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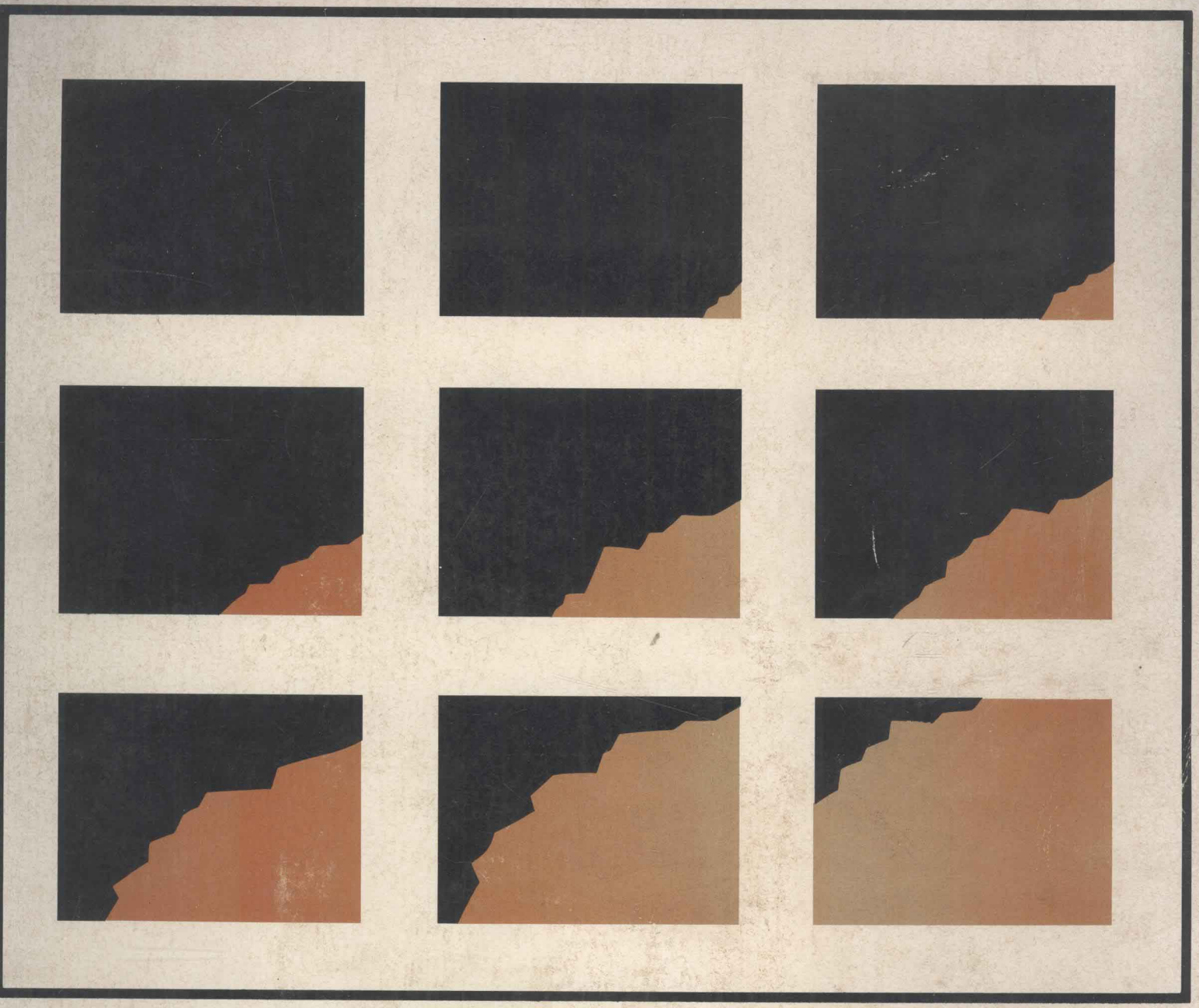

Corrosion Protection, Resistance and Testing

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850208

Corrosion Opinion Poll

Robert E. Luetje
Armco Inc.

ABSTRACT

The American Iron and Steel Institute conducted an opinion poll at the SAE "Corrosion 83" conference to answer specific questions on corrosion and its prevention. The results reported here indicate that vehicle corrosion resistance remains as a major issue. The survey compares the responses of corrosion professionals in three industries (vehicle production, steel production and chemical processing) and shows that there is a common agreement on the definition of the corrosion problem and its solution. In general, metallic coated steels are expected to be the principal factor in the improved corrosion resistance of future vehicles, but there are some concerns about the application of these coated steels on a very broad basis.

