rate and therefore would not be shear-thinning or thixotropic, considering their very low viscosities. In figure 14, the viscosities of Chemlok 252X (neat and thinned), Thixon 532-EF (neat), and Chemlok 6254-LH (neat and thinned) were plotted vs. shear rate on a log/log scale. Chemlok 252X neat and Chemlok 6254-LH neat were very similar with the highest of the viscosities. Thixon 532-EF neat was higher than all of the Chemlok 252X thinned adhesive solutions but lower than the Chemlok 252X neat and Chemlok 6254-LH neat. All of the Chemlok 252X thinned adhesive solutions were more than an order of magnitude lower than the neat Chemlok 252X as expected. The lower viscosity was attributed to the 40 wt. % thinner,

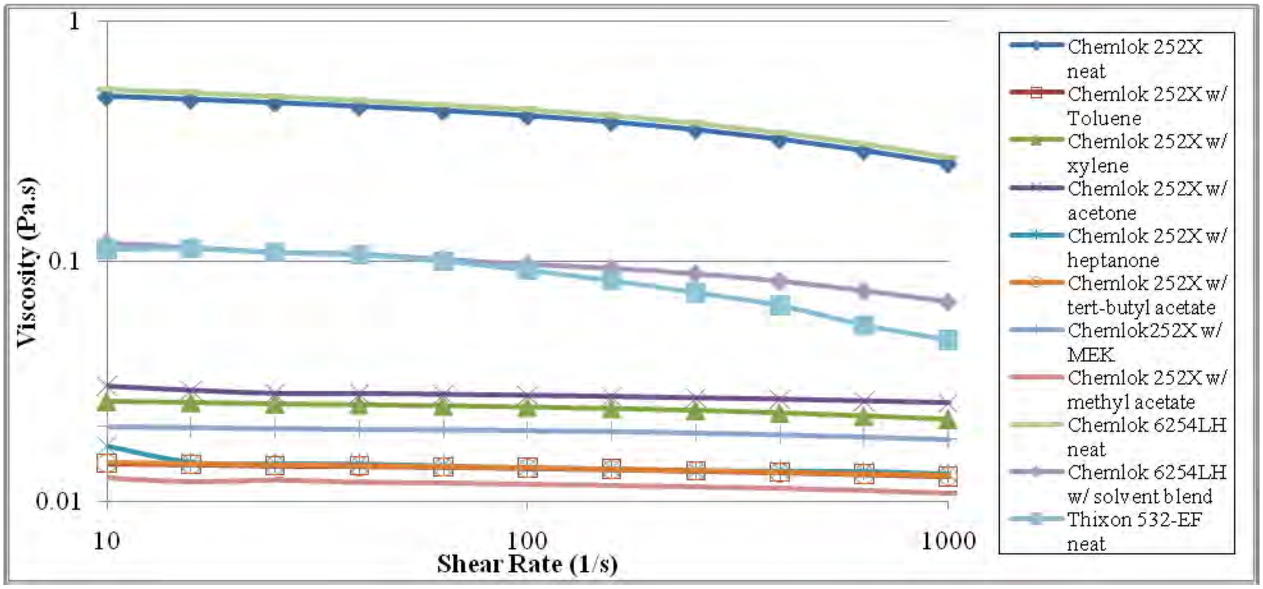

Figure 14. Rheological data for adhesive solutions.

while the other 60 wt. % was neat adhesive. The Chemlok 6254-LH thinned adhesive solution was slightly higher in viscosity than Chemlok 252X thinned and Thixon 532-EF neat solutions because only 20 wt. % was thinner, and the remaining 80 wt. % was neat adhesive, while the baselines used significantly more thinner as recommended by the TDS (*6*, *8*, *11*). The results from the rheological studies demonstrated the similarity in viscosity of the baseline to alternative adhesive solutions. Figure 14 illustrates that the neat adhesives have slight shear-thinning character. Fortunately, the extent and onset of shear thinning is similar. None of the thinned adhesives showed any shear-thinning character in the measured shear rates. There was no measureable thixotropic character for any of the samples.

3.7 Adhesive and Primer Application Findings

All of the adhesives in this test series (except for Chemlok 6411-LH) were successfully applied by spray at room temperature (figure 15). Furthermore, at the time this research was completed, Chemlok 6411-LH adhesive was still experimental and not commercially available. The manufacturer suggested using Chemlok 6411-LH as a low-HAP alternative because Chemlok 6254-LH was discontinued. The manufacturer-prepared panels with Chemlok 205-LH primer and Chemlok 6411-LH adhesive did have a uniform film (figure 4, right). However, the process of preheating panels before spray application of primer and adhesive could be problematic for RRAD implementation. The RRAD process does not allow for preheating of the metal prior to the application of primer or adhesive. Thus “resolvation” of the primer would occur, leaving an irregular film formation of the adhesive and hindering the bonding process (figure 4, left).

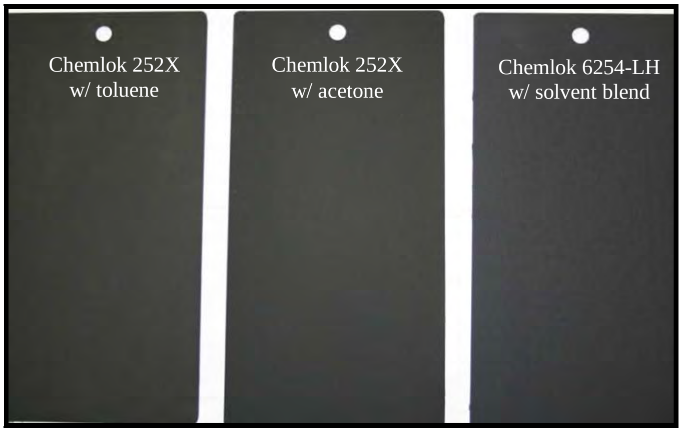

Figure 15. Spray application.

