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NOTICES

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14. ABSTRACT

Advanced military coating technologies have incorporated chemical agent resistance, desirable mechanical properties, and corrosion mitigating properties into CARC systems currently in use. The performance of these coatings is evaluated using MIL-DTL-530721. During the coating application phase and in the field, a tape pull off test is required by MIL-DTL-53072 to gauge adhesive strength of a coating to a primer or substrate. We have investigated the chemical and physical interactions of a variety of tapes used for the verification of coating adhesion with ASTM D33592 on several substrates using tensile pull-testing, infrared-spectroscopy, and contact-angle measurements. A correlation between tape adhesion and surface wetting characteristics has been established. Tapes meeting the minimum performance parameters of 80 inch ounce-force over the selected CARC systems were indentified.

15. SUBJECT TERMS

CARC, coatings, coating adhesion, ASTM D3359, cross hatch, surface wetting, tape adhesion

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CHARACTERIZATION OF TAPE ADHESION TO CHEMICAL AGENT RESISTANT COATINGS

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Abstract: Advanced military coating technologies have incorporated chemical agent resistance, desirable mechanical properties, and corrosion mitigating properties into CARC systems currently in use. The performance of these coatings is evaluated using MIL-DTL-53072[1]. During the coating application phase and in the field, a tape pull off test is required by MIL-DTL-53072 to gauge adhesive strength of a coating to a primer or substrate. We have investigated the chemical and physical interactions of a variety of tapes used for the verification of coating adhesion with ASTM D3359[2] on several substrates using tensile pull-testing, infrared-spectroscopy, and contact-angle measurements. A correlation between tape adhesion and surface wetting characteristics has been established. Tapes meeting the minimum performance parameters of 80 inch ounce-force over the selected CARC systems were indentified.

Keywords: CARC; Coatings; Coating Adhesion; ASTM D3359; Cross Hatch; Surface Wetting; Tape Adhesion

Introduction: Under regulation AR 750-1[3], Army based ground equipment must have a full Chemical Agent Resistant Coating (CARC) system as defined in MIL-DTL-53072, "CHEMICAL AGENT RESISTANT COATING (CARC) SYSTEM APPLICATION PROCEDURES AND QUALITY CONTROL INSPECTION". Several performance test requirements for CARC are specified in MIL-DTL-53072. One such performance requirement is adhesion testing of the system in accordance with ATSM D3359 Methods A and B, "Standard Test Methods for Measuring Adhesion by Tape Test". The primary test for coating adhesion is the cross-hatch tape adhesion method described in ASTM D3359 Method B. Applicators of CARC at OEM's, depots, and suppliers can provide objective quality evidence (OQE) that the integrity of the CARC adhesion is within the established limits of MIL-DTL-53072.

Recently, reports from the users in the field indicate that there is a significant fault with the tape adhesion testing used on Army assets[4,5]. More specifically, many of the tapes that are currently used in dry adhesion testing of CARCs reportedly do not adhere well to CARC topcoats containing polymer-beads used for gloss reduction[6,7]. In prior revisions of ASTM D3359 a single tape was specified for use in adhesion testing. Without adequate tape adhesion to the CARC surface, false positive results of satisfactory CARC adhesion to the substrate can easily result in unacceptable fielded materiel, thereby exposing the warfighter to significant risk of IR detection and a coating system that is no longer resistant to chemical agents. To emphasize the problem more clearly, a schematic representation of a tape pull-off test on identical substrates with different tapes is shown in Figure 1. The performance specification, MIL-DTL-53072 does not specify the type of tape that should be used for adhesion testing or the required peel strength needed to verify the coating adhesion. In order to mitigate this risk, it would require the closing of the technology gap by identifying suitable tapes for dry adhesion testing and developing a fundamental understanding of their adhesive properties with respect to various CARC surfaces.

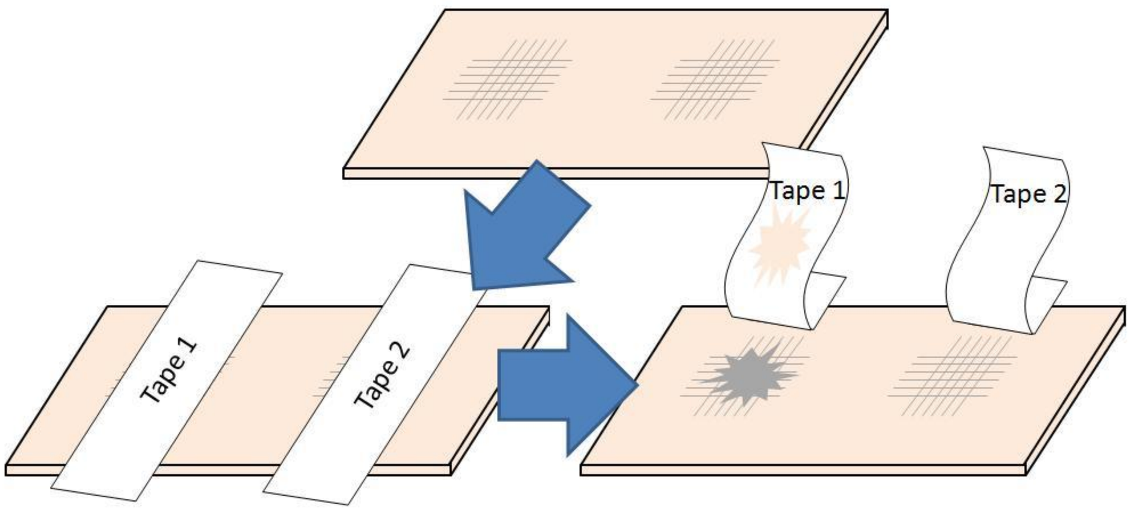

Figure 1: Diagram displaying differences in tapes used in cross hatch adhesion

In this research, the adhesion of several commercially available tapes to various CARC surfaces was evaluated. These tapes were selected based on interviews with several OEMs and military coating applicators as to which are commonly used in the field for adhesion testing[8,9,10]. The CARC formulations were varied to investigate the relationship between the tapes and the different types of CARC's available for use by OEM's and depots. More specifically, each tape was tested on water dispersible and solvent borne polyurethane topcoats in the two most common colors (Green 383[11] and 686A Tan[12]) that were prepared and provided by four different paint manufacturers. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to investigate chemical differences in the adhesives used for each tape. Advancing water contact angles were measured to provide insight on variations in the surface energies of various CARCs and the adhesive backing on the tapes.

Performance criterion for tape adhesion has been set by the CARC Commodity Manager at 80 inch ounce-force using IAW ASTM D 3330, Peel Adhesion of Pressure Sensitive Tape, which used a 180 degree pull angle and 1-inch wide tape [13] Tapes that meet or exceed the 80 inch ounce-force minimum on CARC systems will be recognized by ARL for qualifying the adhesion strength at interfaces within the CARC system. Typically, adhesion throughout the various interfaces in this system is verified using IAW ASTM D 3359.

That the governing specification for tape adhesion testing has become less precise with respect to what tapes are acceptable for use which has created an opening for many different types and brands of tapes with varied adhesive compositions. These variations in tape adhesive composition can lead to differences in adhesion to a substrate. CARC formulations within the same specification vary between manufacturers and because of this, not all CARCs have similar surface energies. We hypothesize that the wide variation in surface energy of CARCs affects adhesion between various tapes and the substrate.

Experimental:

CARC coated substrates were tested as received from the manufacturers. Table 1 summarizes the manufacturer, specification, type, color, and extender.

Table 1: CARC Information

Manufacturer	Spec	Type	Color	Extender
Hentzen	MIL-DTL-64159A	I	Green 383 686A Tan	Silica Particles/Flake
	MIL-DTL-64159B	I	Green 383 686A Tan	Polymer Beads
	MIL-DTL-53039C	I	Green 383 686A Tan	Silica Particles/Flake
		IV	Green 383 686A Tan	Polymer Beads
NCP	MIL-DTL-64159B	I	Green 383 686A Tan	Polymer Beads
	MIL-DTL-53039C	I	Green 383 686A Tan	Silica Particles/Flake
		II	Green 383 686A Tan	Silica Particles/Flake
	MIL-DTL-53039D	IV	Green 383 686A Tan	Polymer Beads
Sherwin Williams	MIL-DTL-64159A	I	Green 383 686A Tan	Silica Particles/Flake
	MIL-DTL-64159B	I	Green 383 686A Tan	Polymer Beads
	MIL-DTL-53039C	II	Green 383 686A Tan	Silica Particles/Flake
	MIL-DTL-53039D	IV	Green 383 686A Tan	Polymer Beads
Spectrum	MIL-DTL-64159B	I	Green 383 686A Tan	Polymer Beads

Tapes were used as received from the manufacturers. Table 2 summarizes the manufacturer and type of tape used in this work.

