

Optimizing Paint Durability, Part I

The rapid deployment of military force dictates that military assets be readily available in potential areas of conflict. As a means to this end, military equipment is prepositioned on ships. While the combat systems are sequestered in environmentally controlled holding areas, tactical systems are chained to the deck in a harsh marine environment. Following 24–30 months of marine exposure, the vast majority of once new equipment is in need of selective overhaul...

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Army equipment in transit.

The Army paint finish with its epoxy primer and polyurethane topcoat should—by design—provide a good finish. An analysis of the returned equipment, however, indicates some serious performance anomalies. These results coupled with isolated paint blistering on new military vehicles and process control failures, indicate that there were factors not presently addressed in the controlling specifications. As laboratory testing of a product does not always represent production variability, a more direct approach was taken for this failure analysis. A comprehensive review of the painting practices at six paint applicators was made to determine the root causes of the deterioration. Products and practices were identified which created these problems. Options are provided to correct the problems. This report reflects the tremendous impact the paint applicator often has in determining the life and continued function of ferrous military equipment.

What We Found

As the equipment was new the impact of gravel impingement or casual paint damage associated with use was minimized. The environmental demands were real salt spray, humidity, thermal cycling and UV resistance. Although the topside surfaces were subject to extreme exposure conditions, the underbody components were more severely corroded than the topside ([Anomaly #1](#)). The corners, pockets and inside surfaces of channels and tubes were generally corroded on ferrous surfaces. Although some underbody components were severely corroded, some adjoining components looked relatively good ([Anomaly #2](#)).



Anomaly #1

The same design flaw was prevalent on almost all equipment. To save weight and reduce cost, designers are specifying intermittent welds. The skipped areas should have been filled with an inexpensive caulk or an electrocoat primer could have been specified, which has the highest probability of coating the relatively tight faying surfaces in the unwelded segments. These steel edges are impossible to coat with a sprayed application; there is rust bleed through within two weeks of fielding.

Analytical tools at the overhaul facility were limited to paint film thickness and Tooke gages. Although they may appear insufficient for a failure analysis, they provide objective evidence as to the thickness and type of coatings applied to the surface. Due to the obvious color difference between epoxy-urethane, electrocoat primers and the white/off-white sprayed epoxy primers, primer identification was easy. All the surfaces evaluated had sprayed epoxy finishes. The actual primer



Anomaly #2

thicknesses ranged from 0.6–2 mils. There was a significant difference in the thickness of the polyurethane topcoat on the topside versus the underbody components. The topside surfaces had typically 3.5–7 mils of topcoat while the underbody components had 1.5–2.5 mils. The underbody components that showed minimal deterioration had essentially the same paint film thickness as adjacent rusty parts (3–4 mils total dft).

Just-in-Time... Gone Awry

Electrocoat primers, baking enamels and powder coat systems are ideally suited to quick turnaround. Solvent-borne coatings developed for ambient cure are not...or so we thought. Three interrelated practices were responsible for promoting rapid corrosion of the substrate. Specifically, they are high temperature forced curing, inadequate corner coverage and wet-on-wet painting. Due to a general lack of knowledge in coating chemistry, mechanics and the epoxy-urethane interaction, applicators are unknowingly perforating the paint film.

Forced Curing. Forced curing is necessary to be cost effective in today's market. It is practiced by 95%+ of the Army's contractors. The impact of higher throughput on the bottom line is obvious. What is less obvious is the direct impact that environmental initiatives (low VOC primers) have had on the painting process and coating quality. Manufacturing conveyor lines are designed with certain products in mind. Although some flexibility can be introduced with line speed manipulation, quantum changes are difficult without a major overhaul and increase in the manufacturing space claim for the painting process. The original (high VOC) version of the epoxy primer used by the Army was designed with a maximum tack-free time of 15 minutes, which was conducive to high-production rates. In many cases, the primer was tack free in 10 minutes; primed surfaces had a uniform continuous film that easily met performance requirements. Most production lines were apparently designed with this product in mind.

With the low VOC reformulations of the epoxy primer, the tack-free time was doubled to 30 minutes. The tack-free time has major implications when forced curing (oven curing) is involved. The original primer formulation with the quick flash off allowed the primer to enter the oven tack free; now the primer is wet as it enters the oven. When a wet paint film enters a hot, non-zoned oven over 200°F, solvent washing and solvent popping often occur. There is random thinning of the paint film preferentially on vertical surfaces and voids in the epoxy down to the substrate. When some epoxy primers are applied less than 1.0 mil, holidays start to appear. The type and quantity of reducing solvent added to the primer can also contribute to these defects as the tack free time can be greatly increased. Many applicators found that their conveyor length was insufficient to fully cure the paint finish with the slower, more environmentally friendly solvents. The easiest way to compensate for a "short oven" was to increase the temperature. Curing temperatures up to 375°F have been witnessed even though many paint manufacturers recommend a maximum temperature of 180°F. The most efficient way of counteracting these effects is to increase the primer wet film thickness by 50%, i.e. 1.5 mils minimum in the dry film.



Wet-on-Wet. High build

6.3 - 7.5 mils

6 min@75°, 15 min@ 320°F

Erractic Adhesion

Figure 1. Impact of high build, wet-on-wet with forced curing.