3.8 Peel Adhesion Testing

Figure 16 shows a photograph of the rubber substrate pulled upward from the steel panel at a constant 90° angle. The rubber is elastomeric, which is defined as a material that returns rapidly to approximately the initial dimensions and shape after substantial deformation by a weak stress and release of the stress (*23*). Therefore, the rubber elongates substantially compared to the original length while being peeled from the metal substrate but returns to the original dimensions after the rubber is completely peeled from the panel and all stress is alleviated.

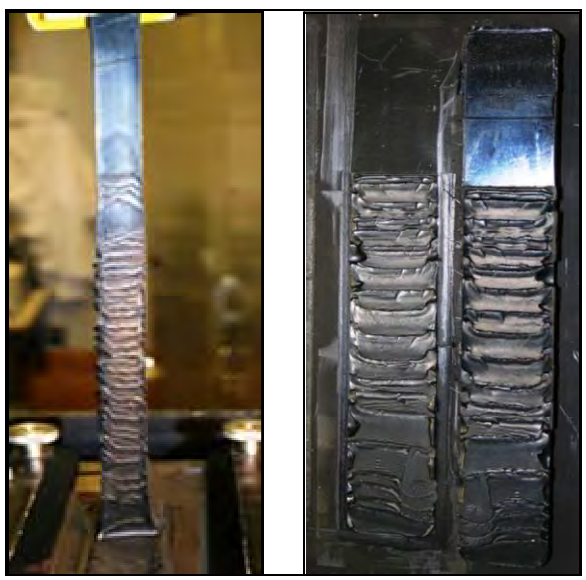

Figure 16. Elongation of rubber substrate during peel test (left) and after peel (right).

If the rubber substrate bonded to the panel started to peel unevenly, a knife blade was used to cut the rubber and correct the symmetry at the rubber-to-metal interface during the peel test. In figure 17, the left side of the interface between the rubber and metal substrates was not symmetrical with the right side. A crescent-shaped bond line is visible. All efforts were made to

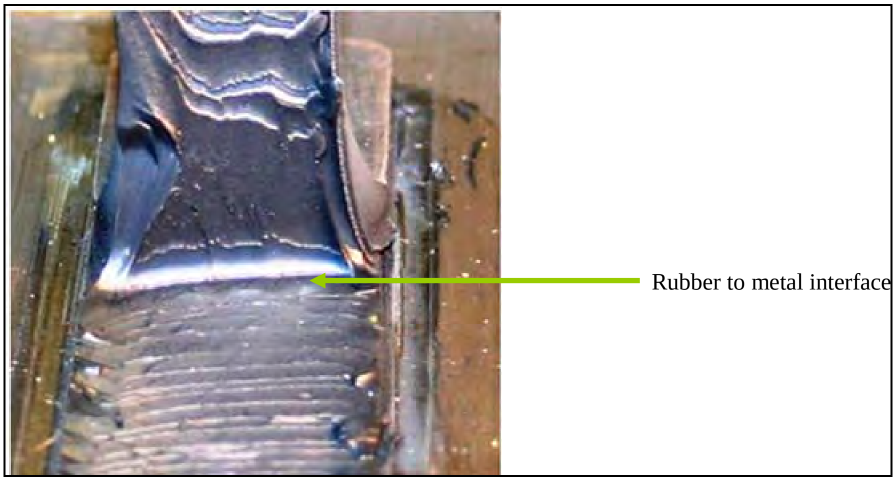

Figure 17. Asymmetrical peel.

maintain a straight bond line that remained perpendicular to the long edges of the substrates. Allowing the asymmetrical peel to continue would have skewed the peel results. The peel must maintain the 90° angle at the rubber-to-metal interface for the duration of the test. Once the rubber strip was completely peeled from the metal panel, the test was complete.

Figure 18 is representative of a typical graph obtained from the 90° peel adhesion testing. The graph highlighted five of the highest peaks and five of the lowest troughs from the plateau portion of the graph. The point in which the failure occurred was recorded to evaluate the adhesion performance of the metal to primer, primer to adhesive, and adhesive to rubber. The type of failure for each assembly was determined by visual inspection after the peel test was completed. The types of failure that could occur were within the rubber substrate (R-failure), at the interface of the rubber to the adhesive (RC-failure), at the interface between the primer and the adhesive (CP-failure), or between the metal and primer (M-failure) (*25*).

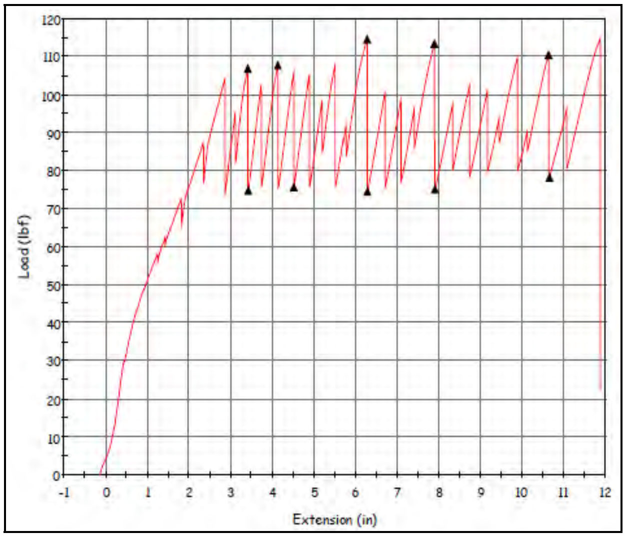

Figure 18. Instron graph produced from 90° peel adhesion test.

