Formulated Didecyl Dimethyl Ammonium Bicarbonate/Carbonate (DDABC), a Multi-Metal Corrosion Inhibitor with Relevance to Commercial Surface Preparation and Coatings Technologies

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Abstract

A new water soluble quaternary ammonium compound, didecyldimethylammonium bicarbonate/carbonate (DDABC), has been evaluated as a corrosion inhibitor via standard electrochemical tests on steel and shown to be highly effective. At the proper dilution, the inhibitor migrates to the metal/solution interface and forms a mono-molecular film on the anodic sites. Preliminary evaluations reported here indicate that DDABC and its phosphate and glycolate anion derivatives also exhibit a remarkable ability to improve the corrosion performance of several commercially relevant coatings including latex, alkyd, and urethane e-coat systems when used either as a pretreatment, sealing rinse, or formulated coatings additive. In some instances, DDABC provides corrosion performance enhancement in B117 salt spray tests of over 300% and creep improvements of 60–75%. Additional observations as an adhesion promoter, wetting agent and flash rust inhibitor are also reported.

Introduction

The danger of corrosion always exists in processes where metal surfaces come in contact with water, whether as liquid water or humid air. Unprotected metals are particularly problematic and corrosion inhibitors either as temporary or permanent agents are often employed. Thus, a very large market for corrosion inhibitors exists in the manufacturing, chemical, and petrochemical industries.[1] There has been much study into the mechanisms by which corrosion inhibitors reduce corrosion,[2,3] and many inhibitor categories exist including film-forming, anodic, cathodic, oxidizing, non-oxidizing, organic and inorganic.[4] Anionic inhibitors comprise the majority of corrosion inhibitors, but organic cationic corrosion inhibitors are also known.[5,6] These corrosion inhibitors can work either alone as flash passivation agents on metal surfaces for temporary corrosion protection or in conjunction with a more permanent coating system whether organic, inorganic, or some combination thereof.

Coatings commonly provide a means of barrier corrosion protection on bare metal surfaces, but steel for example does not form a good bond with organic coatings. Thus, conversion coatings are often used to both inhibit corrosion and to assure good paint adhesion. In this context a conversion coating refers to a protective barrier film or layer on the metal substrate surface simultaneously capable of promoting both corrosion inhibition and paint adhesion. The conversion coating may be comprised of either (i) an organic film, (ii) an inorganic oxide resulting from a metal etching and redeposition process, (iii) an inorganic oxide resulting from a true deposition process, or (iv) any mixture thereof. The most widely used conversion coatings are inorganic and derived from chromating, phosphochromating and iron or zinc phosphatizing processes and these are typically applied by either immersion or spraying. Chromate or phosphate conversion coatings are chemically reacted with the steel to form a rough surface structure with metal-phosphate platelets that provide both mechanical and chemical keying (adhesion) of an organic coating to the metal surface.[7] While chromate and phosphochromate based systems are commonly used, health, safety and environmental concerns require other alternative types of conversion coatings such those based on organic thin films.[8]

Quaternary ammonium compounds containing chlorides are known to be both surface active materials and biocides, but typically exhibit high corrosivity with metals. Recent literature reports demonstrate replacement of the chloride with bicarbonate/carbonate anions results in an effective corrosion inhibitor capable of passivating a wide range of commercially relevant metals including steel, aluminum, copper, zinc, brass, tin and silver.[9] Specifically, didecyldimethylammonium bicarbonate/carbonate (DDABC), Figures 1 & 2, is reported to be particularly effective as a multi-metal corrosion inhibitor.

Important for this work, DDABC also has the potential to react with protic acids such as phosphoric and acetic found in several commercial coatings and pretreatments. This reaction formally liberates CO_2 and results in true anion replacement according to
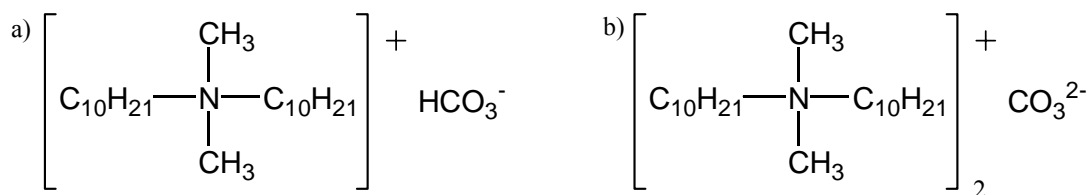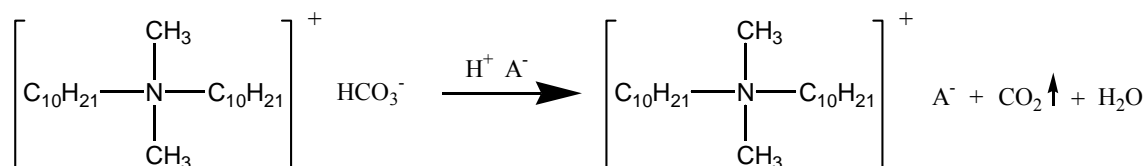

Figure 1: The chemical structures for didecyldimethylammonium a) bicarbonate and b) carbonate. Commercial materials typically contain mixtures of both a and b and are referred to here collectively as DDABC.

Figure 2: Corrosion performance of 1010 steel panels partially immersed in DI water for nine months with the different inhibitors at 0.10% active level: a) didecyldimethylammonium chloride (DDAC) and b) didecyldimethylammonium bicarbonate/carbonate (DDABC).

Equation 1. Note that the reaction equilibrium lies far to the right and is driven to completion by liberation of CO_2 gas.

$$\left[C_{10}H_{21}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}}-C_{10}H_{21} \right]^+ HCO_3^- \xrightarrow{\;H^+\,A^-\;} \left[C_{10}H_{21}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}}-C_{10}H_{21} \right]^+ A^- + CO_2\uparrow + H_2O$$

Eqn. (1): Anion replacement affected by reaction of a protic acid H^+A^- with DDABC.

This paper presents the corrosion inhibition mechanism for DDABC and reports unique aqueous concentration dependent behavior relevant to formulation work. Also presented are preliminary results probing the use of DDABC as a surface finishing compound either as a flash rust inhibitor, a metal surface pretreatment, a sealing rinse over iron phosphated steel, or as a coatings additive in several organic coating systems.[10] Specific attention is given to relevant anion replacements including phosphate and glycolate where appropriate.

Results and Discussion

Corrosion Inhibitor Evaluation

Concentration Effects on Thin Film Formation – The film-forming tendencies of neat DDABC at two levels were tested on 1010 steel in deionized water using electrochemical impedance spectroscopy (EIS), Figure 3. The observed data indicates a significant difference in behavior between the high and low DDABC concentrations. The low 0.05% DDABC level showed a measurable capacitive effect at the low frequencies (left side of Figure 3) indicative of a barrier film. If the film is approximated as a parallel
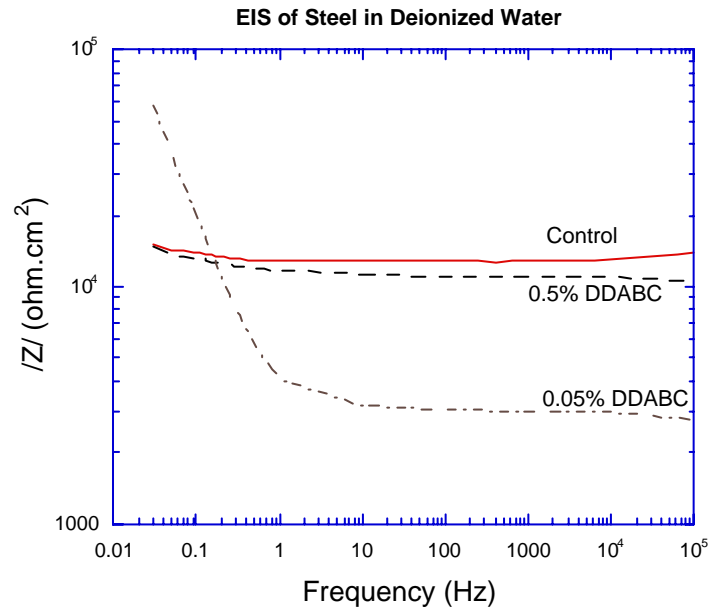
EIS of Steel in Deionized Water