Corner Coverage. Part size and geometry dictate the fan size of the spray pattern. Tight corners and accessibility problems are always an issue for the paint applicator. While the best approach would be to have two paint spray guns available to the painter (one with a narrow fan to stripe the corners and edges and the other with a wide fan for maximum efficiency), this is the exception rather than the rule. When a large spray pattern is used and the painter attempts to get complete coverage in tight corners, high-film builds tend to be created on the adjacent areas due to multiple spray passes. This would be an acceptable approach, if wet-on-wet painting and high-temperature force curing were not practiced.

To demonstrate the impact of this technique, test samples were made on the production line to duplicate actual production sequencing. After a relatively high build of epoxy primer, the wet panels were overcoated with 2K urethane five minutes after the primer application (wet-on-wet). Six minutes later, the panels were run through the curing oven at 320°F. In comparison, a second set of test panels was primed with the same technique but allowed to flash off for 25 minutes (tack free) prior to urethane topcoat application. After a six-minute flash off the panels were run through the same curing oven. The test panels that were allowed to flash off for 25 minutes prior to topcoating had a good visual appearance and good adhesion (cross-hatch/tape test). The wet-on-wet sample displayed mixed results (see Figure 1). While one area had good adhesion, two inches away there was

almost no adhesion. The top corner displayed a large crack in the paint from extensive solvent popping. A section of the paint finish had delaminated from the zinc phosphate pretreatment. These results reinforce the painting techniques noted at some facilities...the corners tend to receive minimal primer coverage. High builds tend to

create obvious paint defects, which must be repaired, affecting delivery schedule and cost. The impact of this painting practice is readily apparent on the returned equipment where extensive corrosion in the corners is evident.

Many applicators familiar with commercial urethane primers were under the impression that good coverage with the urethane topcoat in the corners would adequately compensate for thin primer coverage in the corners. That belief is incorrect.

Wet-On-Wet Painting. When this practice is coupled with forced curing, gross defects as noted in Figure 1 can occur or can result in blistering as depicted in Figure 2. This photo depicts a common approach in the solvent-borne paint industry to keep film builds to a minimum—solvent additions. Common solvents are methyl amyl ketone (MAK), methyl isobutyl ketone (MIBK) and acetone for the epoxy primer up to 20% by volume. The film thicknesses are typical for production. This blistering has been noted on random surfaces of new vehicles. Some manufacturers believe that they have unlimited rights to manipulate the application process provided they pass a film thickness and adhesion test.

Although Figures 1 and 2 display paint defects at the macroscopic level, the impact at the microscopic level with wet-on-wet epoxy-urethane painting practices is catastrophic. The solvent package used in the epoxy is chemically incompatible with the urethane. Wet-on-wet practices bring the epoxy solvent package to the unreacted urethane. Technically, both the 2K and 1K urethane topcoats demand water-free solvents (less than 0.2% by weight) with the 1K resin even more sensitive to water contamination than the 2K urethane. The epoxy primers typically contain both an ether alcohol (butanol) and an ester alcohol (propylene glycol methyl ether). Both of these alcohols can contain unacceptable levels of water unless reagent grade alcohols (0.1% water maximum) are used by the paint formulator. (The product specification does not control the contamination level of the solvents.) Water is a serious contaminant to urethane/urea curing reactions as it reacts with the isocyanate in the urethane. Through a series of intermediate reactions carbon dioxide is emitted leaving micropores in the urethane film. It can also inhibit cross-linking. Even if reagent grade alcohols are used, PM glycol ether is hydrophilic and a hydroxyl donor. The hydroxyls react with the isocyanates in the urethane significantly degrading cross-link density i.e., chemical agent resistance has now been seriously compromised. Furthermore, with the paint applicator using aftermarket solvents to reduce the paint viscosity, there is a high probability that the solvent could have unacceptable levels of water. Only “urethane grade” solvents should be used. There is no cure for wet-on-wet painting. Don't do it!



Optimizing Paint Durability, Part II

It is not uncommon for military tactical systems to spend anywhere from 24 to 30 months in harsh marine environments. Consequently, the vast majority of once new equipment is in need of selective overhaul. Part two of this article discusses production methodologies for improvement of paint durability on these systems, with an emphasis on pretreatment and topcoat...

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What is a Military Paint Finish?

Applicators have a variety of options when it comes to a paint finish on ferrous tactical and combat vehicles. Pretreatment can range from a surface blast (lowest level of performance) to a zinc phosphate pretreatment (highest level). Abrasive blasting is limited to relatively thick gauges of steel to preclude deformation in the blasting process. Paint can be applied by conventional means or electrostatically to provide enhanced edge coverage. Primers range from sprayed epoxy primers (lowest level) to epoxy-urethane electrocoat primers (highest level).

The benchmark for the pretreatment/primer system is the ability to withstand a 336-hr neutral salt spray after being scribed per ASTM D1654 to the substrate. Primed test coupons are scraped with a metal putty knife after a 24-hr recovery period to quantify scribe creep/paint delamination from a paint film defect and rust in the field. To date, only paint systems involving a zinc phosphate pretreatment have been able to meet this performance objective. Electrocoat primer systems are held to a significantly higher performance benchmark (ability to resist 1,000 hr of neutral salt spray).

When it comes to topcoats, two aliphatic polyurethane options are available. There is a 1K system and a 2K system. The former relies on humidity in the air for curing, and is the preferred topcoat by most applicators due to ease of use. Both primer and topcoat have unique military performance requirements imposed, which preclude "commercial equivalents" from being used. Some of the newer Army systems mandate galvanized steel, zinc phosphate pretreatments and electrocoat primers. Many of the Army systems, however, are legacy systems whose designs were finalized 15 or more years ago and are still being manufactured to the standards of that era.