Table 2: Tape Information

Manufacturer	Product Name	Adhesive Type	Cost/roll
3M	250 Flatback Masking Tape	Rubber	~$55
3M	396 Super Bond Polyester Film Tape	Rubber Resin	~$13
Intertape	LA-26 Polyester/Rope-Fiber Laminate Tape	Thermosetting Rubber	~$16
SEMicro	Cross Hatch Tape (CHT)	Synthetic Rubber	~$35

An Instron model #8871 load frame mechanical test system was used to measure pull-off forces of the different tapes on various CARC surfaces. The Instron was equipped with a +/- 5kN dynamic load cell, a 90° panel clamping apparatus, and a pulling arm which gripped and performed the 180° tape pull. The Instron was connected to a personal computer (PC). This PC served as both digital controller and data logger. A picture of the experimental set-up is shown in Figure 2. The tape was pressed onto the CARC surface using an applicator in accordance with ASTM D3359. A suitable length of tape was used to cross the surface of the test panel and double back 180° up into the test fixture. A photo of this can be seen in Figure 3. Air bubbles were removed from the tape/surface interface by applying an even pressure with the backside of a plastic spoon until no air pockets could be seen. A common plastic spoon was selected and a limit of 10 seconds was established to remove air pockets so as to make every application as consistent as possible and to establish an accommodating reference for future field applications. The tape covered sample was clamped into place on the panel mount at the base of the Instron. After the test panel was properly secured, and tape attached to the tape pull apparatus, the tape was pulled from the surface over 25mm at a rate of 125mm/s. A total of 18 pulls were collected for each coating specification, type, color, and vendor tested. All data was recorded utilizing the Instron WaveMatrix[14] software suite and output to excel files.

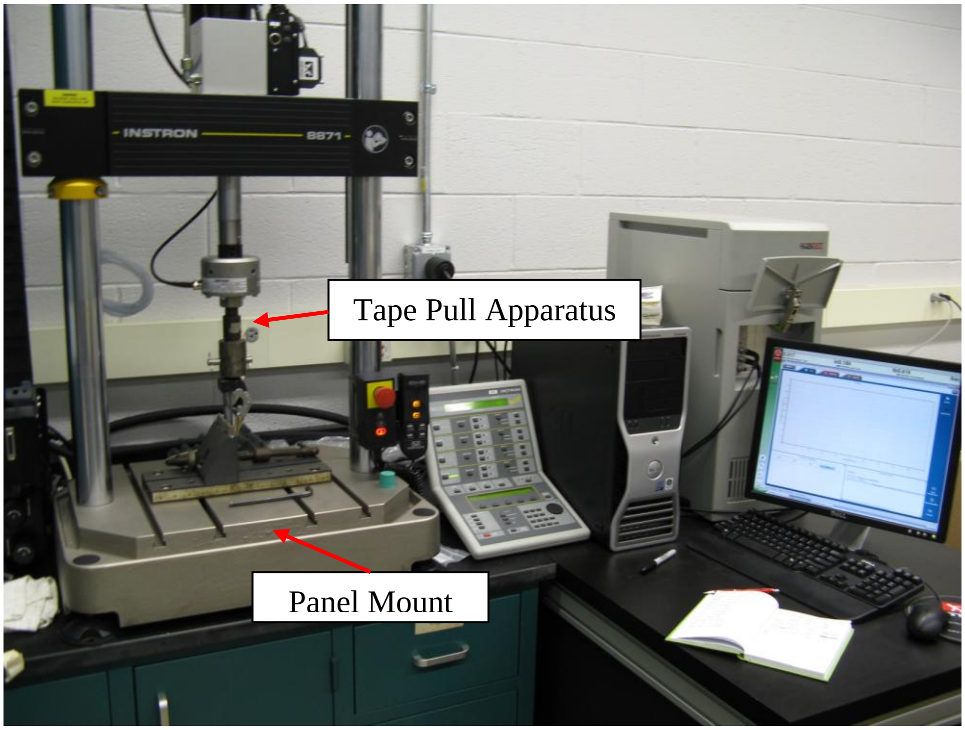

Figure 2: Instron load frame, panel mount, and tape pull apparatus

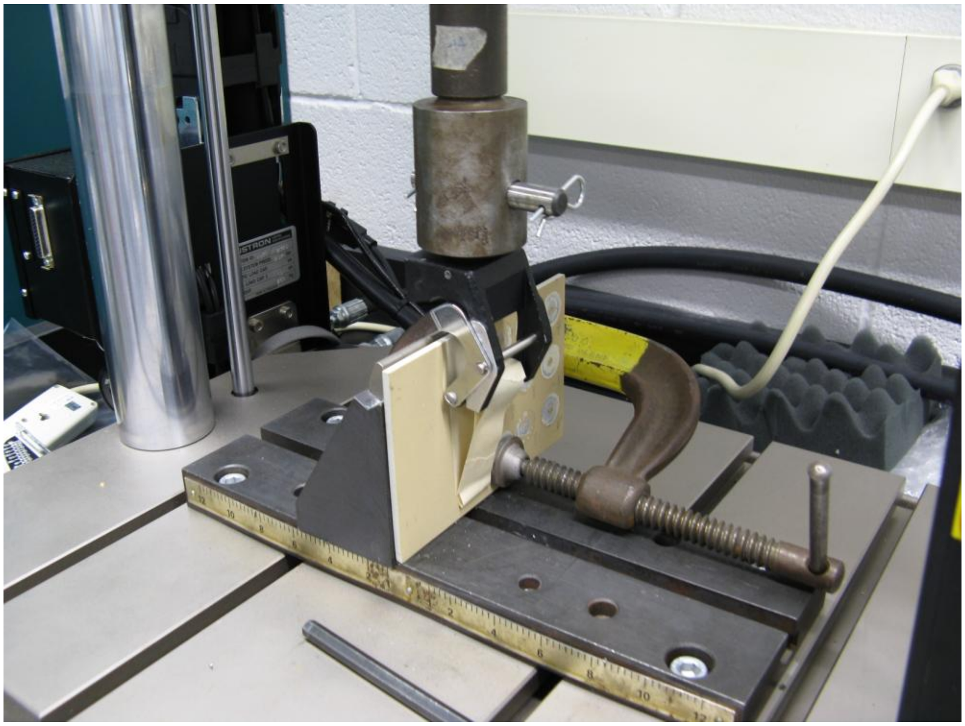

Figure 3: Close-up of panel mount and tape pull apparatus.

A Nexus 870 (Thermo-Nicolet) FTIR spectrophotometer was fitted with a Gateway ATR accessory (Specac). The accessory was allowed to purge with dry nitrogen for 10 minutes prior to collecting a background spectrum of the ZnSe crystal that was mounted in the accessory. Tape was applied onto the crystal and air bubbles were removed with finger pressure. The entire assembly was placed onto the ATR accessory through the sliding window in the FTIR sample compartment. The accessory compartment was purged with N_2 for 10 min prior to collecting the spectrum. The spectra were the summation of 32 scans collected between 650 and 4000 cm^{-1} at a 2 cm^{-1} resolution.

Advancing contact angles were measured using a Rame-Hart Model 290 Automated Contact Angle Goniometer. Water was used as the probe liquid and was purified before use to 18 MΩ cm using a Milipore water purification system. A droplet of water was placed on the surface and the volume of the water droplet was increased until the 3-phase contact line advanced. After an equilibrium angle was observed (i.e.- the drop edge stopped advancing), a measurement was recorded. Five drops were measured at random locations across the sample surfaces.