Figure 3: EIS measurements of DDABC at various concentrations in DI water on steel.

plate capacitor, then the thickness of the film may be estimated.[11] All estimates show that the film is only 0.5 nm in thickness (assuming a dielectric constant of water, $\varepsilon = 80$), and in the present case, this correlates to an absorbed film of approximately one monolayer thick.[12] However, the higher 0.5% DDABC level clearly exhibits no such measurable thin film and behaves in fashion similar to the water control. Significantly, DDABC also exhibits an interesting concentration dependent behavior with respect to polarization resistance (Rp) measurements in the same concentration region. As shown in Figure 4, both dilute and concentrated DDABC solutions exhibit very low Rp, but at an optimal level of ca. 0.05% exhibits extremely high resistance. Polarization resistance correlates directly with corrosion resistance, and taken together these observations indicate a thin film capable of imparting high resistance at optimal concentrations. However, at either low or high concentrations no such thin film results. It is also noteworthy that this film can be destroyed or damaged by polarizing the metal either −20 mV or +20 mV. Indeed, the Rp for 0.05% DDABC is off-scale for the first measurement, but the test disturbed the surface film and the second Rp measurement resulted in the lower value plotted at point #2.

Figure 3 also suggests a potential explanation for this concentration dependent behavior. The solution resistance range (the high frequency impedance on the right side,
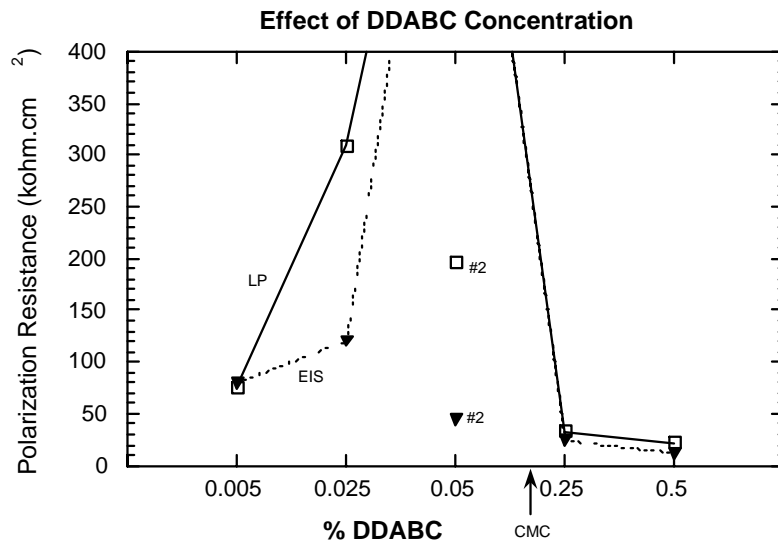
Effect of DDABC Concentration

Figure 4: Polarization resistance as measured by EIS and LP as a function of DDABC concentration in DI water on steel.

Figure 3) shows a minimum (3,000 ohm) for 0.05% DDABC. This indicates that at 0.05% DDABC, sufficient carbonate anions and quaternary cations remain in solution, increasing its conductivity. However, the 0.5% DDABC only shows three times higher resistance (10,000 ohm) despite the fact it is ten times more concentrated. DDABC molecules which are clustered in micelles at high concentrations provide one potential rationale for this discrepancy. The critical micelle concentration (CMC) was determined by measuring the surface tension and was estimated to be 0.10% DDABC.[13,14] However, a recent report demonstrates a more complicated equilibrium behavior in solution with at least three distinct micelle and aggregate structures present.[15] Figure 5 provides the relevant pictorial explanation that at high concentrations DDABC forms micelles which aggregate the majority of the inhibitor molecules into a rod shaped aggregate. In this form, DDABC is not energetically available to adsorb onto the metal surface. However at low and moderate concentrations, trimeric aggregates exist in kinetic equilibrium with spherical micelles in solution which are able to interact with the metal surface. As long as sufficient concentration exists to afford an effective, continuous, thin film, corrosion inhibition will result. Thus the observed DDABC concentration dependence on corrosion performance can be understood in terms of both solution micelle behavior and sufficient thin film formation.
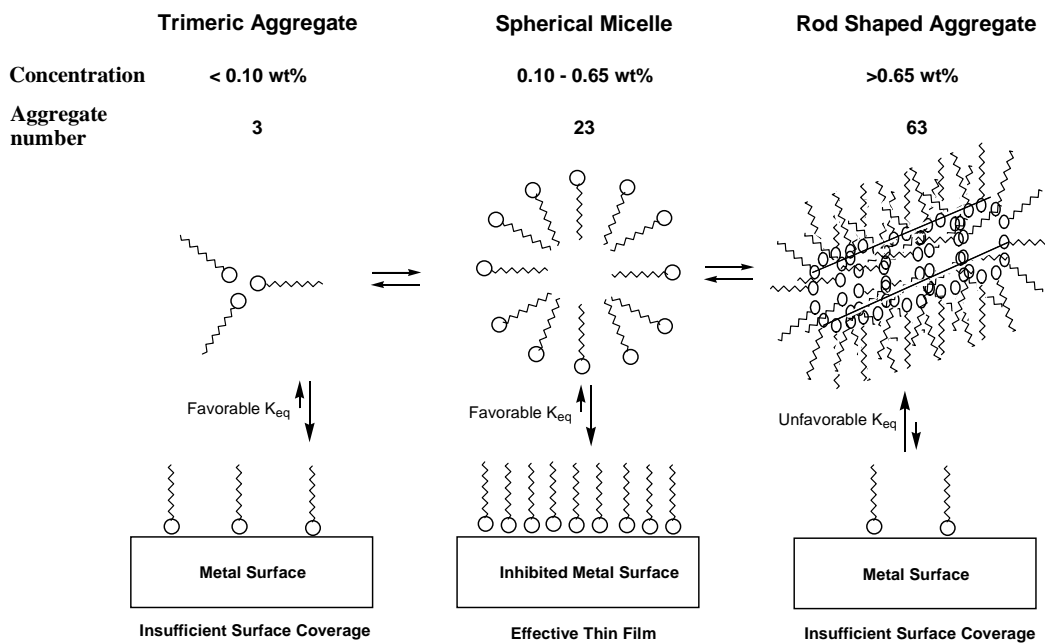
Trimeric Aggregate	Spherical Micelle	Rod Shaped Aggregate

	Trimeric Aggregate	Spherical Micelle	Rod Shaped Aggregate
Concentration	< 0.10 wt%	0.10 - 0.65 wt%	>0.65 wt%
Aggregate number	3	23	63

Favorable K_{eq} Favorable K_{eq} Unfavorable K_{eq}

Metal Surface	**Inhibited Metal Surface**	**Metal Surface**
Insufficient Surface Coverage	**Effective Thin Film**	**Insufficient Surface Coverage**

Figure 5: Schematic revealing complex DDABC aggregation and micelle behavior changes as a function of concentration.