All of the failures during the 90° peel adhesion testing were categorized as R-failures. This implies that the adhesive bond was capable of withstanding loads greater than the limit of the rubber. Adhesive with a layer of rubber substrate remained bonded to the metal substrate (figure 17). Each rubber compound tested left similar amounts of bonded rubber regardless of the adhesive or thinner used. Samples with good adhesion would stretch and tear the rubber in small increments, leaving a serrated appearance to the bonded side of the rubber strip shown in sample A of figure 19. Moderate adhesion had a less jagged appearance and a steadier tear. Samples with poor adhesion generally exhibited a smooth peel but still "R-failure" with very little elongation, shown in sample B of figure 19. The smooth peel may also indicate a vulcanizing/molding process issue rather than an adhesion issue. Due to the characteristic trends observed for each rubber compound, regardless of adhesive, the peel results for all adhesives were grouped by rubber compound.

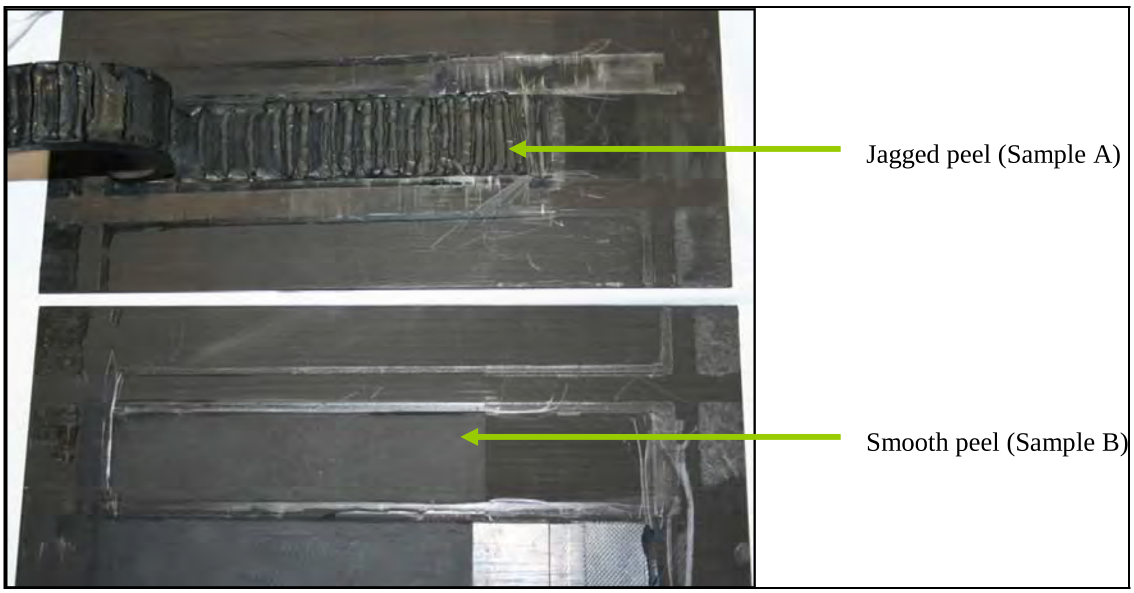

Figure 19. Test panels after 90° peel adhesion testing.

Due to the labor-intensive nature of sample preparation for peel testing, toluene was used as the sole baseline thinner in order to narrow the test series. Xylene (a.k.a. dimethyl benzene) is chemically similar to toluene (a.k.a. methyl benzene). This is also supported on the TDS, which suggests either toluene or xylene can be used to dilute the adhesive (*6, 11*). Therefore, toluene was deemed solely sufficient to represent the baseline thinners. For adhesives thinned with either methyl acetate or tert-butyl acetate, some of the rubber strips instantly snapped, and the samples could not be restarted or pulled long enough to obtain results. The vulcanized rubber seemed to become brittle after molding to the metal substrate using adhesives thinned with either methyl acetate or tert-butyl acetate and resulted in a peel similar to that of figure 20.

Figure 20. Peel sample with brittle rubber substrate.

Except for the acetate thinners used, we found that adhesive performance depended more on the rubber compound used in the bonding process than the thinner used for applying the adhesive. Figure 21 is a compilation side-by-side comparison of the average maximum 90° peel test results. The values for each bar were the average peel results per adhesive mixture and rubber compound.

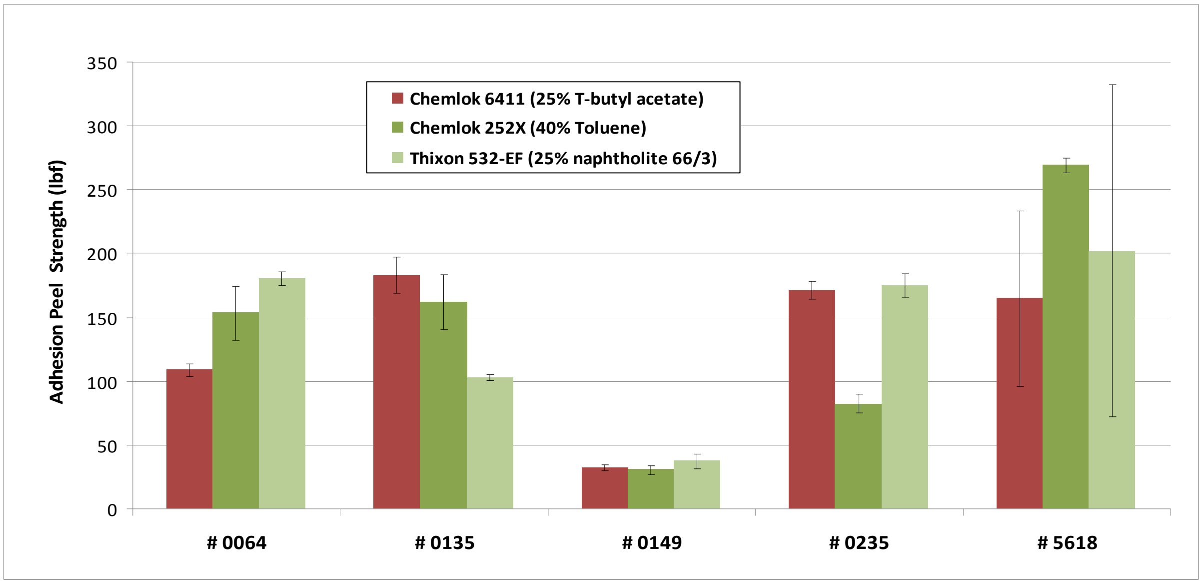

Figure 21. Comparison of adhesion strength after 90° peel testing on selected adhesives for the various rubber compounds.