Improving the Pretreatment

A durable paint finish that can resist paint film defects requires a strong foundation. A clean surface followed by a zinc phosphate pretreatment or one of the new dry-in-place pretreatments provides the ultimate receptor for the primer. Two seemingly "invisible" aspects of this process need to be addressed —the seal rinse and the final water rinse prior to primer application.

The best overall performance is obtained with hexavalent chromium-based seal rinses. Although the functional mechanism is still controversial, it works. Many platers who provide zinc phosphating services are familiar with controlling this heavy metal in their effluent. Most paint applicators, however, do not want the environmental burden.

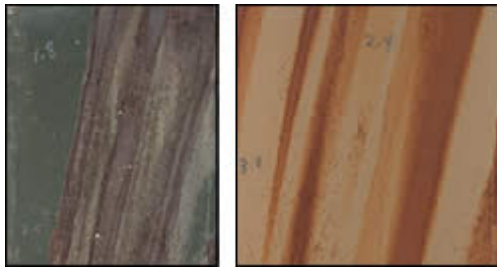


Figure 1 (left): Green 1K Urethane after 336 hours of neutral salt spray.

Figure 2 (right): Tan 1K Urethane after 336 hours of neutral salt spray.

Many non-chromium-based seal rinses will also meet the performance requirements. One approach that does not work is what might be best described as "hot dog technology."

These are rinses based upon the salt, sodium nitrate. This is an excellent preservative for hot dogs but does nothing but promote osmotic blistering when used in conjunction with a pretreatment system. Considering the fact that paint finish societies such as the Steel Surfaces Painting Council (SSPC) go to great lengths to remove all residual salts prior to painting, the fact that some applicators were rinsing parts in salt water was unanticipated. The process controls within the pretreatment specification, TT-C-490E, provide an effective screening tool for selecting an appropriate seal rinse.

Regrettably, some applicators were improperly interpreting the requirements. Process control samples are only meaningful if they duplicate production variables. When process control coupons receive 3–4 mils of primer but production receives 1.0–1.5 mils, salt spray test results are moot. Other salt spray coupons were found unscribed, overcoated with polyurethane topcoat, or not scraped after salt spray exposure. These alterations to the required protocol give a false positive when testing.

If you only process coil or sheet goods (no chemical drag-out between pretreatment stages) or live in a soft water region like Camden, CT (where the conductivity of the water is 100 $\mu\text{S}/\text{sq cm}$), the purity of your rinse water is not an issue. For everyone else, adding a clean water (reverse osmosis or deionized) rinse prior to painting will provide a significant improvement to long term paint performance. The benefit of this rinse is often not evident when conducting acceptance testing but is readily apparent when test coupons are tested to failure. A DI rinse is standard practice with electrocoat primers to minimize contamination to the paint tanks. The primary advantage of this additional operation is to remove/dilute unreacted chemicals from previous steps that are often trapped in the recesses of production parts. The other advantage is that it mitigates hard water deposits and other conductive salts which contribute to osmotic blistering. Applicators in Indiana where the water conductivity measurements are 670 + $\mu\text{S}/\text{sq cm}$ and Ft Worth, TX (1,050 + $\mu\text{S}/\text{sq cm}$) are especially aware of these problems.

The Topcoat Contribution

Army topcoats were developed for military unique performance requirements: visual and spectral camouflage, chemical/live agent resistance and resistance to the decontamination solvent DS2. Automotive-type paint performance is secondary (i.e. nice-to-have but not mandated). Conventional wisdom dictates that for maximum exterior durability you need a high gloss (low pigment volume concentration-PVC) resin system that is UV stable, resistant to moisture permeation (void free) and flexible. The Army topcoats are flat gloss with a high PVC. The

green color has a higher PVC than the tan. Considering the fact that the product literature alludes to "excessive porosity"² in some of the topcoats and some topcoat formulators' technical bulletins warn of "blistering under hot and humid conditions," the benefit of the topcoat to corrosion resistance was questionable.

To determine the basic film formation properties of the 1K and 2K topcoats, the acceptance protocol followed by the epoxy primer and commercial polyurethane primers was duplicated—a 336-hr neutral salt spray over zinc phosphated test panels with waxed edges. Four paint applicators and one paint manufacturer applied the topcoats to sets of test panels. The topcoats were cured identical to production painted parts. All testing was conducted at the U.S. Army Test Laboratory at Rock Island, IL.

In all instances, the 2K urethane provided a void free, quality finish. The 1K urethanes were found to be extremely porous (rust spots) with the green being significantly more porous than the tan ([see Figures 1 and 2](#)). After the first phase of testing, it was unknown as to whether all the applicators had water contaminated paint delivery systems or if there was a problem with the formulation. Pigments used in the formula can contain adsorbed moisture. If there is an insufficient quantity of a moisture scavenger such as isophorone diisocyanate in the formula, the adsorbed moisture will present itself as porosity.³ In the second phase, curing methods, flash off times and reducing solvents were varied, but yielded the same results. Increasing the film build to five mils significantly reduced—but did not totally eliminate—the voids. The most effective means of creating a continuous urethane barrier was to double coat the test panels with a partial cure between coats.