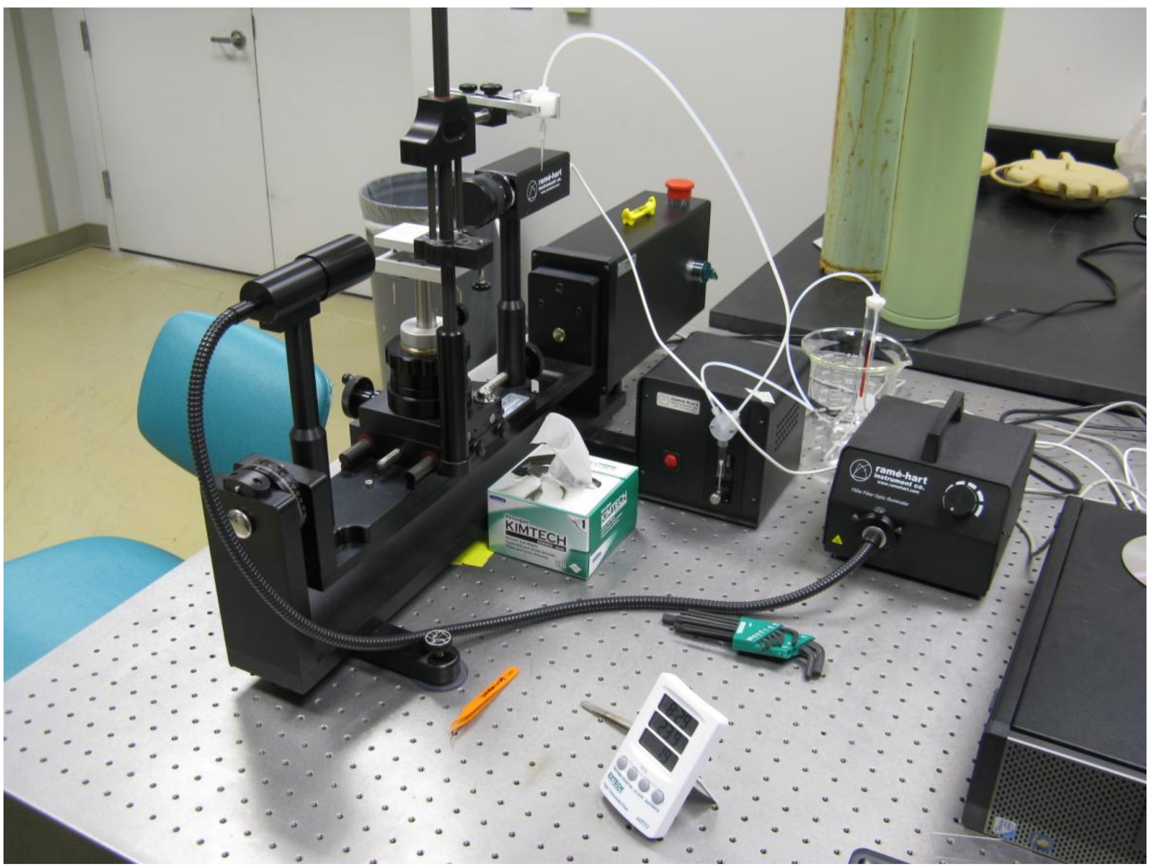

Figure 4: Rame-Hart Model 290 Automated Contact Angle Goniometer

Results and Discussion

Table 3: Average Pull-off Adhesion Strengths for Tapes on Hentzen Coatings

		Green 383	686a Tan
	Tape ID	Adhesive Torque (inch oz-F)	
64159A	3M 250	116.4343418	115.5536483
	3M 396	209.9502469	131.2387126
	CHT	75.30919954	98.0246156
	LA-26	170.2137478	172.8680479
64159B	3M 250	118.3693817	142.2385995
	3M 396	102.3657472	162.7249841
	CHT	80.23762291	100.8733565
	LA-26	165.0913277	193.604993
53039C TI	3M 250	143.5390277	137.2690834
	3M 396	195.0037631	191.8542441
	CHT	154.3933372	156.001803
	LA-26	200.3762747	198.6664471
53039C TIV	3M 250	131.3566168	136.2262631
	3M 396	190.6538985	186.2936355
	CHT	126.095947	122.2181742
	LA-26	178.2005384	170.9017335