Linear Polarization (LP) Results – Linear polarizations for steel in DI water are shown in Figure 6 where circuit potential versus current density is plotted. Note that a direct relationship between the line's slope and corrosion resistance exists and high positive slope indicates greater corrosion resistance. The data reinforces information from the EIS plots in that low slopes (low corrosion resistance) are observed for high DDABC concentration of 0.5% in the same region where a thin film was not observed. However, the slope's magnitude increases with decreasing DDABC concentration for a maximum at 0.05% in the region where a thin film is expected. The slope then drops again predictably at lower than optimal concentrations of 0.025 and 0.005% presumably due to insufficient thin film surface coverage.

One abnormality in the LP results was noted which is related to the response the thin film to applied voltage. In the first test at 0.05% DDABC, the curve was vertical, or even perhaps negative. In the second test run a few minutes later on the same sample, the curve has a more linear slope, although steeper than the other concentrations. This abnormal response indicates an adsorbed film which was blocking the anodic and cathodic sites, which is then damaged during the polarization. This effect is the same for 0.05% DDABC whether the LP is run in the positive or negative directions. While linear polarization is generally considered a non-destructive, reproducible technique, this appears not to be the case for the 0.05% DDABC. Noteworthy, LP indicates the amount of current passed in 0.05% DDABC (#1) is approximately one electron charge per square nanometer, which would be the magnitude for one adsorbed quaternary ammonium cation per square nanometer.
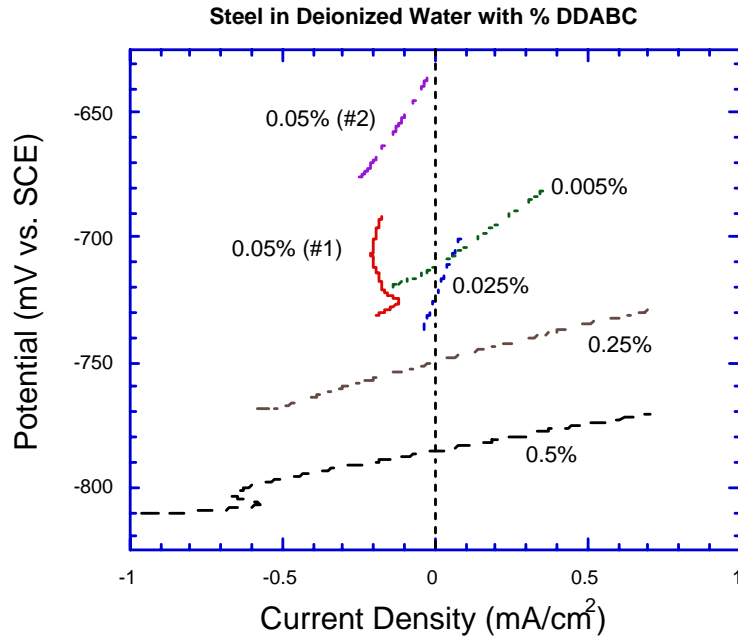
Steel in Deionized Water with % DDABC

Figure 6: Linear polarization measurements on steel at various DDABC concentrations in DI water.

Potentiodynamic Polarization Potentials – The PDP tests for steel in DI water are shown in Figure 7. Consistent with other results, we see that concentrated 0.5% DDABC is almost the same as the uninhibited DI water. However, the 0.05% DDABC has a ten times lower passive current. In this system, the DDABC acts as an anodic inhibitor, lowering the anodic current by ten times.
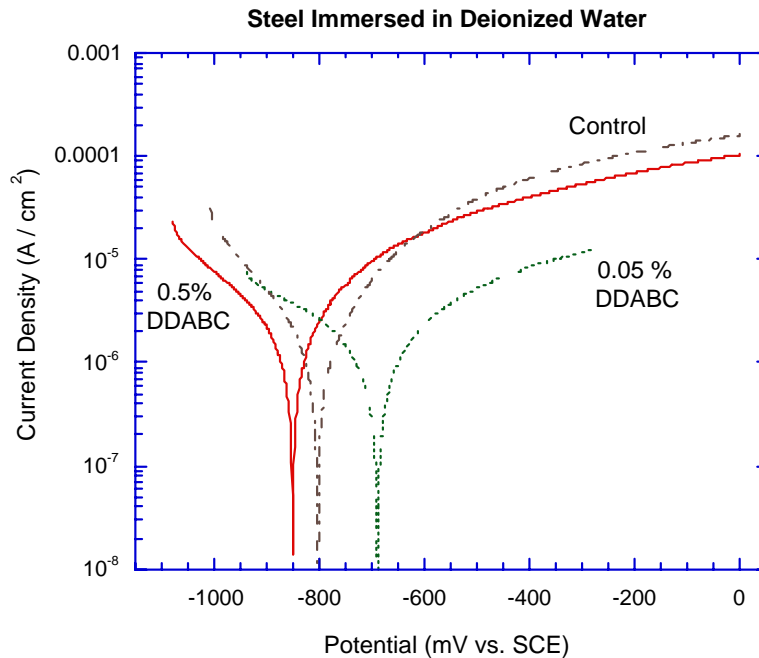
Steel Immersed in Deionized Water

Figure 7: Potentiodynamic polarization measurements on steel at various DDABC concentrations in DI water showing passivation.
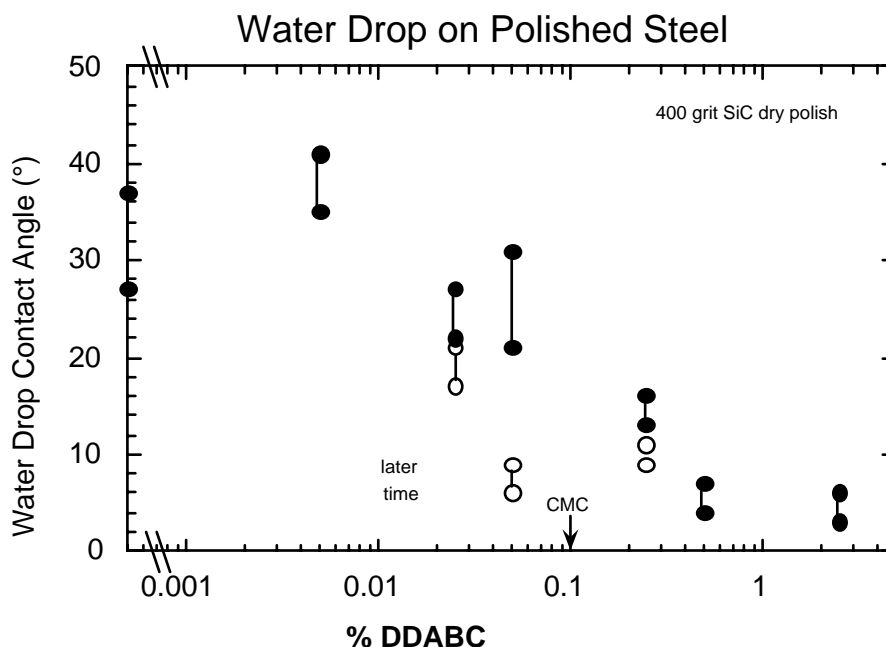
Figure 8: Water drop contact angle measurements on untreated steel at various DDABC concentrations. At midrange concentrations, DDABC exhibits dynamic wetting properties.