Summary

The production methods witnessed at all OEMs thus far indicated that topsides of combat and tactical systems receive two to three coats of topcoat. This approach effectively eliminates the porosity potential in the 1K urethane topcoats and improves the corrosion resistance of the paint finish. Underbody components, however, receive only a single coat of topcoat. This may explain the dramatic difference in corrosion resistance noted between topside and underbody components after "sea duty." Failure to adopt a double coating practice when using these 1K urethanes can have serious consequences to long term paint performance. The pores in the topcoat provide a direct pathway for UV to degrade the epoxy primer.

The 2K urethane provides a much more corrosion resistant coating (all other performance features excluded) than the 1K urethane. If only a single coat topcoat is to be applied, it should be the 2K system to maximize corrosion resistance. The dramatic difference in salt spray resistance between the 1K and 2K urethanes can account for the difference in corrosion resistance between adjacent underbody components as these parts are often supplied by different vendors.

Coating technologies such as electrocoat and powder make it physically impossible to create the problems noted with wet-on-wet and high temperature forced curing which can thin and perforate the coatings. Corners need complete epoxy primer coverage to resist corrosion of the substrate. The reliance on topcoat alone to protect a steel substrate does not work when the topcoat is not designed for that function.

If you are purchasing a simple, easily replaceable commodity, visual paint inspection for gross defects is adequate. When a paint finish takes on a potential life support mission such as camouflage and live agent resistance where soldiers lives can be compromised, higher standards must apply. That simple door panel might not appear that it deserves a premium paint finish, but it may end up as a part of the armor solution in a ballistic door. A loss in material thickness due to corrosion from a faulty paint finish will compromise that armor system; it may no longer defeat that bullet. America's finest are being placed in harm's way. Please give that soldier the paint finish that he/she deserves.

Quantifying Paint System Performance

The ability of a coating to withstand severe duty is a complex function dependent upon the substrate, coating chemistry, pretreatment and application variability. This report benchmarks the methodology the Tank Automotive and Armaments Command is using on select programs to define and quantify the durability of epoxy-based coating systems whose primary performance requirement is to protect the substrate from corrosion...

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How do you know the paint you just bought will actually meet the manufacturer's claims? Because there is no industry standard for ranking or evaluating paint systems, you don't.

The U.S. Army Tank Automotive and Armaments Command is in the process of leveraging commercial technology to improve military coating systems. Innovative approaches with respect to system design and evaluation are necessary to provide the military with a vehicle that lasts longer and requires less maintenance.

We have found that the automotive industry has done an exceptional job developing highly durable coating systems and the test methods to qualify them. In the automotive industry, corrosion and chip resistance are often taken for granted because of the use of galvanized steel, plastic, aluminum and anti-chip coatings. While automotive manufacturers have recognized the value of multi-coating paint systems in conjunction with more corrosion resistant substrates, for the most part, general industry and the military have not made this quantum change. For these industries, total system performance is driven by the pretreatment, or lack thereof, primer and topcoat.

Although some companies have accepted accelerated corrosion testing as a means to establish the durability of their paint/pretreatment system, the durability of an epoxy-based system, based upon accelerated corrosion testing alone, can be extremely optimistic if other safeguards are not exercised.

In the last few years, this has become a more serious issue with the drive to reduce VOCs. Lower VOC primers have higher viscosities and are less efficient as corrosion inhibitors. Consequently, they tend to require greater film thickness to get the same performance level as their higher VOC versions. Although a thicker epoxy provides

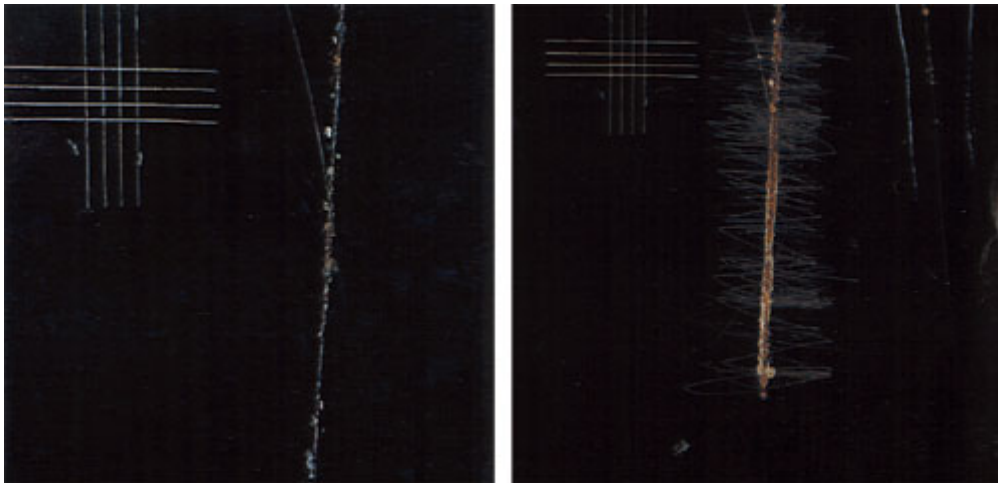
improved corrosion resistance, it is more brittle. Considering the industry's move toward lower VOC coatings, a thorough evaluation of multi-coating systems, substrates and pretreatments is necessary.