The adhesives tested with rubber compound no. 0149 exhibited very low peel strength, very little elongation, and a smooth peel at the adhesive/rubber interface. There are several possibilities to explain the overall low adhesion strength of the no. 0149 rubber compound—for instance, the age of the rubber or uncontrolled exposure to heat and humidity—but the most probable is the molding process. More specifically, RRAD's production process is difficult to duplicate in a laboratory setting. This issue was known and discussed at the start of this research. Compound nos. 0064, 0135, and 0235 had comparable adhesion strengths. No. 5618 clearly had the highest peel strengths for almost every adhesive/thinner/primer combination (table 7). This is likely because this rubber was formulated to have high durability.

Table 7. Adhesive/primer performance compared to baseline.

Adhesive/Thinner	Average Peel Strength (lbf) and STD	Rubber No. 0064	Rubber No. 0135	Rubber No. 0149	Rubber No. 0235	Rubber No. 5618
Chemlok 252X baseline (40% toluene)	Average	153	162	30	82	269
	STD	21	22	4	7	6
Thixon 532-EF baseline (25% toluene)	Average	121	91	63	174	48
	STD	18	2	36	1	6
Chemlok 6254-LH (20% blend)	Average	165	133	17	84	288
	STD	18	49	1	3	9
Chemlok 6411 (25% t-butyl acetate)	Average	109	183	32	171	165
	STD	5	14	2	7	69
Chemlok 252X (40% acetone)	Average	103	85	38	75	219
	STD	4	4	3	7	63
Chemlok 252X (40% MEK)	Average	173	86	31	81	190
	STD	0.30	3	5	5	121
Chemlok 252X (neat)	Average	157	184	31	132	208
	STD	47	7	3	15	91
Chemlok 6254-LH (neat)	Average	16	128	36	160	244
	STD	0.9	9	13	11	61
Thixon 532-EF (neat)	Average	112	180	40	91	17
	STD	10	12	5	2	6
Thixon 532-EF (25% acetone)	Average	104	81	98	94	281
	STD	2	2	0	1	4
Thixon 532-EF (25% MEK)	Average	152	85	39	174	15
	STD	39	0.9	3	6	6
Thixon 532-EF (25% naphtholite 66/3)	Average	181	103	37	175	202
	STD	5	2	6	10	130
Thixon 532-EF (25% toluene) Megum 3911 primer	Average	147	90	169	74	275
	STD	35	7	26	8	8

Color Code:	
Green: sample performed better than both baseline adhesives.	
Blue: sample performed better than 1 baseline adhesive.	
Yellow: sample performed worse than lowest baseline adhesive.	
Red: sample performed very poorly.	

The adhesives tested with rubber compound no. 0064 exhibited moderate peel strengths with less jagged tearing (table 7). The baseline adhesive Chemlok 252X with 40% toluene had a peel strength of ~153 lbf. Chemlok 252X with 40% MEK (173 lbf), Thixon 532-EF with 25% naphtholite 66/3 (180 lbf), and Chemlok 6254-LH with 20% solvent blend (165 lbf) performed slightly better than the baseline. Thixon 532-EF (baseline) with 25% toluene had a peel strength of 121 lbf. Chemlok 252X with 40% acetone (103 lbf), Thixon 532-EF with 25% acetone (104 lbf), and Chemlok 6411-LH were slightly lower than the baseline peel strength.

The adhesives tested with rubber compound no. 0135 exhibited moderate peel strengths with less jagged tearing (table 7). The baseline adhesive, Chemlok 252X with 40% toluene, had the peel strength of ~162 lbf. Chemlok 6254-LH with a 20% solvent blend (133 lbf) performed slightly lower than the baseline. Chemlok 252X with 40% acetone (85 lbf), Chemlok 252X with 40% MEK (86 lbf), Thixon 532-EF with 25% toluene (91 lbf), Thixon 532-EF with 25% acetone (81 lbf), Thixon 532-EF with 25% MEK (85 lbf), Thixon-EF with 25% naphtholite 66/3 (103 lbf), Thixon–EF with Megum 3911 primer (90 lbf) had peel strengths significantly lower than the baseline adhesive, while being close in magnitude to each other. Chemlok 6411-LH adhesive with 25% tert-butyl acetate exhibited sporadic brittleness but had the highest peel strength (182 lbf).

Rubber compounds no. 0149 resulted in poor peel strengths for all adhesives (figure 22, table 7). The baseline adhesive, Chemlok 252X with 40% toluene, had peel adhesion strength of ~30 lbf. Chemlok 252X with 40% acetone (38 lbf), Chemlok 252X with 40% MEK (31 lbf), and Thixon 532-EF with MEK (39 lbf) performed similarly to the baseline. Chemlok 6254-LH with a 20% solvent blend (17 lbf) had the lowest peel strength of all adhesive combinations tested with this rubber compound. Thixon 532- EF with Megum 3911 primer had the highest peel strength (169 lbf) for this series.