Contact Angle/Wetting Ability – Neat DDABC serves as a powerful wetting agent with observed dynamic wetting properties. Water droplets typically bead on steel with a contact angle of about 30°. Increasing concentrations of DDABC employed in the water droplet results in lower contact angles with polished steel to a limit of less than 5°, Figure 8. The mid-range 0.025–0.25% DDABC solutions exhibit true dynamic wetting characteristic of spreading and creeping across the surface with time (5–10 minutes) as indicated by open circles in Figure 8. This effect was most noticeable for 0.05% DDABC and is likely related to a decrease in surface tension expected near the critical micelle concentration (CMC).[16]

Anion Replacement Screening

As discussed previously, DDABC is reactive towards protic acids in aqueous environments, releasing CO_2 via chemical reaction and resulting in anion exchange. Because of the reaction potential within acidic e-coat processes or other pretreatments which employ acids such as mineral or short chain organic, selected DDABC anion replacements were screened for corrosion inhibition properties, Table 1. Since several anions are shown to provide poor DDABC corrosion inhibitor adducts, these anion replacements should be avoided. From this screening work, phosphate and glycolate anions emerged as particularly effective corrosion inhibiting adducts while sulfate, chloride, citrate, and acetate were notably ineffective. Additionally, through the use of more or less than stoichiometric amounts of acid HA, a specific final pH can be targeted. Thus, titration of DDABC concentrate with phosphoric acid to a final pH of 4.0 results in

Table 1: Corrosion performance behavior of several common anion replacements.

Anion (A)[*]	Corrosion Result [§]
DDABC (Carbonate/ Bicarbonate)	no corrosion
Phosphate	no corrosion
Glycolate	no corrosion
Borate	slight corrosion
Acetate	moderate corrosion
Citrate	moderate corrosion
Chloride	heavy corrosion
Sulfate	heavy corrosion

*Neat DDABC material was titrated to a pH of 7.0–7.5 with the requisite conjugate acid, then diluted to a working concentration of 0.10% quaternary active for corrosion screening.

[§]Partial submersion of 1010 unpolished steel in deionized water overnight.

phosphoquat 4.0 (PQ4.0). Likewise, titration of DDABC with glycolic acid to a final pH of 7.5 results in partial replacement of carbonate to provide glycoquat 7.5 (GQ7.5). These materials can then be diluted to active use levels.

Preliminary Pretreatment and Coatings Evaluations

Flash Rust Evaluation: Humidity chamber testing on dip pretreatment samples of 1010 steel provided an indication as to the general flash rust protection afforded by various DDABC derived materials. The data in Table 2 indicates that both the DDABC, phosphate, and glycolate materials are effective flash inhibitors in this system.[17] However, excess acids associated with the PQ4.0 and GQ4.0 materials had a very detrimental effect on flash rust performance, Figure 9.

Table 2: Total flash rust observed in humidity testing at 80°F and 95% relative humidity.

Compound*	Total % Rust at Time (h)			
	2	4	6	8
DDABC	10	15	15	25
PQ7.5	10	15	15	25
GQ7.5	10	15	15	25
Control (D.I. Water)	85	90	100	100
PQ4.0	81	100	100	100
GQ4.0	100	100	100	100

*Dip pretreatment times of 2 minutes on 0.10% active solutions with 1010 steel.

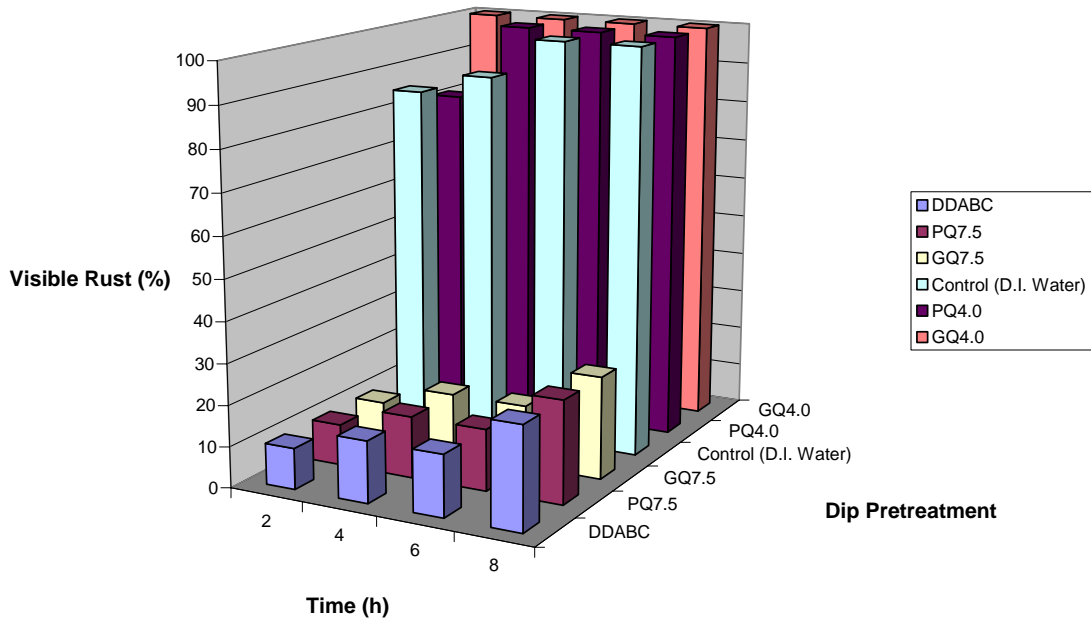**Humidity Test Total Flash Rust at 80F, 95% Humidity**

Figure 9: Humidity test results for flash corrosion on several DDABC derived materials.

E-Coating Pretreatment Evaluations – A series of unpolished 1010 steel coupons were exposed to various pretreatments containing DDABC solutions for 1 hour at room temperature, air dried, then subjected to a commercial urethane e-coating via procedure A. Panels were then evaluated for creep performance, with measurements at periodic intervals, Figure 10. From the data, a very noticeable improvement in peel performance
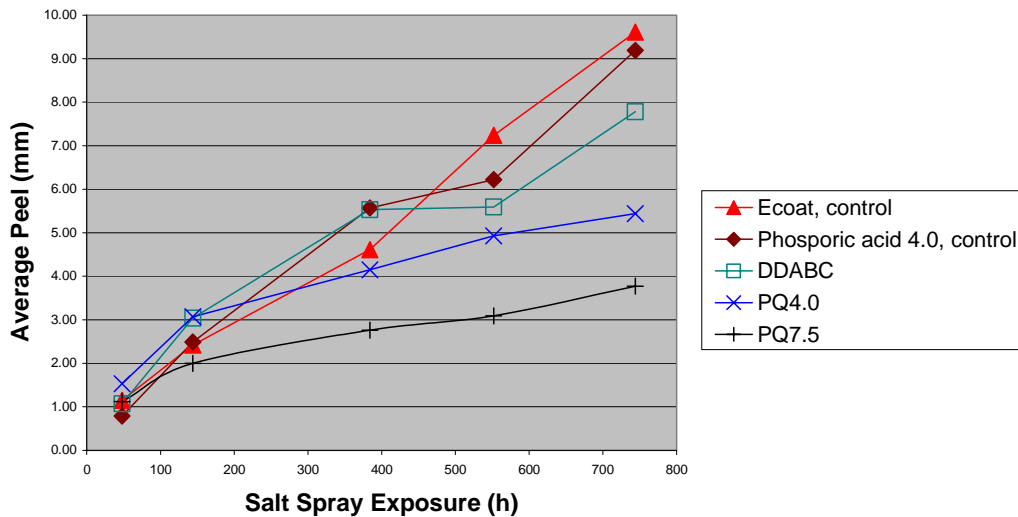
Creep Summary: E-coat Panels

Figure 10: Creep results from ASTM B117 salt exposure on commercial e-coat panels pretreated with various DDABC containing formulations.

is noted. All pretreatments here resulted in statistically significant creep improvements, but in the case of a partially neutralized phosphoric acid salt PQ7.5, the improvement is approximately 60%. Comparison of PQ7.5, PQ4.0 and neat phosphoric acid data suggests that at lower pretreatment pH values *in situ* iron phosphatization may be contributing to the overall corrosion performance but this is clearly not the case for the slightly alkaline PQ7.5 pretreatment.