Therefore, we took the automotive industry's proven methods and made some slight "improvements" to create a quantitative method for evaluating paint performance. Many of our new system contracts have paint and substrate corrosion performance defined in terms of GM 9540P cycles coupled with a gravelometer test for chip resistance and impact test for process control.

Cleaning & Pretreatment - The Variability Begins Cleaning and pretreatment are the foundation for the coating system. Therefore, some general insight into cleaning and pretreatment and the pretreatment methods we used in this study need to be discussed.

Although a cleaning or pretreatment process might perform well in laboratory conditions on flat test panels, the ability to properly clean and pretreat complex structures with multiple metals and surface conditions, corners, edges, cavities, welds and flash/heavy rust is another matter. Temperature control, concentration and contamination levels in the various recycled chemicals need constant monitoring to maintain minimum levels of performance.

Manufacturing processes, such as laser cutting, forming lubricants and corrosion inhibitors to retard flash rusting are sources of constant grief to the finisher. Laser cut edges resist most pretreatments, and some drawing compounds and corrosion inhibitive oils only come off with specific cleaners. Their removal becomes even more difficult if they have been on the surface for considerable periods of time. Welding processes, which deposit a glassy flux on the weld deposit, provide an unreactive surface for both the pretreatment and the primer.



On the left is a test coupon after an "automotive" evaluation. The image on the right is the same test coupon after it had been scraped. The scribe creep goes from an intermittent condition to an almost continuous response along the scribe line.

Problems are often compounded when the finisher, due to a lack of manufacturing floor space, chooses to store parts outside with little or no corrosion inhibitors or water-soluble inhibitors. The general and galvanic corrosion cells created by this practice often result in tenacious corrosion products that require both mechanical and chemical intervention for complete removal.

The typical approach is to use an alkaline cleaner in conjunction with an abrasive blast, iron phosphate, zinc phosphate, chromate conversion, vinyl wash primer or organo-ceramic derivative pretreatment. But, chemical cleaning becomes increasingly more complicated when inorganic contaminants and mixed metals are involved. In addition, some cleaners have wetting agents, which augment the removal of certain contaminants but may hide organic contaminant detection by giving the visual impression of a clean water break. Fish eyes can be prevented with this practice, but overall long-term performance is compromised. There is no "easy" way to determine that the surface is free of all inorganic contaminants, since water break criteria do not apply. Adhesion failures in an accelerated corrosion test of adequate duration are often the only reliable means of contaminant detection. Abrasive blasting is highly regarded by some as providing the optimal "pretreatment" for large platforms. There is no question that for quickly removing old coatings, corrosion and mill scale, various media and blast pressures can be employed to accomplish the task with minimal degradation to the substrate. Complications, however, do

arise when the spent media, old coatings and metallic fines need to be contained or removed from the remainder of the structure to preclude primer contamination.

Unless the process is contained in an environmental booth, this process cannot be easily carried out in a manufacturing environment. Although water delivery systems help to contain the residue, a relatively expensive reverse osmosis water system is necessary to preclude the development of almost instantaneous flash rusting on ferrous surfaces using water sources with high mineral salt content.

However, the greatest deterrent to abrasive blasting is its inherently limited ability to develop chemical bonding between the substrate and primer compared to chemical pretreatments. Good mechanical bonding between the primer and substrate can be obtained if the primer is applied shortly after blasting to the proper surface profile.

Product data sheets, which identify a particular level of coating performance in conjunction with abrasive blasting, can be very misleading. Both surface profile and dwell time from blasting to primer application are critical variables. The difference in performance between a 2-hr dwell time (laboratory test coupon) and a 2-day dwell time (typical production) can be dramatic.

Iron phosphating does not meet Army acceptance standards as a pretreatment but is generally an effective cleaner. Numerous attempts have been made in the past to get various manufacturers' products to pass the military's 336-hr salt spray test on scribed panels with an epoxy primer. Not one has succeeded.

The polyvinyl butyral wash primers are recipe driven pretreatments dictated by DOD-P-15328. They contain hexavalent chromium and typically have a VOC of 6 lb/gal with 10% solids. These factors limit its use in some states. These are two-component products containing a phosphoric acid component. They are touted as adhesion promoters. They have no other performance benefits expressed or implied. They have been used on a variety of substrates but require that the film remain wet a minimum of 2 min to allow the acid component to have maximum effectiveness. Furthermore, the wash primer must cure a minimum of 1 hr before primer application (MIL-C-8507). There have been reports that the chromium component leaches through the paint film and has been detected in the drip line of vehicles. This product has been used by numerous manufacturers and is allowable on many Army systems.

Aside from its significant environmental problems, wash primers suffer from two major weaknesses associated with their application:

1. Coating systems that rely on a "paint" for a pretreatment typically have very poor to minimal cleaning practices associated with them. Chemical pretreatment systems have a controlled cleaning process directly preceding them to assure a reactive surface in conjunction with sufficient rinsing to eliminate chemical cross contamination.
2. Applicators have a tendency to "dry spray" the wash primer, apply wet-on-wet with the primer or apply the incorrect film thickness. All degrade the usefulness of the product.

Zinc phosphating and organo-ceramic derivative pretreatments are the preferred method for obtaining maximum corrosion resistance of the coating system on ferrous and galvanized surfaces. Immersion systems provide coverage to internal as well as external surfaces and are the preferred method for large or complex components.