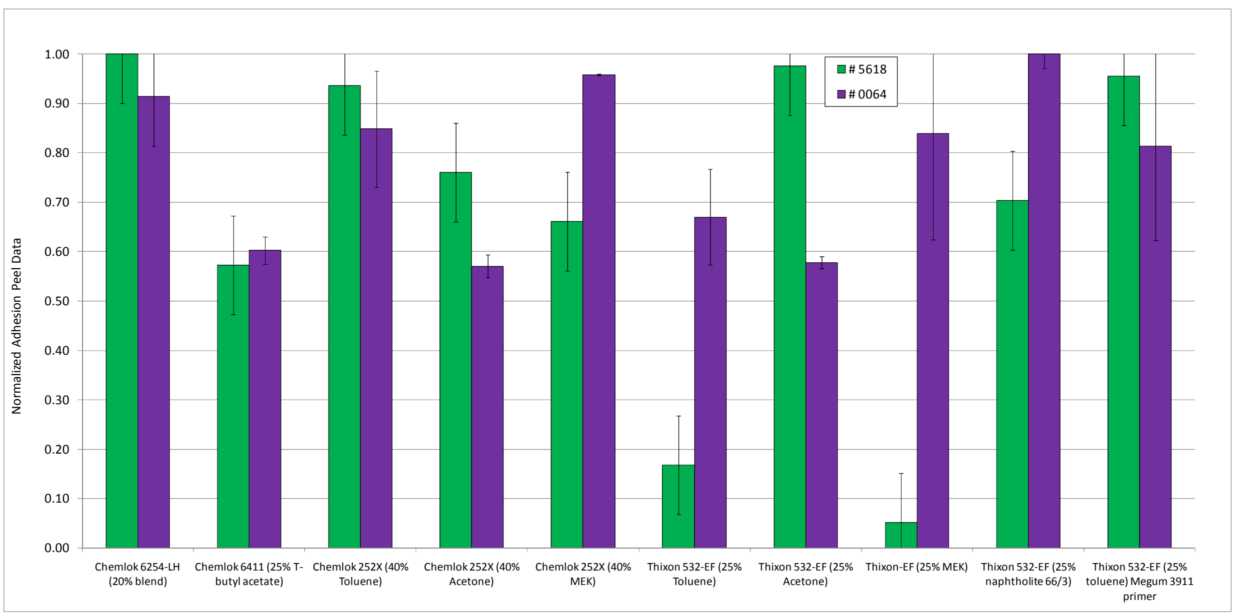

Figure 22. Comparison of normalized adhesion strength after 90° peel testing for selected rubber compounds.

The adhesives tested with rubber compound no. 0235 exhibited moderate peel strength with less jagged tearing (table 7). The baseline adhesive, Chemlok 252X with 40% toluene, had the peel strength of ~80 lbf. Chemlok 6254-LH with a 20% solvent blend (84 lbf), Chemlok 252X with 40% acetone (75 lbf), Thixon 532-EF with 25 % acetone (94 lbf), and Chemlok 252X with 40% MEK (81 lbf) performed similar to the baseline. The baseline Thixon 532-EF with 25% toluene had the peel strength of 173 lbf. Thixon 532-EF with naphtholite 66/3 (175 lbf), Thixon 532-EF with 25% MEK (174 lbf), and Chemlok 6411-LH with 25% tert-butyl acetate (171 lbf) exhibited a peel strength significantly higher than the Chemlok 252X baseline but similar to the Thixon 532-EF baseline.

The adhesives tested with rubber compound no. 5618 exhibited mostly high peel strengths and very jagged tears (table 7, figure 22). The baseline adhesive, Chemlok 252X with 40% toluene, had the peel strength of ~269 lbf. Chemlok 6254-LH with a 20% solvent blend (280 lbf), Thixon 532-EF with Megum 3911 primer (274 lbf), Chemlok 252X with 40% acetone (254 lbf), and Thixon 532-EF with 25% acetone (281 lbf) performed similar to the baseline adhesive. Chemlok 252X with 40% MEK (190 lbf) performed lower than the baseline. Thixon 532-EF with 25% toluene (48 lbf) and Thixon 532-EF with 25% MEK (15 lbf) had a peel strength significantly lower than the baseline.

From figure 22 we can make a few more observations of note. Most adhesives perform well on different substrates. However, Thixon 532/EF using toluene and MEK as thinners did not perform consistently from rubber to rubber. Despite showing this for only two rubbers, this general trend was found for all rubber compounds.

Table 7 allows for a measure of how well a given adhesive performs across the five rubbers by examining the color. Green coloration indicates the best performance, blue indicates better performing than one baseline, yellow indicates a slightly worse performance than the lower-performing baseline, and red indicates poor performance. Of the thinned adhesives, only Thixon 532-EF (25% naphtholite 66/3) did not have any yellow or red color, while Chemlok 6411 (25% t-butyl acetate) had only a single yellow color.

To help determine other good performing adhesives, we devised a rating system to assess the overall performance on all rubbers of a given adhesive. The following equation was used to determine the average normalized strength of a given adhesive, $\sigma_{normalized}^{average}$:

$$\sigma_{normalized}^{average} = \frac{1}{5} \sum_{rubber=i}^{n} \sigma_i / \sigma_i^{\max} \qquad (2)$$

The factor of 5 is to account for the five rubber compounds. σ_i is the peel strength for a given adhesive/rubber combination, and σ_i(max) is the highest adhesive strength for a given rubber. Figure 23 shows the overall performance ranking of adhesive strength for each adhesive/thinner dilution in the test series compared to the two baselines. The best-performing adhesive was Thixon 532-EF with toluene and Megum 3911 primer, followed by Thixon 532-EF/naphtholite and Thixon P-11 primer. Three adhesive/thinner dilutions performed better than the Chemlok 252X baseline, and six adhesive/thinner dilutions performed better than the Thixon 532-EF baseline. Only Thixon-EF with 25% MEK and Chemlok 252X with 40% acetone performed worse than both baselines.