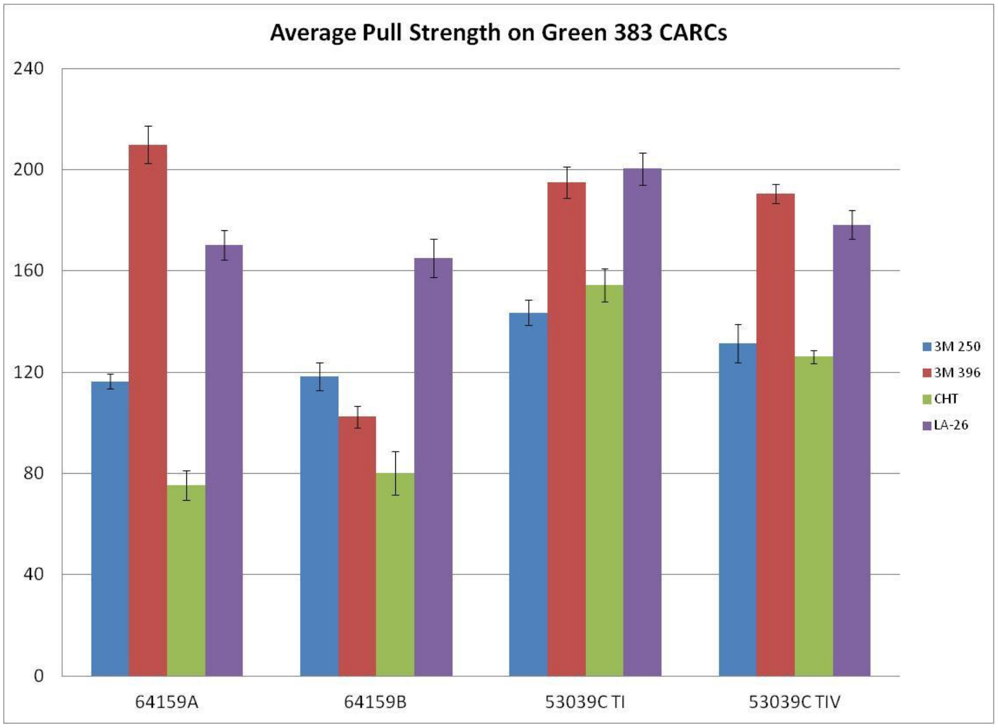

Figure 5: Average Pull-off Strength across Hentzen Green 383 CARCs

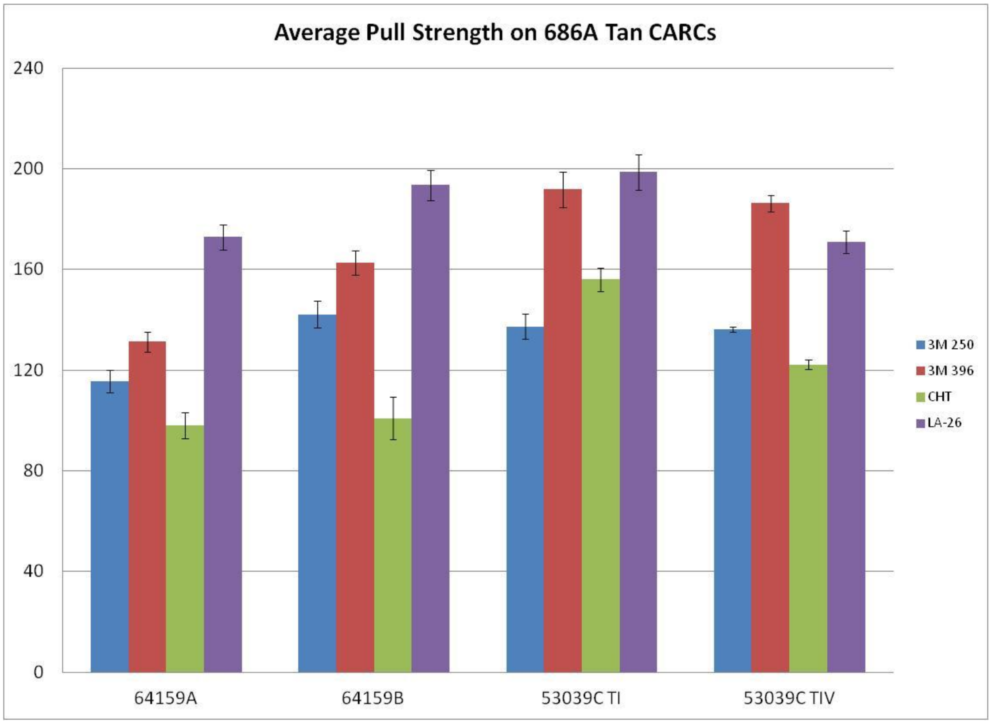

Figure 6: Average Pull-off Strength across Hentzen 686A Tan CARCs

All tapes tested met the established performance criteria of 80 inch ounce-force on all Hentzen coatings with the exception of Cross Hatch Tape over the Green 383 MIL-DTL-64159A. This coating is a silacious flattened waterborne CARC which had an average adhesive strength of 75.3 inch ounce-force, though standard deviation would meet the 80 inch ounce-force threshold. During testing it was noted that the CHT had issues with some adhesive residues left behind on the green silacious waterborne Hentzen coating, at first delaminating from the surface before the Instron was able to initiate the test. The baseline 3M 250 Flatback Masking Tape adhered similarly to each Hentzen coating. The 3M 396 Super Bond Film Tape and the LA-26 Intertape had higher adhesion values than the baseline 3M 250 on each Hentzen coating with the exception of 3M 396 having a lower adhesion strength on the Green 383 Hentzen MIL-DTL-64159B beaded waterborne CARC. The CHT typically had the lowest adhesion strengths of all the tapes tested on the Hentzen coatings with the exception of the type I solvent-borne CARC.

Table 4: Average Pull-off Adhesion Strengths for Tapes on NCP Coatings

		Green 383	686a Tan
	Tape ID	Adhesive Torque (inch oz-F)	
64159A	3M 250	132.7503765	120.9349896
	3M 396	158.3875335	195.7080301
	CHT	192.4183165	173.1846228
	LA-26	119.2778943	88.94703369
64159B	3M 250	125.0854736	99.3807805
	3M 396	202.6268211	208.8347205
	CHT	172.1919435	189.4485205
	LA-26	115.1765149	120.2415306
53039C TI	3M 250	140.4451796	112.6309499
	3M 396	144.2195001	155.3683186
	CHT	177.3376463	163.4457609
	LA-26	111.9850009	90.36489506
53039C TIV	3M 250	98.90985427	83.13689632
	3M 396	63.41534713	77.779158
	CHT	106.9569749	91.40965219
	LA-26	41.97781413	45.33741022

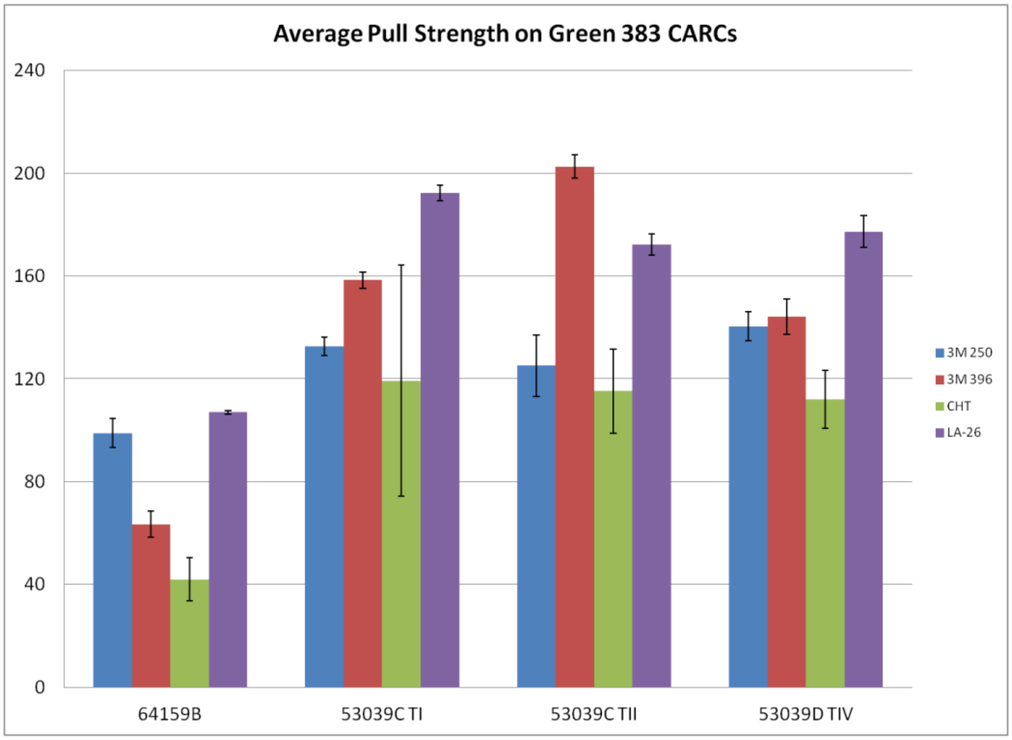

Figure 7: Average Pull-off Strength across NCP Green 383 CARCs

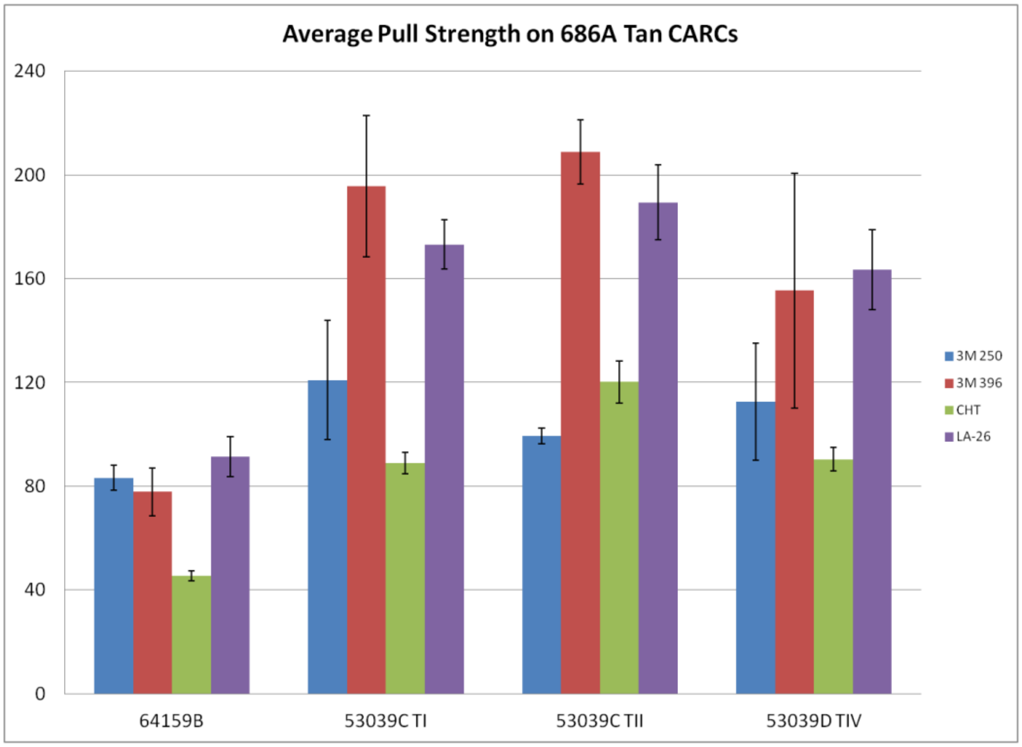

Figure 8: Average Pull-off Strength across NCP 686A Tan CARCs

All tapes tested met the established performance criteria of 80 ounce-force inch on all Hentzen beaded waterborne CARCs with the exception of 3M 396 and CHT. In the case of the 396 on the 686A Tan version of the beaded waterborne CARC, the standard deviation was greater than the margin by which the failure occurred. The standard deviation of the other failures mentioned above were less than the margin of failure. The 396 adhered strongly to the other coatings in the matrix, occasionally in excess of 200 inch ounce-force . The LA-26 adhered strongly to these other coatings as well, and performed adequately on the beaded waterborne CARCs. The baseline 3M 250 performed similarly across all coatings, and with the lower end of standard deviation could have been considered a failure on the beaded waterborne CARCs.