There have been significant advances in the zinc phosphate industry in the last 8 years. Application processes can be run at lower temperature (110F) with less sludging (disposal), which reduces the overall operating cost. Crystal size, morphology and coverage have been optimized to give consistent performance in conjunction with high performance coatings. Functional capabilities have been enhanced.

Low alloy steels previously required a preliminary abrasive blasting operation to remove excessive surface carbon and oxidation products. Failure to perform this operation resulted in surfaces with 20-50% coverage of zinc phosphate crystals and unsatisfactory coating performance. Alkaline cleaning/zinc phosphating technology that can provide the same alloy with 100% crystal coverage at less than 0.5 micron size without the need for abrasive blasting is commercially available.

Improving the chemical robustness of the system has its drawbacks however. Previously both organic and inorganic contaminants often could be detected by the lack of crystal coverage over the contaminated surface on the scanning electron microscope. Now the contaminated surfaces appear to have the same quality and coverage of crystals as the clean surface. It is the bond strength of the zinc phosphate crystal to the substrate that has

been compromised. Failure analysis now requires more stealthy analytical methods to determine the type and degree of contamination.

Chromate conversions (MIL-C-5541) have been the benchmark for pretreating aluminum alloys for the military. Due to the hexavalent chromium content in the chemistry, alternatives are being sought.

Corrosion Resistance Testing

To establish benchmarks that could have high statistical correlation to actual exposure conditions, GM 9540P-Accelerated Corrosion Test (ACT) was selected as the protocol for establishing corrosion resistance.¹ The merit of this protocol is derived from its thermal and moisture cycling, which induces mechanical stresses in the coating system. In other words, this test mimics the real-time fatigue of a coating system in a corrosive environment; it is not just a corrosion test. ACT has become an accepted industry standard and is a readily available protocol at independent test laboratories. Test panel substrates were cold rolled steel (CRS), galvanized steel (G 90), AA 5083-H231 and AA 6061-T6.

Both electrocoat epoxies as well as spray epoxies were evaluated. Products were military approved or commercially advertised as having exceptional levels of corrosion resistance. Seven products from five manufacturers are provided in the listing. It should be noted that comparative data from two additional products was purposely omitted. These two products displayed a significant variation in ACT results at two different test facilities. It is not without coincidence that these same two products have demonstrated significant variations in 336 hr salt spray process control test results over time. The source of the variability cannot be established at this time. It is believed that the variation is more likely attributed to variations in the wet paint (lack of process control, solvent manipulation or additive change or omission by the paint manufacturer) than variations in the test laboratory.

All substrates were cleaned (water break free) and pretreated as noted. Surface profiles were established with replica tape. Some received a combination of both abrasive blasting and chemical pretreatments. One product tested recommended a specific surface profile prior to primer application. Some manufacturers are required to abrasive blast the surface prior to chemical processing due to poor storage/handling conditions that create unacceptable levels of corrosion or purchase hot rolled steel with unacceptable levels of mill scale.

Some test coupons were prepared over knowingly inadequate zinc phosphate pretreatments to assess the impact on performance. An unacceptable pretreatment is considered one that has less than 70% crystal coverage by scanning electron microscope evaluation at 500x. High performance coatings have demonstrated that they are capable of providing adequate protection even with marginal pretreatments. Marginal coatings, however, require almost perfect pretreatment conditions to achieve even a minimal level of performance. Unless otherwise noted, the zinc phosphate pretreatment had 100% crystal coverage. All test panels were cured a minimum of 7 days prior to scribing to assure a fully cured condition.

Testing was conducted at four facilities. In many cases duplicate panels of a particular system were tested at two facilities or at the same facility at different times. Test results were averaged on a minimum of six replicates. Coating dry film thickness was reported as the mean value of the range (six readings per test coupon). The range of coating dry film thickness (dft) was a function of the application process. Electrocoated test coupons had the same dft (relative to dft readings recorded to the nearest 0.1mil) over the entire test surface. On sprayed test panels the range varied from 0.2-1.7 mils on a single panel. Typically, the higher the solids content of the coating the greater the applied range.

A significant limitation of the GM 9540P protocol is the method of evaluation after exposure. The test panels are typically rinsed and subjected to high-pressure air to remove any loose primer; occasionally the air nozzle tip may be used to loosen the corrosion scab. Many coating systems fail by cathodic disbondment. This current automotive method was not considered adequate to address this failure mechanism. Consequently, the evaluation protocol was modified.

All test coupons were scraped at a 30-degree contact angle to the test surface with a blunt-edged, 1.5-inch-wide metal putty knife prior to evaluation. To demonstrate the difference in evaluation techniques, Figure 1 shows a test coupon after an "automotive" evaluation. The opposing image is the same test coupon after being scraped. The scribe creep goes from an intermittent condition to an almost continuous response along the scribe line. The maximum scribe creep measured from one side of the scribe increased from 1.6 mm to 1.7 mm.

The failure criteria for steel and galvanized surfaces was the same criteria used since 1985 by the Tank Automotive and Armaments Command (TACOM) for the system of pretreatment and primer contained in TT-C-

490, "Cleaning Methods for Ferrous Surfaces and Pretreatments for Organic Coatings." If any of the following four conditions was met, the test coupon was considered to have reached "failure:"

1. Primer creep, blistering or loss of adhesion relative to a scribed line applied prior to corrosion testing was equal to or exceeded 0.125 inch at any point at the scribe (maximum creep measured from one side of the scribe).
2. Corrosion in the field exceeded rust grade No. 9, ASTM D610 on ferrous surfaces.
3. There were more than five blisters in the field in any 24 in² area.
4. Any single blister exceeded 1 mm.