Additional Pretreatment Evaluations – A series of unpolished 1010 steel coupons were dip pretreated with DDABC derived solutions for 1 hour at room temperature, air dried, then subjected to a commercial aerosol spray coating via procedure C. Creep performance from subsequent ASTM B117 testing is reported in Table 3. The data indicate very noticeable creep improvements of 40–60%. Of special note, the partially

Table 3: ASTM B117 salt exposure creep results from pretreated panels subsequently coated with commercial aerosol spray.

Water Used in Pretreatment	Pretreatment (1h, rt)	Paint System*	Creep Rating (mm) at 144h B117 salt spray	% Improvement over control
D.I. Water	PQ7.5	Commercial Aerosol	5.71	62%
D.I. Water	0.1% DDABC	Commercial Aerosol	7.63	50%
D.I. Water	Phosphoric acid 4.0 (control)	Commercial Aerosol	8.86	42%
D.I. Water	0.1% active PQ2.5	Commercial Aerosol	9.87	35%
D.I. Water	0.1% active PQ4.0	Commercial Aerosol	9.98	34%
None	None	Commercial Aerosol	13.89	NA
D.I. Water	None	Commercial Aerosol	15.20	NA
5% Salt Water	0.1% DDABC	Commercial Aerosol	7.36	40%
5% Salt Water	None	Commercial Aerosol	12.36	NA

*Alkyd based Rust-Oleum® high performance enamel (hunter green) according to procedure C.

anion exchanged PQ7.5 treatment afforded roughly similar creep improvements of ca. 60% both here and in the previous e-coat series. Comparison of PQ7.5, PQ4.0 and neat phosphoric acid data again suggests that at lower pretreatment pH values *in situ* iron phosphatization may be contributing to the overall creep performance, but this is clearly not the case for the slightly alkaline PQ7.5 pretreatment.

Sealing rinse evaluation on iron phosphated steel – A series of phosphated steel coupons (Q-panel, R-36-1) were exposed to various pretreatments containing DDABC solutions for 1 minute or 5 minutes at room temperature, air dried overnight, then subjected to humidity chamber testing at 80°F, 75% humidity for 12 h to determine flash rust performance. The results indicate that DDABC and its PQ7.5 analog provide very significant sealing rinse enhancements at both dip times tested, Figure 11. More importantly, these improvements translated into observable coating system enhancements when the panel was overcoated with a commercial aerosol spray (Rust-Oleum® brand aerosol spray professional high performance enamel, Hunter Green, procedure C). Indeed, corrosion results in ASTM B117 salt spray testing indicates

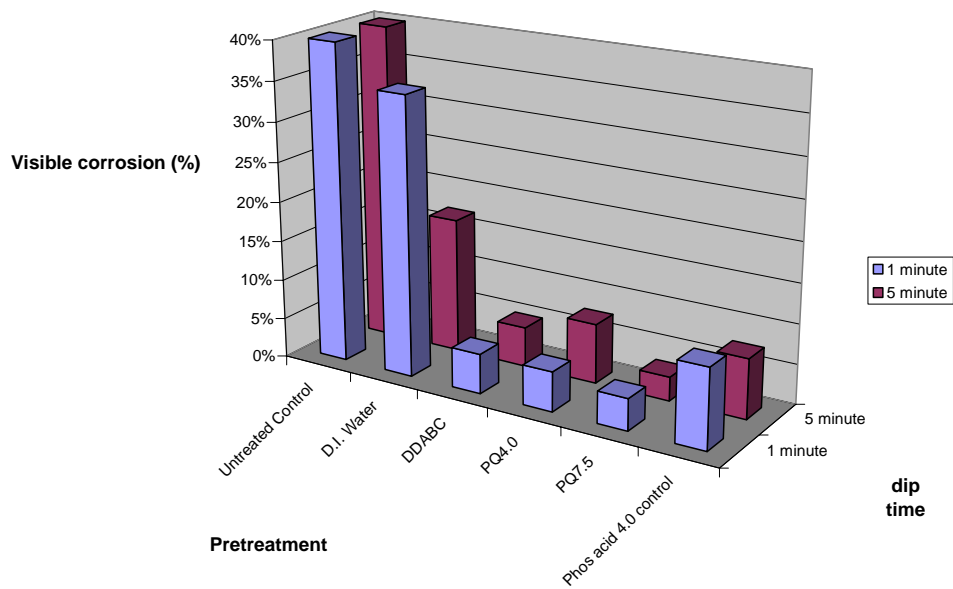## Humidity Test Results - Iron Phosphated Panels

Figure 11: Humidity chamber test results (12h, 80°F, 75% RH) on commercial iron phosphated panels subjected to various sealing rinses for 1 and 5 minutes at room temperature.

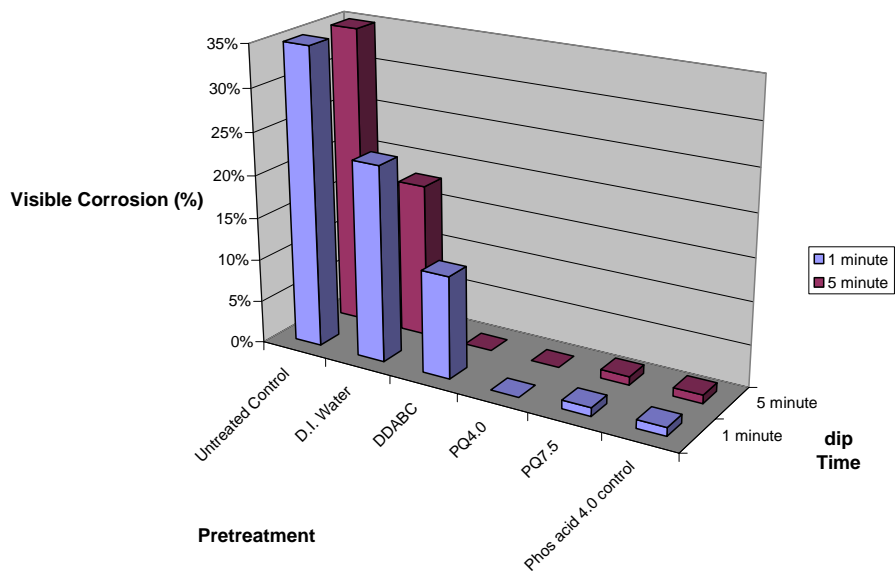## Salt Spray Results of Sealed, Coated Panels

Figure 12: ASTM B117 salt spray results on analogous panels from Figure 11 which were subsequently painted with a commercial alkyd aerosol spray.

parallel performance to that shown on the dip pretreatment panels, Figure 12. Thus corrosion performance associated with the sealing rinse also translated into the finished coating system performance when employed with a compatible paint system.