Table 5: Average Pull-off Adhesion Strengths for Tapes on Sherwin Williams Coatings

		Green 383	**686a Tan**
	Tape ID	Adhesive Torque (inch oz-F)	
64159A	3M 250	121.924166	126.2662192
	3M 396	143.1628696	121.4726765
	CHT	99.86779499	92.92666367
	LA-26	161.7851218	154.8465372
64159B	3M 250	98.1758155	86.83773152
	3M 396	68.95000138	52.87354516
	CHT	27.07132894	13.84469814
	LA-26	125.8186814	129.0627346
53039C TI	3M 250	144.8774794	129.4325893
	3M 396	188.2608935	160.4740078
	CHT	137.1784956	114.8251067
	LA-26	183.5808988	138.7905794
53039C TIV	3M 250	128.1307735	119.04685
	3M 396	152.6848133	149.5709988
	CHT	110.9296079	104.1712998
	LA-26	149.5745858	138.7905794

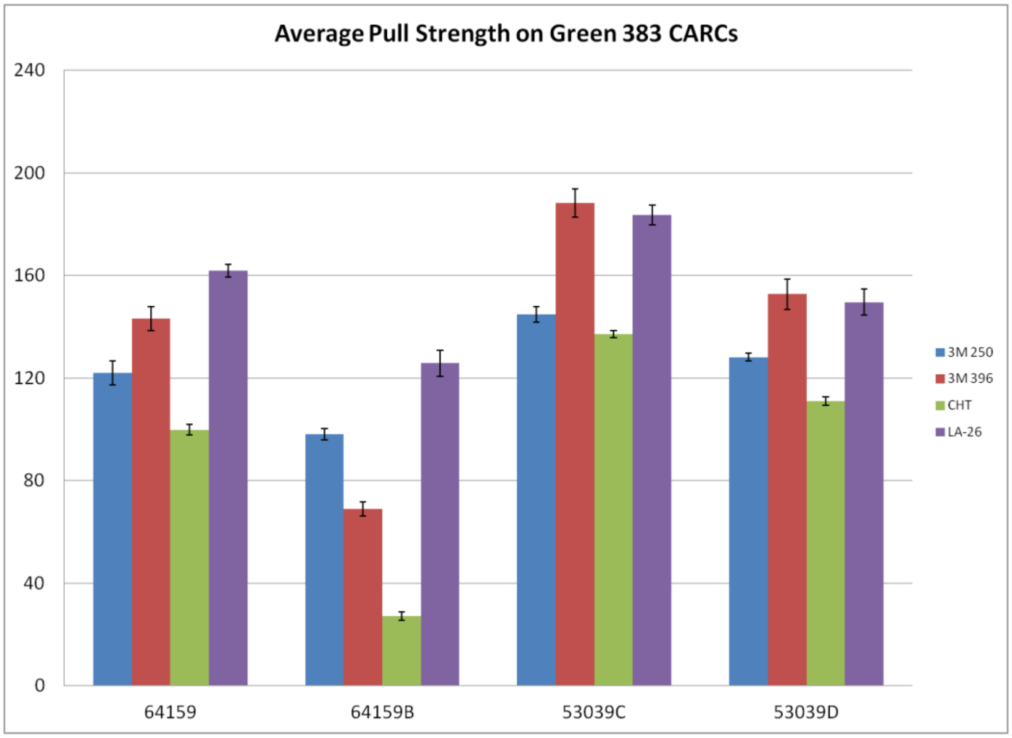

Figure 9: Average Pull-off Strength across Sherwin Williams 383 Green CARCs

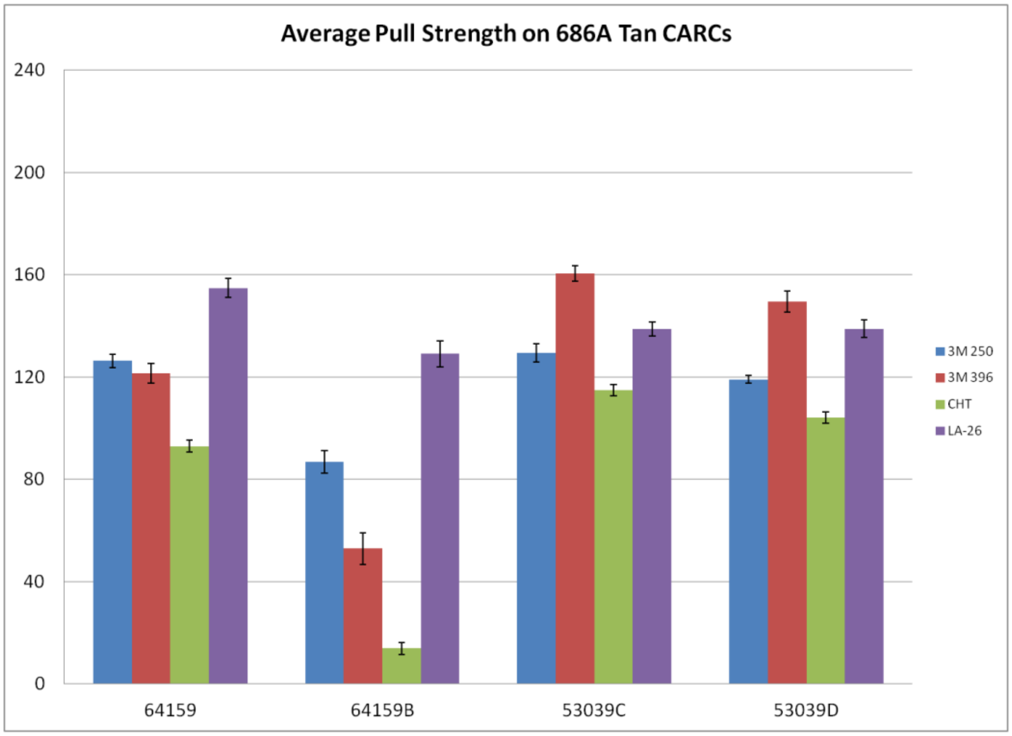

Figure 10: Average Pull-off Strength across Sherwin Williams 383 Green CARCs

The baseline 3M 250 met and exceeded the established performance criteria of 80 inch ounce-force on each of the Sherwin Williams coatings, as did the LA-26. The 396 and CHT met/exceeded 80 inch ounce-force on each of the Sherwin Williams coatings except for the beaded waterborne CARCs. The standard deviations do not exceed the margin of failure in the case of either the 396 or the CHT.

Table 6: Average Pull-off Adhesion Strengths for Tapes on Spectrum Coatings

	Green 383	686a Tan
3M 250	126.12747	134.24676
3M 396	98.256272	77.959094
CHT	73.289886	62.05658
LA-26	165.85749	171.37503