These criteria are considerably more liberal than most current automotive standards.

The benchmark for aluminum systems was established from a prior internal study using two aluminum alloys, two epoxy primers and two thickness criteria. 160 cycles of GM 9540P were required on AA 5083 and AA 6061 test coupons with a chromate conversion before any primer could be scraped from the scribe. There was no degradation in the field.

The test coupons were generally kept in the ACT cabinet until failure criteria had been met (test to failure). When the corrosion scab or paint eruption met the 0.125 inch criteria, the coupon was scraped. Some coupons were removed at a predetermined stop point such as 40 or 80 cycles.

The epoxy coating on the galvanized and aluminum coupons normally does not erupt around the scribe line as on CRS. These materials must be scraped to determine coating failure.

TABLE I - Primer System Longevity

Substrate	MIL-C-5541	Abrasive Blast (MIL)	Wash Primer	Zinc Phosphate	Primer ID	VOC (lb/gal)	dft (mils)	Cycles to Failure	Comments
AA 5083						4.3	1.3		0.0 scribe creep
AA 6061	X				H1	4.3	1.2	160+	0.0 scribe creep
AA 5053	X				H1	4.3	1.3	160+	0.0 scribe creep
AA 6061	X				R1	4.3	1.2	160+	0.03-in scribe creep
AA 6061	X				R1	0.3	0.8	160	0.0 scribe creep
AA 5083	X				P1	0.6	3.9	160+	96-hr delay after blast before prime
		1.6			D2			48	0.07-in scribe creep
G90				X		0.3	0.6		0.03-in scribe creep
G90				X	P1	4.3	1.1	80+	
G90				X	H1	2.8	5.9	40+	
CRS				X	S3	4.3	2.1	26*	
CRS				X	H1	3.2	3.4	63	
CRS		0.9		X	H2	0.3	0.8	59*	field failure
CRS				X	P1	0.6	4.4	53	
CRS		1.2		X	D2	3.2	1.5	52	
CRS		0.9		X	H2	0.6	1.2	44	
CRS				X	P2	0.6	1.2	44	field failure
CRS		1.2		X	P2	3.2	0.9	35	
CRS		0.9	X		H2	3.2	3.6	28*	
CRS		0.9		X	H2	0.6	3.2	24*	
CRS		1.2		X	D2	3.2	3.5	23	poor quality treatment
CRS			X		H2	3.2	2.0	23*	
CRS		0.9			H2	0.6	3.7	18	
CRS		1.2	X		D2	3.2	1.7	15	
					H2			12	

Notes:

1. Dft is direct reading. There was no correction for surface profile. The reported value is the mean of the range.
2. * Indicates extensive coating disbond from scraping as compared to the visual observation for blistering and corrosion at the scribe line. Cycles to failure was reduced based upon this observation.
3. Scribe creep is rated from one side of the scribe line at the maximum value.

4. 40 cycles (40 days) of GM 9540P is approximately equal to 5 year performance with respect to corrosion.
5. The alpha designator in the primer ID identifies the paint company.

Once the coupon was scraped, the test panel was retired from further corrosion testing. If the failure criteria had not been met at this interval, a plus (+) designation was added to the duration. Noting the scraping procedure, the amount of scribe creep could be considerably greater than that visually observed in the cabinet at the point of removal. Those coupons whose scribe creep increased by scraping more than 0.031(1/32) inch than that recorded prior to scraping were so noted by an asterisk following the number of cycles. The number noted represents a deduction of 4 cycles for every 0.031 inch increment greater than 0.156 inch of scribe creep (for example, a maximum scribe creep of 0.236 inch after scraping would have 10 cycles deducted from the original rating).

Beyond Corrosion Resistance

An appropriate engineering decision could be made with respect to a given coating system from this data alone only if the following two conditions are met: 1) the coated product was in a static application not subject to flex or chipping conditions and 2) the product was not subject to direct sunlight (UV exposure).

TABLE II - Flexibility

Primer ID*	dft	Direct Impact (in-lb)	Reverse Impact (in-lb) **
P1	0.8		160
P1	1.0	160	160
P1	1.2	160	160
H1	1.2	120	6
H1	1.7	50	< 4
H3	1.0	40	4
H3	1.3	50	< 4
N2	1.5	35	6
N2	3.1	45	< 4
S2	1.6	40	8
S2	2.1	40	< 4
S2	2.6	40	< 4
S2	3.4	16	< 4
		8	

* VOC of H3, N2 and S2 primers is 3.5 lb/gal

** A coating with an impact value less than 6 in-lb is categorized as brittle (ASTM D 2794). All test coupons were a minimum of 30 days.

Although epoxies are known for their exceptional corrosion and fluid resistance they suffer from two weaknesses. Epoxies show an inverse relationship between dft and flexibility. Consequently, if you need to increase the dft to get corrosion resistance, you are compromising chip resistance in the process. Various tests are used by the industry to assess flexibility of the coating. Those that best accommodate high strain rates reflective of stone pecking damage are the impact tests per ASTM D2764, STM for Resistance of Organic Coatings to the Effects of Rapid Deformation (Impact) and the various automotive gravelometer tests based upon SAE J400, Test for Chip Resistance of Surface Coatings. A comparison of five epoxies with respect to direct and reverse impact is provided in Table II. The criteria for rating were no cracking by unaided visual observation or disbond (tape) of the coating.