Spiked additive evaluations on commercial systems: In light of the performance observed as a flash inhibitor and as a sealing rinse, additional experimentation designed to probe performance as a coating additive was performed. Here the 1010 steel coupons employ no pretreatments, but rather three levels of active ingredient are spiked into a commercial aqueous latex formulation (Rust-Oleum Painter's Touch®, Hunter Green, procedure D). Noticeably better wetting, spreading, and fisheye performance occurred during panel preparation. Corrosion data (B117) in Figure 13 indicates that the optimal DDABC level of 0.5% active affects a very significant delay in the onset of visible rust of approximately 300% from 24 hours to nearly 300 hours. However, it is also clear that the high and the low active levels afford insignificant changes to corrosion onset times.

We attribute the strong concentration dependent behavior to the same kind of gross micelle structure behavior illustrated in Figure 6. As in the case of efficient thin film formation in neat water, a sufficient minimum DDABC concentration to afford adequate surface coverage is required. However, as previously seen in aqueous systems, the prevailing micelle structure (spherical versus rod-shaped) may also energetically limit the availability of the DDABC to interact effectively with the substrate surface resulting in an ineffective thin film. Thus, DDABC concentration optimization is critical since formulation ingredients may impact the effective DDABC concentration by altering the

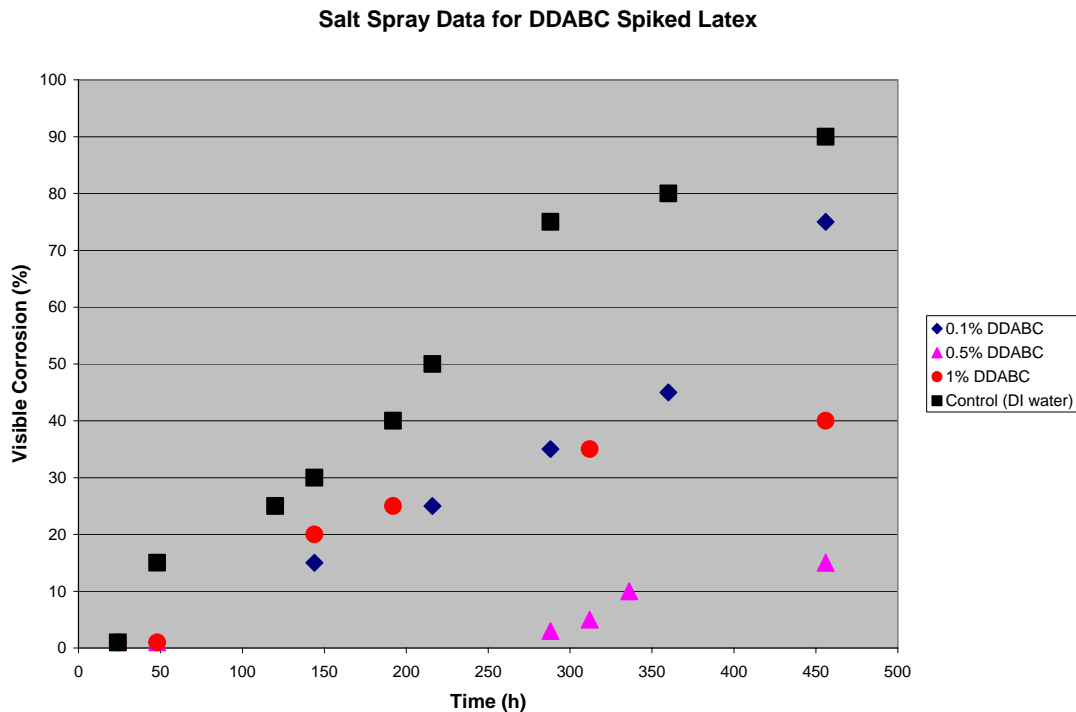**Salt Spray Data for DDABC Spiked Latex**

Figure 13: Onset of visible corrosion in ASTM B117 testing on commercial latex samples spiked with DDABC at three levels. Note that at optimal DDABC loadings, an improvement of over 300% is noted.
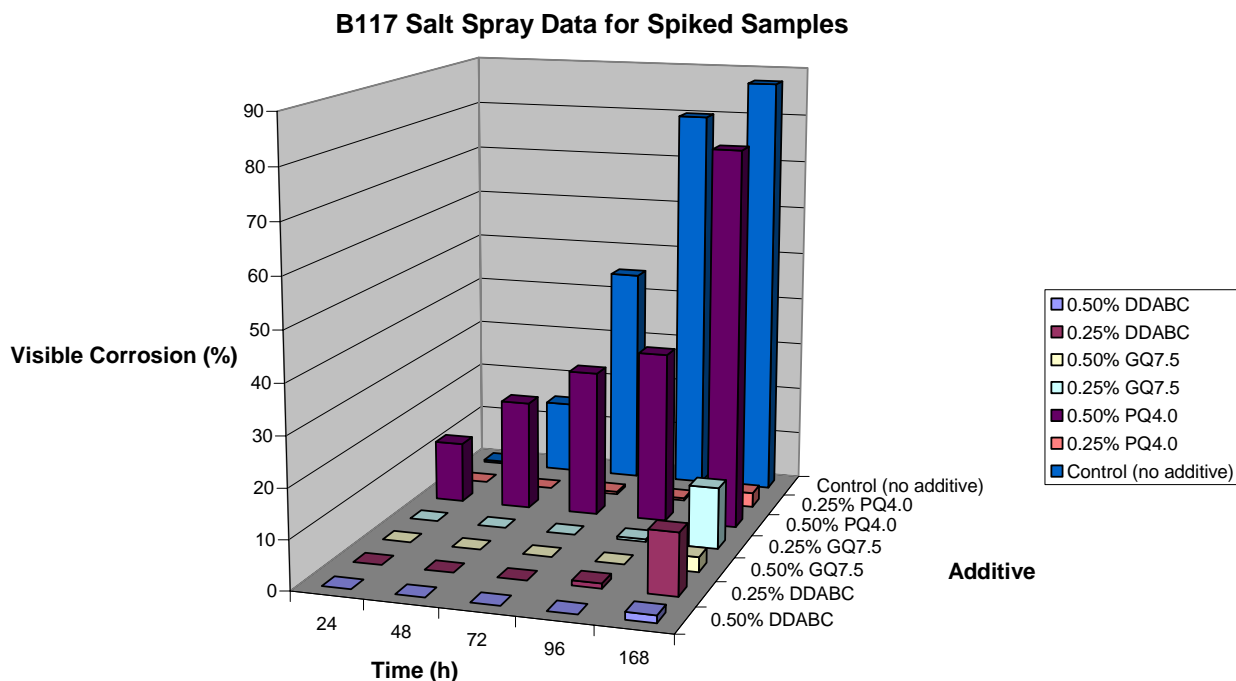
B117 Salt Spray Data for Spiked Samples

Figure 14: Onset of visible corrosion in ASTM B117 testing on commercial aerosol samples spiked with DDABC derivatives. At proper loadings, both DDABC, phosphoquat, and glycoquat analogs were able to significantly delay onset of visible corrosion by as much as 300%..

gross micelle structure and subsequent film forming tendencies in non-obvious ways.

The basic corrosion offset behavior noted above on an aqueous latex system also duplicated during similar spiking experiments on a solvent born enamel system, Figure 14. Again here the 1010 steel coupons employ no pretreatments, but rather two levels of active DDABC based ingredients spiked into the commercial solvent borne alkyd formulation (Rust-Oleum® Gloss Protective Enamel, Hunter Green). Significantly, examples of both carbonate anion based DDABC, phosphate anion and glycolate anion derivatives provide similar corrosion enhancement behavior in the systems studied.