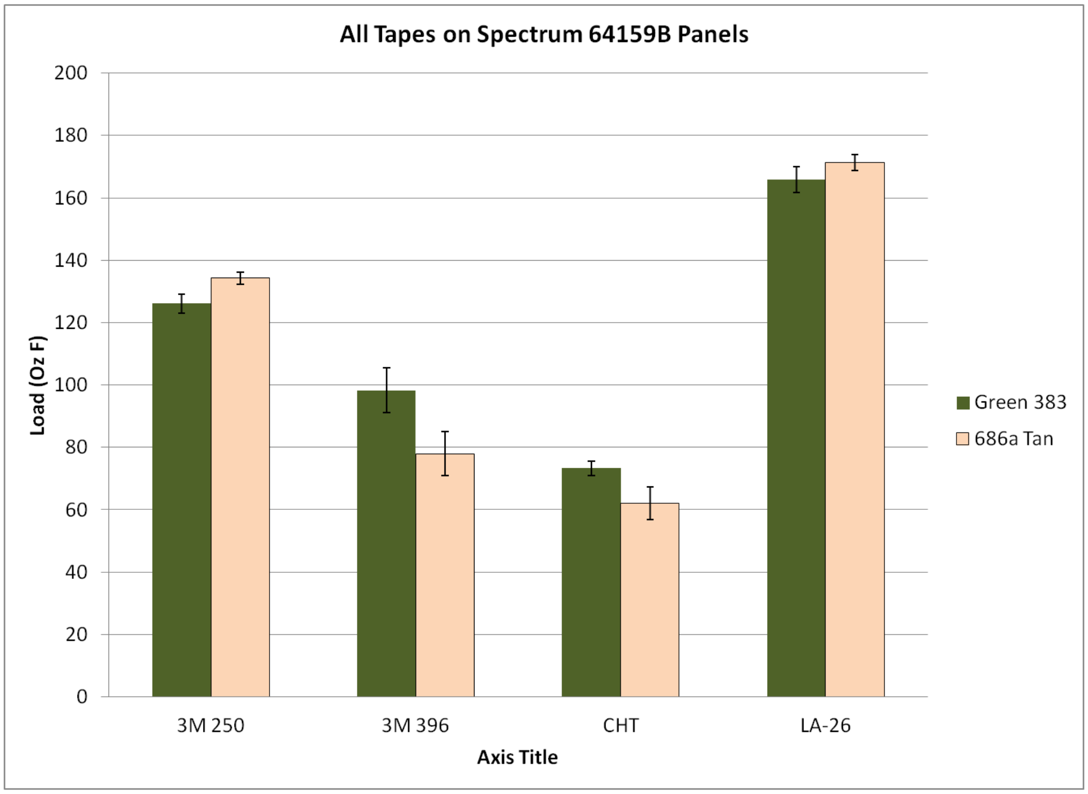

Figure 11: Average Pull-off Adhesion Strength across Spectrum 64159B CARCs

Table 7: Water Break Test Results

			250	396	CHT	LA-26
Sherwin Williams	64159A	Green 383	PASS	PASS	PASS	FAIL
		686A Tan	PASS	PASS	PASS	FAIL
	64159B	Green 383	PASS	PASS	PASS	PASS
		686A Tan	PASS	PASS	PASS	PASS
	53039C	Green 383	PASS	PASS	PASS	PASS
		686A Tan	PASS	PASS	PASS	PASS
	53039D	Green 383	PASS	PASS	PASS	PASS
		686A Tan	PASS	PASS	PASS	PASS
Spectrum	64159B	Green 383	PASS	PASS	PASS	PASS
		686A Tan	PASS	PASS	PASS	PASS
Hentzen	64159A	Green 383	PASS	FAIL	PASS	PASS
		686A Tan	PASS	PASS	PASS	PASS
	64159B	Green 383	PASS	PASS	PASS	PASS
		686A Tan	PASS	PASS	PASS	PASS
	53039C I	Green 383	FAIL	FAIL	Marginal	FAIL
		686A Tan	FAIL	FAIL	FAIL	FAIL
	53039C IV	Green 383	PASS	PASS	PASS	FAIL
		686A Tan	PASS	FAIL	PASS	PASS
NCP	64159B	Green 383	PASS	PASS	PASS	PASS
		686A Tan	PASS	PASS	PASS	PASS
	53039C I	Green 383	PASS	PASS	PASS	PASS
		686A Tan	PASS	PASS	PASS	PASS
	53039C II	Green 383	PASS	PASS	PASS	PASS
		686A Tan	PASS	PASS	PASS	PASS
	53039D IV	Green 383	PASS	PASS	PASS	PASS
		686A Tan	FAIL	FAIL	FAIL	FAIL

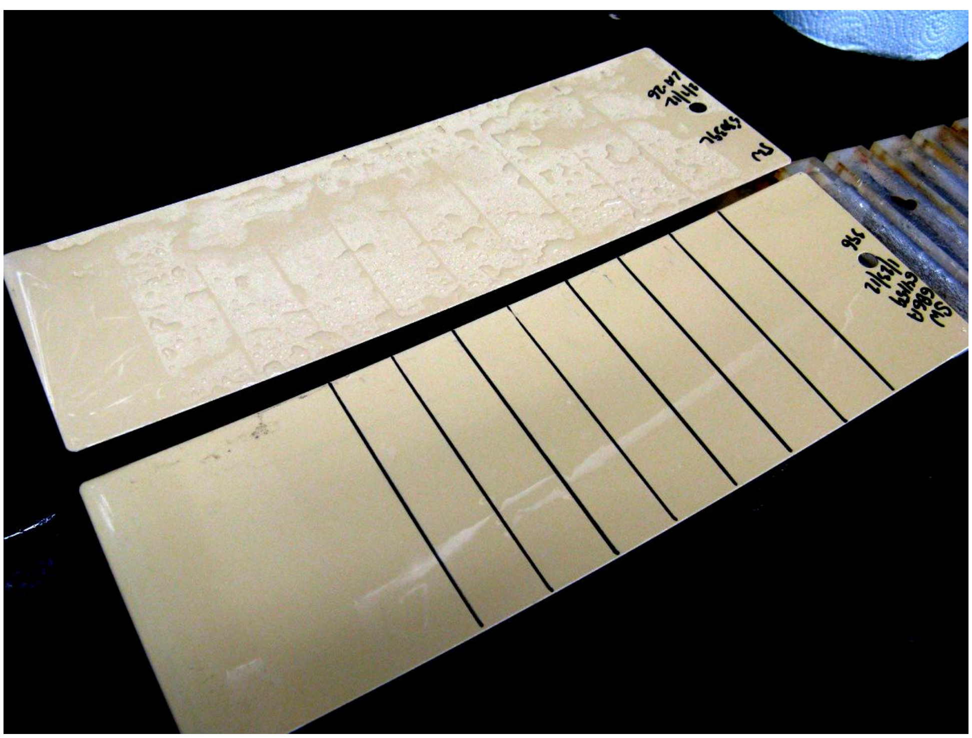

Figure 12: Example of Failed Water Break Test (Top) and Passed Water Break Test (Bottom)

The water break testing was done by running DI water over the test panels after the tape testing had been completed. For the purposes of this test, water that beaded up over the areas where tape had been applied to the surface was considered a failure and can be seen on the upper panel in Figure 11. The lower panel in Figure 11 in which you can see the water evenly spread out over the panel surface is an example of a pass. The instances in which failure occurs are attributed to adhesive residue left on the surface of the panel. These results could affect field application whereby these tapes would be used for masking during painting operations. There were few failures in the water break testing and were limited to LA-26 over Sherwin Williams' silacious waterborne CARCs, 396 over Hentzen's silacious waterborne (green only), every tape over Hentzen's silacious solvent-borne, 396 over Hentzen's beaded solventborne, and every tape over NCP's 53039D beaded solventborne (tan only).

Surface properties such as roughness, chemical composition, and homogeneity are well known to influence the wettability of surfaces. CARC topcoats used by the Army can exhibit a wide range of surface properties that result from subtle differences in formulation,, from variations in application parameters, and even ambient conditions, andGenerally, systems formulated to be water dispersible produced films that were slightly hydrophilic (water contact angle < 90°) whereas systems formulated with organic solvents that are not miscible with water cured to yield polymer films that were hydrophobic (water contact angle > 90°) (Table 8).

Table 8: Average water contact angle of various CARC systems.

	advancing contact angle of water (degrees)	
	waterborne polyurethane	*solventborne polyurethane*
silica extender	80 +/- 5	112 +/- 8
polymeric bead extender	79 +/- 9	106 +/- 4

The results in Table 8 also suggest that the type of extender has little or no impact on the wettability of the virgin polyurethane surfaces. A comparison of wetability for 686 tan and 383 green pigmented polyurethane coated samples obtained from several different vendors is shown in figure 12.