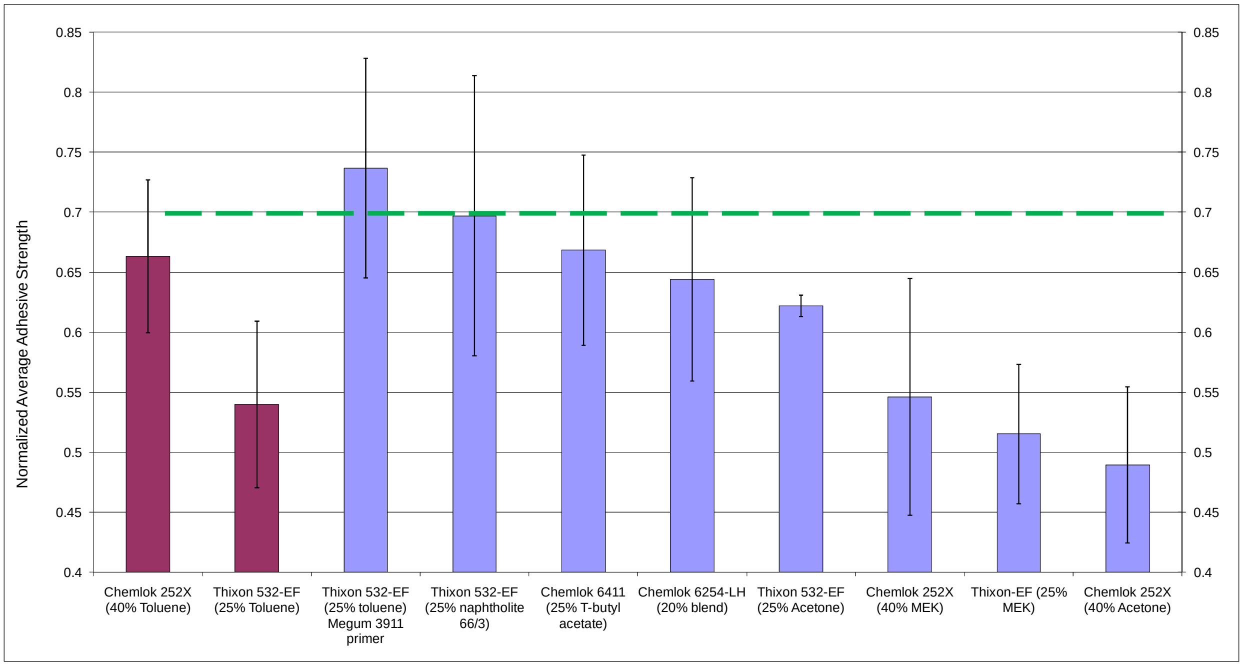

Figure 23. Ranking of normalized average adhesion strength.

Figure 24 illustrates the use of a point system to graph the adhesive performance compared to the baseline. An adhesive that performed better than 1 standard deviation of both baselines received four points. An adhesive that performed within 1 standard deviation of both baselines received three points. An adhesive that performed better than 1 standard deviation of one baseline (but worse than the other baseline) received two points. An adhesive that performed within 1 standard deviation of the lower-performing baseline received one point. An adhesive that performed below 1 standard deviation of both baselines received zero points. These scores were averaged for each adhesive across all five rubber compounds. As such, an average score above two indicated better performance than the baselines, while a score below indicated inferior performance. These results show that five adhesives have superior performance relative to the baselines. Thixon 532-EF/naphtholite performed the best, followed by Thixon 532-EF with toluene and Megum 3911 primer.

Considering all ranking systems (table 7, figures 23 and 24), we can judge which adhesives performed well relative to the baselines. Overall, Thixon 532-EF thinned with naphtholite was the top performer, followed by Thixon 532-EF thinned with toluene using Megum 3911 primer. Chemlok 6411-LH performed third best. Yet, some sporadic brittleness occurred with rubber no. 1035 and Chemlok 6411-LH thinned tert butyl acetate. Both low-HAP adhesive alternatives in conjunction with the appropriate low-HAP primers performed better than the baseline adhesives with low-HAP thinners (table 7). Chemlok 6254-LH/20% t-butyl acetate performed fourth best, and Thixon 532-EF/25% acetone performed fifth best.