THE ACAP (AUTOMOTIVE CORROSION AND PREVENTION) Committee of SAE sponsored a major technical meeting, "Corrosion 83", December 5-7, 1983, at the Hyatt Regency Hotel in Dearborn, MI. The Transportation Department of the American Iron and Steel Institute conducted a written "Corrosion Opinion Poll" survey during this meeting and the results are reported here.

The purpose of the survey was to generate subjective information on automotive corrosion from a relatively large group who are well versed on the subject. While corrosion is clearly a major concern in the automotive industry, at times there seems to be a wide difference of opinion on problems and solutions. Data from accelerated testing is subject to different interpretations and real-time data always seems to be five years away. Users and suppliers of automotive steels as well as those involved with associated chemical processes are all stakeholders who have somewhat different interests. This survey helps answer some of these questions.

The survey included 18 questions and it was distributed to 207 of the approximately 375 people attending the meeting. Some were returned on-site and some were mailed back to AISI. A total of 60 surveys were returned and are part of this data.

Respondents were asked to identify their job function and their industry. By function, 49% were in engineering, 31% in research and 20% other. Regarding place of employment, 30% were vehicle producers, 23% were ferrous material producers, 27% were chemical processing and 12% other.

For purposes of analyzing this survey, three groups called "Car Makers", "Steel Makers" and "Chemical Treaters" were separated for comparison. "Car Makers" include vehicle and component producers. "Steel Makers" are ferrous material producers and "Chemical Treaters" include paint suppliers, chemical suppliers and phosphate producers.

CONCLUSIONS OF THE SURVEY

The results are given in the figures that follow, but some general conclusions can be made as follows:

There was generally good agreement within and between the three groups on most questions indicating that corrosion authorities have a common understanding of the issues regardless of their industry or company affiliation.

The public is still concerned about corrosion and vehicle producers perceive a need for further improvement, especially in body components. It is unlikely that paint systems will improve to the point where coated steels and rustproofing are not needed.

A large majority felt that outer body panels need a metallic coating on the exposed side.

The quantity of coated steels used in a typical car will increase about 50% from 1983 to 1990.

When considering the use of galvanized steel in place of cold rolled steel, the primary concern is surface quality and the least concern is cost.

When asked to compare hot dip and electrogalvanized steels, electrogalvanized was characterized as superior relative to surface quality and uniformity, while hot dipped was cited for lower cost and heavier coating.

The most important factor in corrosion resistance is vehicle design followed by the use of coated steels, phosphating, paint system and rust-proofing.

In accelerated testing, salt spray was often used as a part of a test series but only two respondents used salt spray alone to evaluate coated steel components. The three groups use different corrosion tests as their primary one; specifically, car makers rely most often on proving ground tests, steel makers on cyclic tests and chemical treaters on the salt spray test.

While car makers rated the North American steel industry on a par with others in developing new coated steels, there is a major concern about availability of some of these products.

There was a wide variety of opinion on the need for "rust-proofing" on salt belt cars but a stronger indication that it may not be cost effective.

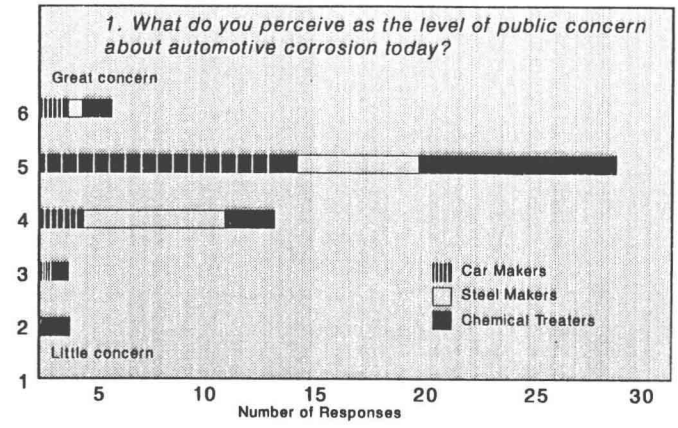
Aluminum coated steel was named as the best choice for mufflers and tailpipes but, when asked to rank a variety of materials for corrosion resistance only under-vehicle, the results were somewhat different. Type 409 stainless was clearly first, while galvanized and aluminum-zinc coated were nearly tied for second followed by aluminum then aluminum coated. Long terne and Zincrometal were lowest ranked.