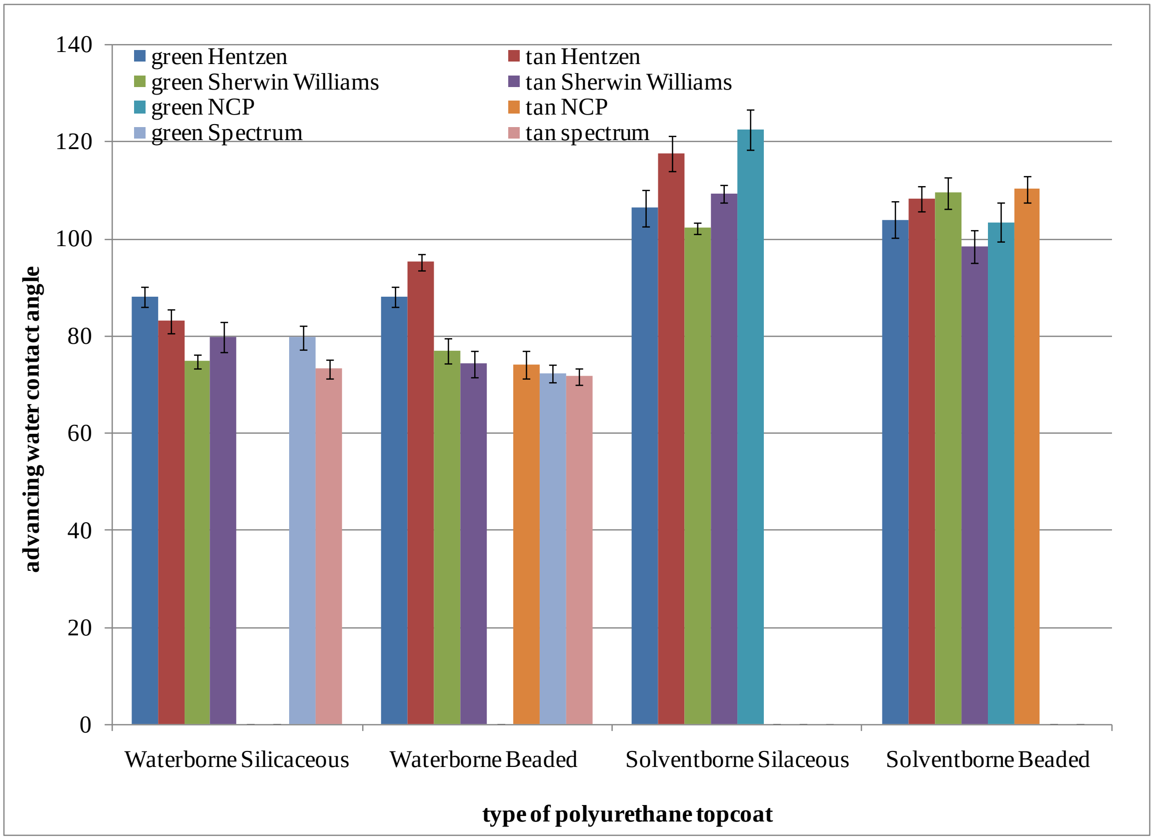

Figure 13: Advancing water contact angles of polyurethane topcoats formulated in tan and green from four different vendors.

There is little or no difference in the water contact angle measured on samples differing only in pigment composition. Although this observation suggests that pigment does not affect surface properties, additives used to disperse the pigments and extenders may preferentially migrate to the surface of the coating. Similarly, surfactants utilized for increasing the solubility of urethane precursors in waterborne formulations may reside at the surface preferentially. A more detailed and systematic study on a model system should provide clarity regarding surface segregation of particular additives used in formulation. Our research clearly shows waterborne polyurethanes have lower contact angles (higher surface free energies) than their solvent borne counterparts.

The relationship between wettability and work of adhesion is described by the Young-Dupré equation:

$$W_{SVL} = \gamma_{LV}(1 + \cos\theta), \qquad (1)$$

where W_{SVL} is commonly referred to as the work of adhesion, γ_{LV} is the interfacial free energy at the liquid-vapor interface, and θ is the contact angle at the three-phase contact line. From this equation we expect the work of adhesion between a liquid and solid to decrease as the contact angle increases as shown in Figure 13.[15]

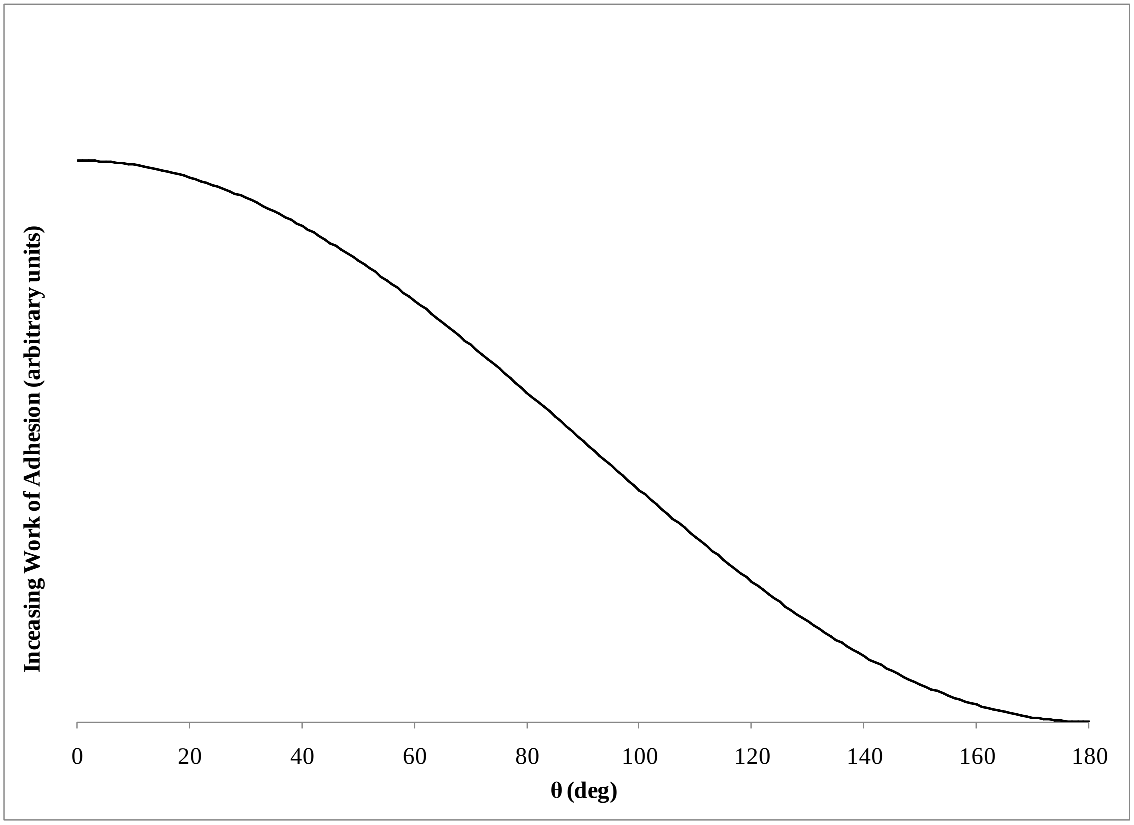

Figure 14: Theoretical behavior of the work of adhesion with respect to contact angle based on the Young-Dupré equation.

Extending this expected behavior to a solid-solid system such as an elastomer/polyurethane interface is more complicated. The Johnson-Kendall-Roberts (JKR)[16] and the Derjaguin-Muller-Toporov (DMT)[1718] theories are typically used to describe the work of adhesion for polymer-solid systems. Although these relationships will be useful in fundamental studies that model our system, they are beyond the scope of this report and are mentioned here to highlight the relationship between work of adhesion, pull-off-force, and contact angle. In our research the lack of a clear correlation between contact angle and pull-off strength is most likely due to the complexity of the systems studied.

Attenuated total reflectance-fourier transform infrared spectroscopy was used to identify chemical differences in the adhesive of the tapes used for pull-off tests. Figure 14 shows the region of the spectrum where –CH , –OH, and -NH stretching vibrations occur. Small stretches observed at ~3280 cm^{-1} for the adhesive on the 3M® 250 tape and 3330 $cm^{-1}$for the LA-26 tape indicate –OH or –NH groups within the adhesive or adsorbed water. Hydroxyl, amine, or amide functionality within an adhesive can hydrogen bond with free chain ends of the urethane and with the oxide surfaces of pigment particles and hydroxyl groups may have enough mobility to chemically react with any residual isocyanate groups present at the polyurethane surface. The likelihood that these hydroxyl groups would contribute significantly to tape pull-off forces is low due to the relatively low intensity of the normally strong –OH stretch. It is common, however, for –NH groups of secondary amines to be quite weak. Other evidence that supports the presence of –NH groups is seen in figure IRB (*vide infra*). Evidence for the presence of vinyl groups in all of the tape samples analyzed is seen by the –CH stretch just above 3000cm^{-1}. Although vinyl functionality may contribute to an increase in the overall adhesion to a substrate that contains thiol groups, the low intensity of this stretch complicated quantification of the differences in –C=C concentration between the various tapes.