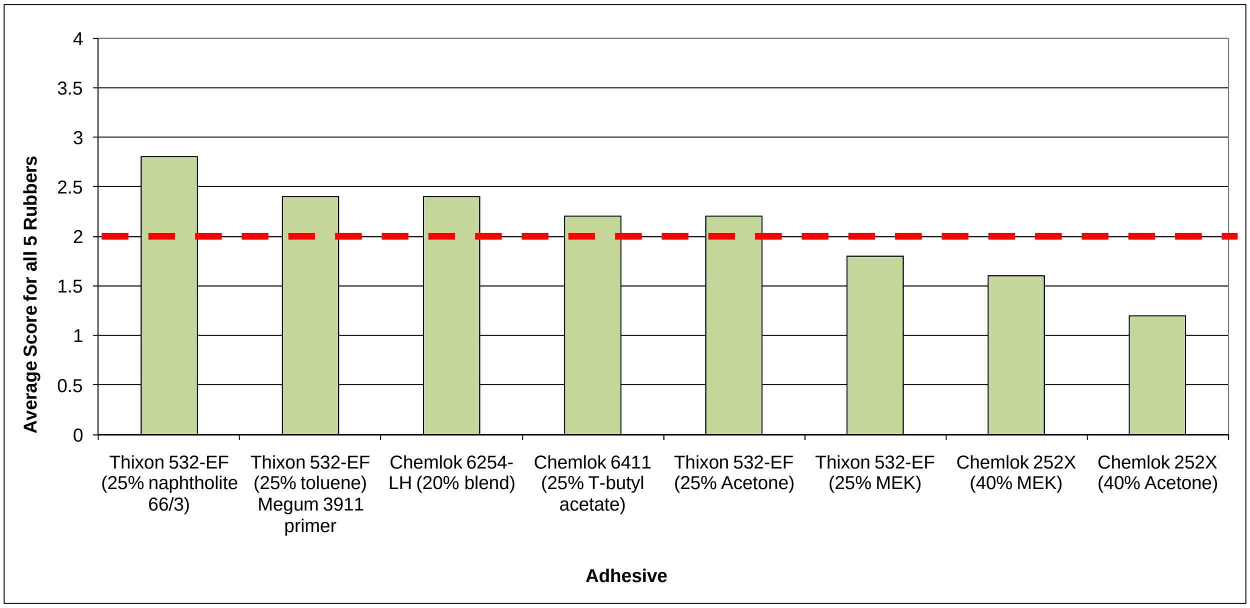

Figure 24. Performance of adhesives graphed by point system.

3.9 Potential Emissions Reduction

Table 8 lists the HAP content of the neat adhesives, the adhesives thinned with a manufacturer-suggested HAP solvent (toluene or xylene), and the adhesives thinned with a HAP-free solvent. There was not a HAP-thinned version of Chemlok 6254-LH or Chemlok 6411-LH adhesives because the TDS recommended solvents that are HAP-free (*8*).

Table 8. Total HAP content (including inorganic HAPs) in adhesives.

Adhesive/Primer Name	HAP Content Neat (wt. %)	Dilution (wt. %)	HAP Content Thinned With Toluene (wt. %)	HAP Content Thinned With non-HAP Solvent (wt. %)
Chemlok 252X (baseline)	85	60/40	91	51
Thixon 532-EF (baseline)	80	75/25	85	60
Chemlok 6254-LH (alternative)	25	80/20	NA	20
Chemlok 6411-LH (alternative)	15	75/25	NA	11
Chemlok 205 (baseline)	~75	75/25	81	56
Thixon P-11 (baseline)	~75	75/25	81	56
Chemlok 205-LH (alternative)	~11	80/25	NA	9
Megum 3911 (alternative)	~12	85/15	NA	10

Table 9 contains the estimated pounds of primer usage per year for RRAD. The baseline primers are currently thinned with MEK, which is non-HAP. MEK was delisted as a HAP by the EPA in 2005 but is still considered a VOC. These primers are used in the amount of 7357 lb/yr, producing 5518 lb/yr HAP emissions and 7908 lb/yr VOC emissions. The two low-HAP primers in table 9 could reduce HAP emissions by ~ 4000 lb/yr. VOC emissions would be reduced slightly by ~380–2100 lb/yr depending on the low-HAP primer used.

Table 9. Estimated primer HAP and VOC emissions (lb/yr).

Primer Name	Estimated Usage (lb/yr)	HAP Content Neat (lb/yr)	HAP Content Thinned With non-HAP solvent (lb/year)	Estimated Reduced HAPs (lb/yr)	VOC Content Neat (lb/yr)	VOC Content W/Thinner (lb/yr)
[a]Chemlok 205 (baseline)	7357	5518	5518	2452	5456	7908
[a]Thixon P-11 (baseline)	7357	5518	5518	2452	5534	7986
Chemlok 205-LH (alternative)	7357	809	809	6548	5685	7524
Megum 3911 (alternative)	7357	883	883	6474	4570	5868

[a]The total amount of Chemlok 205 and Thixon P-11 primers used together equals 7357 lb/yr depending on which baseline primer/adhesive RRAD chooses to use, as both are qualified for the application.

Table 10 contains the estimated pounds of adhesive used per year by RRAD. These adhesives are used in the amount of 9636 lb/yr and produce 10,900–14,600 lb/yr HAP emissions and 10,500–13,800 lb/yr VOC emissions. Replacing the baseline with the low-HAP Chemlok 6411-LH could reduce emissions by ~13,100 lb/yr. VOC emission reductions would amount to ~450–3800 lb/yr. Using HAP-free thinners with the baseline adhesive would reduce HAP emissions by ~3200–6400 lb/yr. However, the VOC emissions would remain the same as in table 10 because the non-HAP thinners used are considered VOCs. A combination of low-HAP primer and low-HAP adhesive could reduce total HAP emissions by ~ 20,100 lb/yr and VOC emissions by ~3800 lb/yr.

Table 10. Estimated adhesive HAP and VOC emissions (lb/yr).

Adhesive Name	Estimated Usage (lb/yr)	HAP Content Neat (lb/yr)	HAP Content Thinned With Toluene (lb/yr)	HAP Content Thinned With non-HAP Solvent (lb/year)	Estimated Reduced HAPs (lb/yr)	VOC Content Neat (lb/yr)	VOC Content With Thinner (lb/yr)
[a]Chemlok 252X (baseline)	9636	8191	14,615	8191	6424	7416	13,840
[a]Thixon 532-EF (baseline)	9636	7709	10,921	7709	3212	7287	10,499
Chemlok 6254-LH (alternative)	9636	2409	NA	2409	12,206	7093	9502
Chemlok 6411-LH (alternative)	9636	1445	NA	1445	13,170	6836	10,048

[a]The total amount of Chemlok 252X and Thixon 535-EF adhesives used together equals 9636 lb/yr depending on which primer/adhesive RRAD chooses to use, as both are qualified for the application.

4. Conclusions

Miscibility of methyl acetate, MEK, acetone, heptanone, Oxsol 100, tert-butyl acetate, THF, IPA, and ethanol as HAP-free thinners were compared to the baseline thinners toluene and xylene in the test series. Verification of solvent miscibility eliminated IPA and ethanol from the test series due to the solidification of the resin. Heptanone and THF were eliminated from further testing due to the formation of white precipitate in the miscibility samples. Oxsol 100 was removed from further testing due to the high cost of the material relative to other promising candidates. The down-selection process resulted in two solvents remaining (MEK and acetone). Table 11 contains a summary of thinner down selection tested.