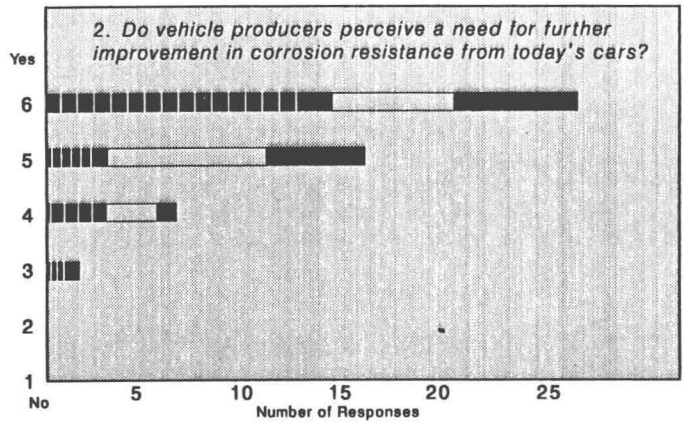
There was not very good agreement on the degree of corrosion resistance that is lost in fabricating galvanized parts. Bare edges, stretching and spot welding may have a detrimental effect on the coating performance, but some felt it was serious and some felt it was insignificant.

RESULTS

The following figures record actual results of the survey. Each figure phrases the question exactly as it was stated in the survey and histograms are used wherever possible to illustrate the distribution of responses. For brevity and to show the response of the group as a whole, all three groups are combined in each figure. Response of each of the three subgroups can be distinguished by the different shading. In every case, car makers are indicated by the vertical shaded bar (varying widths of individual bars is not significant), steel makers by the open bar and chemical treaters by the solid bar.

On all questions where the answer was a matter of degree, a scale of 1 to 6 was used to "force" respondents to circle a number which was either above or below midscale.





3. How much is a "5 year cosmetic/10 year perforation" warranty worth to the consumer?

	Average	Range
Car Makers	$731	$100 - $3000
Steel Makers	$407	$75 - $600
Chemical Treaters	$1284	$100 - $10,000

4. What component in current vehicles is most likely to experience a premature corrosion problem?

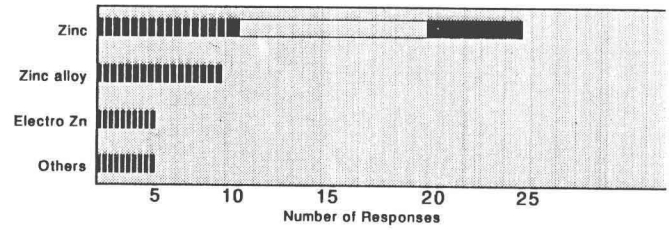
	Body Parts	Exhaust	Chassis
Car Makers	9	4	3
Steel Makers	13	2	
Chemical Treaters	13	1	

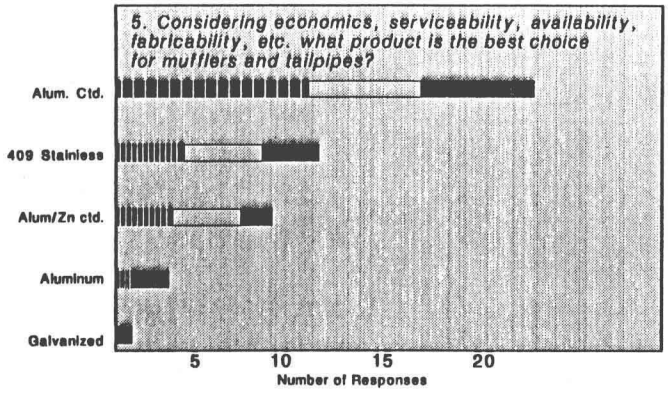
Numerous individual components were mentioned but those body parts most frequently specified were: doors (13); fenders (10); quarters (5); hood or deck (5); rockers or sills (3).

7. Do you believe steel outer body panels need a metallic coating of some kind on the exposed side under the conventional paint system?

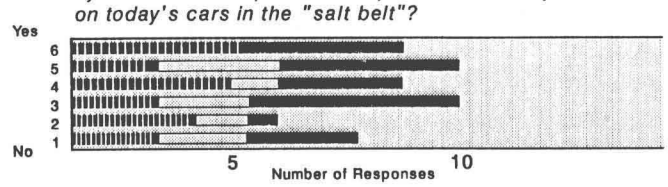
	Yes	No
Car Makers	18	5
Steel Makers	14	0
Chemical Treaters	9	7

What type of coating?