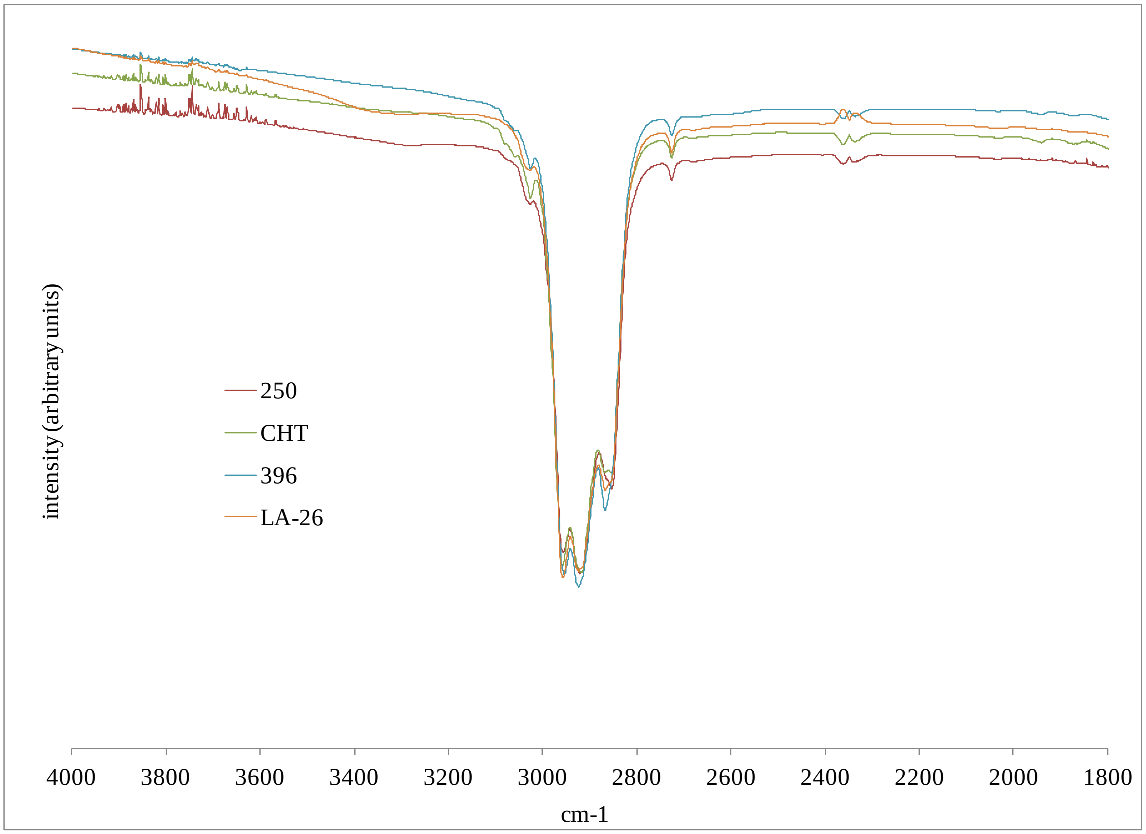

Figure 15: ATR-FTIR spectra of various tapes in the region of 4000-1800 cm^{-1}

Spectra from 650 – 2000 cm^{-1} for of each tape are seen in figure 15. Once again there is evidence that the 3M® 250 and the LA-26 tape contain chemical functional groups consistent with hydrogen bonding groups such as the – NH bend of an amide (~1585 cm^{-1}), an amine (1218 and 1236 cm^{-1}) for LA-26 and 3M® 250 respectively, and a strong stretch at 911 (3M® 250) and a weaker one at 918 cm^{-1}(LA-26) that is indicative of the double bond of an acrylate functional group. Several smaller peaks are present in spectra of the tapes that are difficult to confidently assign functionality to without complementary analytical techniques.

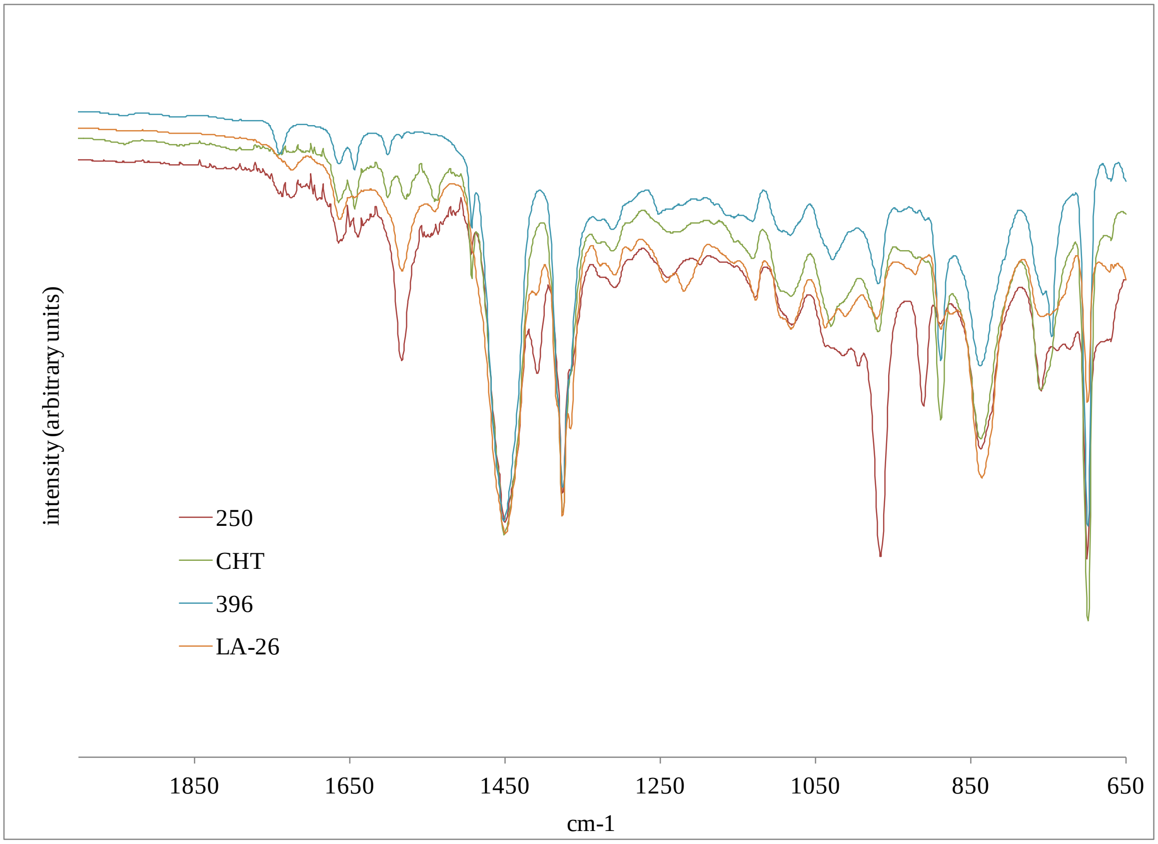

Figure 16: ATR-FTIR spectra of various tapes in the region of 650-1950 cm^{-1}

Conclusions

1) Waterborne formulations have lower advancing contact angles (higher surface free eneries) than solvent borne counterparts.
2) There is no clear difference in the wettability of CARC that contains polymeric beads and a CARC system that contains silica as an extender. The caveat here is that each system has unique additives (dispersants, surfactants, solvents) that allow for a final film with specific properties and these variables may be the underlying cause of the similarities in contact angles.
3) Green and tan pigments do not affect the wettablilty of the cured film. The same caveat that is described in #2 applies here.
4) Tapes that contain functional groups such as hydroxyl, amine, amide, or vinyl typically correlate with higher pull off forces on most samples.
5) A more fundamental study is needed to develop a more fundamental understanding.

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