Fully formulated prototype coatings formulations – Two prototype formulations including aqueous borne latex and a solvent borne alkyd were prepared with DDABC included at two arbitrary formulation levels of 0.25 and 0.50% active and evaluated. Appendix A provides detailed composition information on these systems which were formulated from scratch. For each formulation, both pre-treated and non-pretreated samples were prepared in triplicate according to procedure b and evaluated for creep and adhesion. Data shown in Table 4 confirms the ability of DDABC to improve creep performance in both systems. As seen previously, these creep data also indicate an important concentration dependence. The lower level of 0.25% DDABC affects a more significant creep improvement in the latex rather than in the alkyd where the higher level of 0.50% DDABC affects the greatest change. Also noteworthy, the dip pretreatment on the alkyd system provides all of the improvement DDABC afforded by inclusion into the formulation. This was not the case with the latex system where inclusion into the

Table 4: Summary of creep data observed in selected formulations. (in millimeters)

	Creep Control	0.25% DDABC	0.50% DDABC	Best % Improvement over control
Latex	1.06	0.25	1.18	76%
Pretreat Latex*	1.13	0.4	0.83	65%
Alkyd	0.56	0.41	0.37	34%
Pretreat Alkyd*	0.23	0.44	0.23	59%

* DDABC dip pretreatement times of 2 minutes were employed.

formulation gave the more significant improvement. Adhesion data presented in Table 5 confirms DDABC's ability to enhance adhesion in both systems. However, this data set presents a much more complicated juxtaposition of results between formulation level and pretreatment performance. This data also confirms other unreported results which suggest that optimal DDABC performance is very formulation and application specific.

Table 5: Summary of adhesion data in selected formulations. (in psi)

	Adhesion Control	0.25% DDABC	0.50% DDABC	Best % Improvement over control
Latex	1331.5	1561.8	1525.1	17%
Pretreat Latex*	1227.6	1485.3	1547.5	26%
Alkyd	2569.3	2486.8	3054.2	19%
Pretreat Alkyd*	1796.1	2655.5	1838.8	48%

* DDABC dip pretreatement times of 2 minutes were employed.

Materials and Methods

Test Solutions
All concentrations are expressed as percent active DDABC ingredient unless otherwise indicated.

Commercial DDABC – 50% concentrate (Tradename CarboShield® 1000), produced according to the Lonza Inc. process was used as received. DDABC is a 50wt% aqueous concentrate consisting of a nominal 50wt% DDABC, 40wt% water, and 10wt% propylene glycol. The bicarbonate to carbonate ratio is proprietary and an approximate molecular weight of 380 is employed in stoichiometric calculations. All amounts reported here are as percent active ingredient. Thus, a 0.10% active DDABC solution was prepared by dissolving 0.20 wt% DDABC in relevant water samples at room temperature with stirring; i) deionized water ii) tap water (Allendale, NJ) or iii) 5% Salt (NaCl) Water

Phosphoquat solutions – These are comprised of di-*n*-decyldimethylammonium (hydrogen) phosphate(s) prepared by adding to neat DDABC the requisite amount of 85% aqueous phosphoric acid required to obtain a specified pH. Additions are performed at ambient temperature in a magnetically stirred beaker at such a rate as to control foaming.

Glycoquat−solutions – These are comprised of di-*n*-decyldimethylammonium glycolate(s) prepared by adding to neat DDABC the requisite amount of glycolic acid required to obtain a specified pH. Additions are performed at ambient temperature in magnetically stirred beaker at such a rate as to control foaming.

Electrochemical tests

Steel (ASTM A366, 0.037% C, 0.19% Mn, 0.18% Cr) and (black, 0.030%C, 0.31% Mn, <0.10% Cr), aluminum (6061-T6, 0.6% Si, 0.3% Cu, 1.0% Mg, 0.2% Cr) were tested in 3.5% NaCl (salt content equivalent to seawater), and deionized water. The surfaces of the test samples were first dry sanded using 400-grit SiC, with the exception of the galvanized steel, which was tested in the as-received condition. Glass O-ring joints (20 mm ID) were clamped to the sanded surface with the O-rings lightly coated with Apiezon L vacuum grease. The glass joints were filled with 25 mL of the test solution. The open circuit potential (OCP) was measured immediately after the solution was poured in the tube using a saturated calomel electrode (SCE). The samples were covered and then allowed to equilibrate overnight, and tested the next day using the three-electrode method and the standard electrochemical methods described below.

Electrochemical Impedance Spectroscopy (EIS) – Impedance was measured at the OCP using a 5 mV root mean square sine wave, with frequencies starting at 100 kHz, ending at 0.01 Hz. The EIS tests were conducted with an EG&G 263A Galvanostat/Potentiostat and an EG&G 5210 Lock-in Amplifier, using EG&G 298 impedance software.

Linear Polarization (LP) – was used to estimate the corrosion rate of a metal. A potential is applied to the sample at 20 mV negative of the OCP. The potential is then ramped at 0.167 mV/sec to 20 mV above the OCP. The result is typically a straight line with a slope equal to the polarization resistance, Rp. The larger the resistance, the more effective the inhibitor. The LP tests were conducted also with an EG&G 263A using EG&G 352 corrosion software. Both the EIS and LP are considered nondestructive tests.

Potentiodynamic Polarization (PDP) – PDP is similar to the linear polarization, however, the potential is ramped from 250 mV below the OCP to several hundred millivolts above the OCP, a much larger range, at a faster scan rate of 1 mV/sec. The PDP can measure the cathodic and anodic rates and the passive current density. The PDP tests were also conducted with an EG&G 263A using EG&G 352 corrosion software.

Water Drop Contact Angles – were determined visually through the use of digital photographs of water droplets placed on the metal. Photos were obtained from a relevant side angle and digitally enlarged to reveal the contact angle measurement.

Pretreatment Dip Procedure – Panels requiring pretreatment dip preparation were prepared in the following manner using a circular plastic or equivalent tank 11″ in diameter and 11″ in height. The tank was filled with 9,600 grams of test solution and typically stirred with magnetic stir bar. Test panels 10.16 cm×15.24 cm×1.59 mm (4″×6″×$^1/_{16}$″) with a mounting hole of 6.35 mm (¼″) in diameter located 6.35 mm (¼″)

from the top edge were treated by placing a plastic pipette through the hole in the panel. Up to three panels were mounted using the same pipette. This allowed for the panels to stand upright, with only the bottom of the panel touching the tank. If needed, the tank could also be placed in an oven for time at temperature treatments. After requisite times, panels were removed from the tank, hung dried at ambient temperature overnight, then treated according to subsequent procedures.

Coating Formulation Preparation – Detailed formulations for latex and alkyd formulations are provided as Appendix A. Formulations were allowed to stand a minimum of 48 hours before use. Spiked commercial samples (both liquid and aerosols), were prepared by placing known amounts of materials in a 250 mL beaker, mixing 2 h with magnetic stir bar, then used immediately without further preparation. DDABC additions were calculated based on total formula weight unless otherwise noted. The following commercial samples were purchased from a retail store and used as provided from the manufacturer. Rust-Oleum® brand's Professional High Performance Enamel (Hunter Green) spray paint; Painters Touch® (Hunter Green) latex paint; and Gloss Protective Spray Enamel (Hunter Green).

Coating & Test Procedures
Following panel pretreatment where required (see above), panels were coated using one of several coatings procedures. Samples were prepared in duplicate or triplicate.