Table 11. Down selection of thinners.

Thinner	Eliminated	Reason for Elimination
Acetone	No	NA
Ethanol	Yes	Immiscibility with adhesive
Heptanone	Yes	White precipitate formation
IPA	Yes	Immiscibility with adhesive
MEK	No	NA
Methly acetate	Yes	Made some rubber compounds brittle
Oxsol 100	Yes	Additional expense, halogenated
Tert-butyl acetate	Yes (except for use with Chemlok 6411-LH)	Made some rubber compounds brittle
THF	Yes	White precipitate formation
Toluene (baseline)	Yes	HAP thinner
Xylene (baseline)	Yes	Similarity to Toluene

Dry time analysis showed that methyl acetate, MEK, acetone, and tert-butyl acetate-thinned adhesives were comparable to the baseline adhesive due to similar vapor pressures. Nonvolatile content analysis confirmed that all adhesives in this test series were 22%–26% solids. TGA of Thixon 532-EF neat and thinned confirmed that low-HAP dilutions were chemically similar to the baseline. Rheological data collected for both neat and thinned versions of Chemlok 252X, Thixon 532-EF, and Chemlok 6254-LH were similar in viscosity. Peel samples prepared with methyl acetate or tert-butyl acetate exhibited sporadic brittleness, and peel strength could not be collected. Consequently, methyl acetate and tert-butyl acetate were eliminated from further testing. However, the manufacturers' suggested thinner for Chemlok 6411-LH was tert-butyl acetate (25%), which also resulted in sporadic brittleness for some of the rubber compounds.

All adhesive/primer combinations appeared to have very low peel strength values when used with rubber no. 0149 compared to the other four rubber compounds in the test series. The peel strength was increased significantly with the no. 5618 rubber by more than 50 lbf compared to the other four rubber compounds. Rubber no. 5618 was reformulated to have high durability, and these adhesion results support that finding.

Both low-HAP primers performed very well with both low-HAP and baseline adhesives for all rubber compounds. Therefore, it appears that the low-HAP primers Megum 3911 and Chemlok 205-LH could be used to replace the baseline primers. The best-performing reduced-HAP adhesive formulations include Thixon 532-EF thinned with naphtholite 66/3, Chemlok 6411-LH, Chemlok 6254-LH, Thixon 532-EF thinned with acetone, and Chemlok 252 thinned with MEK. These adhesives performed as well as the baseline products. Although Chemlok 252X was the preferred adhesive for RRAD operations, Thixon 532-EF outperformed this adhesive when used with non-HAP thinners. However, Dow/Rohm & Haas would not approve the use of thinners other than Naphtholite 66/3 for Thixon 532-EF. In addition, Chemlok 6254-LH has recently been discontinued by the manufacturer. Furthermore, the special process required for application of Chemlok 6411-LH (preheating the panels) may prove problematic for use at RRAD.

Although several combinations performed well, only vendor-approved mixtures were submitted for first article testing at RRAD. Table 12 contains the various combinations of primer, adhesive, and solvent approved by the manufacturers to be field tested at RRAD. If none of these adhesives/primers prove satisfactory, some of the adhesive/primer combinations with poorer laboratory performance could be examined at RRAD. However, we will not demonstrate/validate adhesives/primers at RRAD that are not approved by the manufacturer.

Table 12. Low-HAP alternative combinations to be tested at RRAD.

Type	**Adhesive**	**Thinner (low HAP)**	**Primer**
Low-HAP	Chemlok 252X (baseline)	MEK	Chemlok 205-LH (low HAP)
Low-HAP	Thixon 532-EF (baseline)	naphtholite 66/3	Megum 3911 (low HAP)
Low-HAP	Chemlok 6411-LH (alternative)	t-butyl acetate	Chemlok 205-LH (low HAP)

The low-HAP primers and adhesives, and the use of HAP-free thinners, will significantly reduce HAP emissions from this bonding operation at RRAD. The baseline primers have ~81 wt. % HAP content when thinned, and the baseline adhesives contain 85–91 wt. % HAP. Using the HAP-free thinners would reduce HAP content to 56 wt. % in the primers and 51–60 wt. % in the adhesives. Using low-HAP primers and adhesives would reduce HAP content to 9–10 wt. % in the primers and 11–20 wt. % in the adhesives. Based on the results contained in this research, it seems likely that HAP emissions could be reduced by ~3200–6400 lb/yr by using low-HAP primers and HAP-free thinners. If the Chemlok 6411-LH low-HAP adhesive can be successfully transitioned, HAP emissions could be reduced by ~20,100 lb/yr.

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List of Symbols, Abbreviations, and Acronyms

ASTM	American Society for Testing and Materials
DLSME	Defense Land Systems and Miscellaneous Equipment
DSC	Differential Scanning Calorimetry
EPA	Environmental Protection Agency
HAP	hazardous air pollutant
IPA	isopropyl alcohol
kPa	kilopascal
lbf	pound-force
MEK	methyl ethyl ketone
MIBK	methyl isobutyl ketone
mil	one thousandth of an inch
MPK	methyl propyl ketone
MSDS	material safety data sheet
NESHAP	National Emission Standard for Hazardous Air Pollutants
P/B	pigment to binder
psi	pounds of force per square inch
RRAD	Red River Army Depot
RTMB	rubber-to-metal bonding
SPOTA	Sustainable Painting Operations for the Total Army
STD	standard deviation
TDS	technical data sheet
TGA	thermogravimetric analysis
THF	tetrahydrofuran
VM&P	Varnish Makers and Painters

VOC	volatile organic compound
wt. %	weight-percent

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