A more insidious problem with epoxies is their poor UV resistance, which degrades the performance of the coating (commonly referred to as chalking) via direct degradation or photolytic oxidation.^{2,3} Although it is general knowledge that you don't expose epoxies to UV, there is the belief that applying a topcoat will always shield the epoxy. This assumption can have devastating consequences. There is no accepted method for accelerating UV exposure with a real-time correlation. The best protocols are developed around xenon arc or the use of mirrors to track and intensify light exposure in a desert climate coupled with moisture. Many use the UV test protocols to measure changes in color or gloss over time. The serious damage occurs when the topcoat is transparent to UV transmission allowing the epoxy to degrade and generate a disbond between the primer and topcoat.⁴

Many manufacturers have consequently added proprietary UV absorbers or reflective pigments in their topcoats to protect the epoxy. As the user can't readily verify this addition there must be considerable trust in both the topcoat suppliers chemistry and manufacturing controls to provide a consistent, compliant product. Adding excessive pigment to a topcoat formulation (flat gloss) in the belief that it will block the UV photon is not a valid remedy.

Two problems are associated with flat topcoats:

1. It has been theorized that when the pigment volume concentration (PVC) exceeds approximately 50%, close packing of the pigment particles generates scattering within the coating rather than reflection of the UV energy. The generation of more free radicals increases the probability of degrading the binder.⁵ The low binder content of low gloss coatings inherently provides for lower resistance to UV degradation.
2. Heavily pigmented topcoats may exceed the critical pigment volume concentration (CPVC) due to variations in product batching or improper mixing ratios by the applicator in 2K systems. High PVC topcoats have been found to have microcracking in field systems. The microcracking not only makes cleaning difficult but also generates crevice corrosion problems. The topcoat deterioration also provides a pathway for the UV to contact the epoxy primer.

Results Based on this research, we can draw some definite conclusions:

1. The use of abrasive blasting as the sole surface pretreatment for epoxy primers does not provide adequate protection to the substrate-coating system when the surface is subject to flex and chipping. An aggressive surface profile dictates the use of even greater dry film thicknesses to cover the substrate peaks, which further degrades epoxy flexibility.
2. Wash primer is the worst possible option for a surface pretreatment on steel. It not only has serious environmental issues but also provides no significant performance improvement to the coating system. If the only two options are abrasive blast and wash primer, the abrasive blast option is the preferred approach.
3. The more passive the substrate, the longer the coating system is capable of lasting.
4. Due to the limited film thickness capabilities of electrocoat primer (without special modification of the process parameters), the use of abrasive blasting in conjunction with electrocoating will reduce the performance capabilities of the system. It is still preferred to the alternative approach of trying to coat directly over corrosion.
5. A poor quality zinc phosphate pretreatment can decrease the longevity of an epoxy primer by more than 50%.
6. Environmental constraints have forced paint manufacturers to reduce the VOC of their primers. Unfortunately, all sprayed primers tested to date show a significant drop in the performance level of their low-VOC epoxies compared to the higher VOC versions. The typical response has been to often increase the dft by 50% or more to obtain comparable corrosion performance. The solvent/surfactant package in the wet paint has a major impact on film adhesion properties. Surface wetting facilitates chemical bonding to the pretreatment. Too much wetting, however, can be just as detrimental as not enough.⁶ Thin film, high-solids coatings appear to suffer from poor surface wetting. When high-solids epoxies are applied at thicker levels, the tack time tends to increase. This longer tack time indicates a higher solvent concentration per unit surface area of substrate, allowing for film leveling and surface wetting. The over zealous use of tail solvents alone is not the solution but rather the intelligent blending of various solvents/diluents to obtain a fully cured, homogeneous film. The solvent blends, however, must be compatible with the curing facilities of the applicator. Numerous field coating failures have been noted where the excessive primer film build in conjunction with inadequate curing have created adhesion failures due to solvent entrapment.
7. The lowering of VOC levels with the resultant increase in dry film thicknesses have resulted in finished products with continually receding levels of chip resistance and flexibility. This may be a direct response to formulators lowering the molecular weight of the resin. The response to this situation in conjunction with unquantifiable levels of UV resistance provided by a topcoat warrants a change in coating system design. The addition of a flexible UV barrier or the replacement of sprayed epoxies with thermoset polyurethane primers are possible options. A third option is to use curing agents that improve flexibility by decreasing the cross link density.⁷
8. There are no two epoxy primers tested thus far with equivalent levels of performance at the same film thickness.

The reliance on the salt spray test (which has no correlation to real time exposure) for product development and qualification may be responsible for many misconceptions in the non-automotive coatings industry. Coating formulation is highly complex chemistry, and the degradation mechanisms are no less complex. The formulator at a minimum must have knowledge and control of the molecular weight of the resin, crosslink density of the cured

polymer, plasticizer and surfactant additives and pigment type/concentration. These factors have a major impact on the adhesion, corrosion resistance, fluid resistance (for example, water, gasoline, hydraulic fluid or decontamination solvent) and flexibility of the final film. The coating chemist must rely on meaningful physical testing to confirm the actual performance of his engineered product. The variables involved and possible synergisms, either positive or negative, are too complex to intuitively predict any outcome.