Procedure a) Commercial E-coating was performed in a double blind fashion by Royal E-Coat (Costa Mesa, California), using a proprietary commercial process and a urethane based (black) coating supplied by Hawking Technologies. Panels were specifically not subjected to detergent washing before the coating procedure, but rather subjected directly to the coating procedure. Panels were cured at approximately 170°C for 30 minutes. Coating thickness was a minimum 7.5 microns.

Procedure b) Panels received one application of coating with #44 wire wound draw down bar, giving a wet film thickness of 4.4 mils. Where 1 mil = .001 inch. Leneta charts were coated with a 3 mil bird bar giving a dry thickness of approximately 3 mils. Taber panels received two coats, with two hour dry time between coats, and second coat applied in a perpendicular direction to the first. The following panels from Q-Panel were utilized in coatings testing: i) Dull matte-finish steel (3x6 Q-panels stock # R-36) ii) Phosphate treated steel (3x6 Q-panels stock # R-36-I)

Procedure c) For spray paints, panels were laid flat end to end and spray painted with sufficient material, after drying overnight, to afford approximately 1.0 g of paint (dry weight) per surface. A total of one paint coat per side was applied.

Procedure d) The paint was applied with a foam roller to the steel panels with sufficient material, after drying overnight, to afford approximately 1.0 g of paint (dry weight) per surface coat. A total of two coats per side was applied.

Humidity Chamber Testing – Samples were evaluated according to standardized ASTM D-1735 humidity testing (method variation to 80°F, 75% humidity) for 12 h by Assured Testing Services (224 River Rd., Ridgeway, PA 15853).

B117 Salt Spray Testing - Painted samples were evaluated according to standardized ASTM B117 tests by Assured Testing Services (224 River Rd., Ridgeway, PA 15853) or by the University of Missouri – Rolla Coatings Research Institute (1870 Miner Circle, Rolla, Mo. 65409-1020). The panels were coated as described above, and allowed to dry 7 days. Panel edges were typically treated with either wax or epoxy (7 day curing) to prevent edge effects. Unscored panel surfaces were periodically evaluated for total visible rust and rated from 0 to 100%.

Creep Data Measurements – Creep data panels were scored in an X design just prior to subjecting to B117 salt spray conditions. The score was made so that the bottom of the cut was 2 inches up from the bottom of the panel with a 90° intersection in the middle of the score. Panels were placed into racks in a random order, and then placed into the B117 chamber. Scored samples were evaluated by measurement (in mm) in 5 different locations and reported as an averaged value.

Adhesion Data Measurements – After allowing a 7 day dry time on coated panels, the surface of the panels were slightly roughened with 400 grit sandpaper, and an aluminum puck was glued directly to the coating with 3M brand 'Scotch-Weld' DP-420 thread side up. The force required to twist off the puck was recorded in inch pounds and converted to PSI. The digital torque wrench used in this test was the Computorque II made by CDI model number 2502CI II. Modes of failure were reported as specified in ASTM D 4541-02. A percent cohesive failure and a percent adhesive failure, and the PSI values are all reported and detailed in the torque data table. Measurements were made by the University of Missouri – Rolla Coatings Research Institute.

Summary

A new water soluble quaternary ammonium compound based additive, didecyldimethylammonium bicarbonate/carbonate (DDABC), has been evaluated as a corrosion inhibitor via standard electrochemical tests on steel and shown to be highly effective. A strong concentration dependence with respect to corrosion performance is observed both in aqueous environments as a neat ingredient and in multiple formulated coatings systems. This concentration dependence is believed to be related to bulk solution micelle structure behavior which effects DDABC's ability to deposit an efficient thin film. In aqueous systems, the optimal concentration range is approximately 0.05 to 0.65% active weight percent in the concentration region where a trimeric and spherical micelle aggregates prevails. Above this threshold concentration, a rod-shaped micelle structure effectively solubilizes DDABC into the bulk liquid preventing thin film formation. DDABC was also shown to lower the surface tension of water, allowing for very low wetting angles on sanded steel and improved coatings performance. Phosphate and glycolate anion DDABC derivatives also exhibit good performance as a corrosion inhibitor while other anions including sulfate, chloride, citrate and acetate provide lackluster to detrimental corrosion impact.

Preliminary coatings evaluations reported here indicate DDABC and its derivatives exhibit a remarkable ability to improve the corrosion performance of several

commercially relevant coatings including latex, alkyd, and urethane e-coat systems when used either as a pretreatment, sealing rinse (over iron phosphatized steel), or formulated additive. In some instances, DDABC affects corrosion performance enhancement in B117 salt spray tests of over 300% and creep improvements of 60–75%. When formulated into latex and alkyd formulations, DDABC exhibits significant performance enhancements to creep and adhesion. Significant variability with respect to formulation level, coating system, and the use as pretreatment versus coatings additive is also noted and this demonstrates optimal DDABC performance is very formulation and application specific. However, preliminary results presented herein clearly warrant additional work to further elucidate the general utility of DDABC in additional coating systems.

Acknowledgement

Grateful acknowledgement is made to Prof. Michael Van de Mark at the University of Missouri Rolla Coating Research Institute for coatings formulation work reported in Appendix A.

Appendix A: Detailed Prototype formulations from Tables 4 & 5.

Alkyd Formulations

Paint Identification		
Lonza Alkyd 2	Master Control No CS	
Single batch		
Material	Formula (grams)	Actual (grams)
Setal 21-1491	292.10	292.2
Troysol 98C	11.25	11.3
MIBK	200.00	200.0
Bentone SD-2	12.50	12.5
CR 822	500.00	500.0
Minex 7	375.00	375.0
Grind		
Setal 21-1491	1124.15	1124.2
12% Cobalt Hexcure	5.38	5.4
12% Zirconium Hexcure	18.75	18.8
Active 8	4.23	4.2
Skino #2	8.00	8.0
Byk 300	2.15	2.2
MIBK	370.50	370.8

Control this formulaiton
CS Low added 2.23 g CS-1000
CS High added 4.78 g CS-1000

Latex Formulations

Formulated by Dr. Michael R. Van De Mark

Paint Identification				Paint Identification	Master Control has no CS 1000	
Lonza Latex 1	Master Control has 0.25% CS-1000			Lonza Latex 2		
Double batch				Double batch		
Material	Formula (grams)	Actual (grams)		Material	Formula (grams)	Actual (grams)
Water	112.0	224.1		Water	112.0	224.0
Propylene Glycol	33.0	66.0		Propylene Glycol	33.0	66.0
Natrosol 250 HBR	2.0	4.0		Natrosol 250 HBR	2.0	4.0
AMP 95	2.0	4.0		AMP 95	2.0	4.0
CS 1000	2.6	5.2		Triton CF10	2.6	5.2
Tamol 731A	6.0	12.1		Tamol 731A	6.0	12.0
Colloid 640	2.0	4.0		Colloid 640	2.0	4.0
CR 822	160.0	320.0		Can Guard 327	2.5	5.1
Minex 7	160.0	320.5		CR 822	160.0	320.0
Grind to 6+				Minex 7	160.0	320.0
UCAR Latex 625	460.0	920.0		Grind to 6+		
Archer RC	23.0	46.0		UCAR Latex 625	460.0	920.0
Water	90.0	180.0		Archer RC	23.0	46.0
Acrosol RM 825	2.0	4.0		Water	90.0	180.0
CS Low is Master Control **CS High 2.44 g CS-1000**				Acrosol RM 825	2.0	4.0

CS Low is Master Control
CS High 2.44 g CS-1000

Latex Control is Master Control
Latex Nitrite added 2.39 g Sodium Nitrite

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17   Additional benchmarking experiments against commercial flash inhibitors confirm this conclusion.