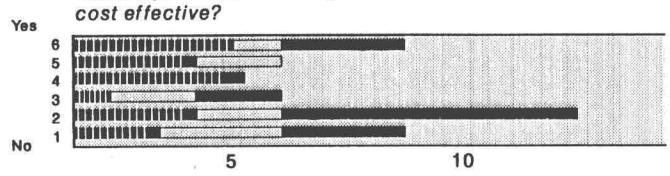


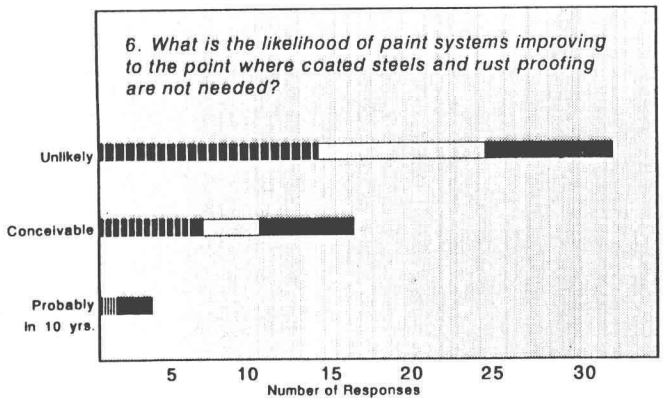


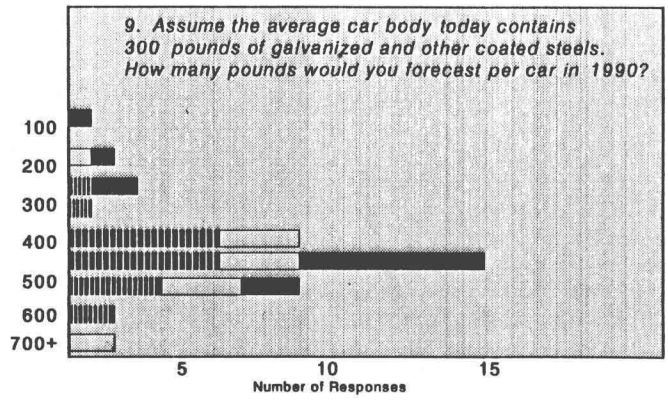
8. Do you believe "rust proof" treatments as applied by dealers or independent shops are necessary on today's cars in the "salt belt"?



8A. Do you believe "rust proof" treatments are cost effective?







10. Considering only corrosion resistance, how would you rank these materials for underbody service? (Please rank #1 for best, etc.)

Material	Composite ranking	Car Makers	Steel Makers	Chemical Treaters
Type 409	1.7	1.5	1.3	2.2
Alum-Zn Ctd.	3.2	3.4	2.8	3.4
Galvanized	3.3	3.3	3.2	3.3
Aluminum	3.6	3.7	4.0	3.0
Alum. Ctd.	4.0	4.0	4.2	3.9
Zincrometal	5.3	5.7	6.0	4.2
Terne	5.6	5.2	5.5	6.4

11. When considering the use of galvanized panels in place of cold rolled steel, do you have any concern in the following areas:

(Rank in decreasing order; Major concern (6), No concern (1))

Concern	Composite ranking	Car Makers	Steel Makers	Chemical Treaters
Surface Quality	4.9	4.9	4.9	5.0
Paintability	4.6	4.8	3.9	4.9
Weldability	4.6	4.6	4.7	4.5
Formability	4.1	4.7	3.3	4.0
Availability	4.1	4.4	3.3	4.4
Cost	4.0	4.1	3.2	4.4

12. Please list some adjectives to describe these two types of coatings

(Note: Only responses offered more than once are recorded below)

Car Makers

Hot Dip Galvanized		Electrogalvanized	
Affordable	5	Better Surface	9
Rough	4	Uniform	5
Heavy Coat	3	Consistant	4
Available	3	No effect on props.	3
Good Protection	2	Expensive	3
Thick. Variation	2	Good Corr. Protect.	3
Spangled	2	Paintable	2
		Better Forming	2
		Thin	2

12. Please list some adjectives to describe these two types of coatings

(Note: Only responses offered more than once are recorded below)

Steel Makers

Hot Dip Galvanized		Electrogalvanized	
Heavy	6	Uniform	7
Better Corr. Resist.	5	Light Coat	7
Cheaper	4	Smooth	6
Sacrificial	3	Formable	4
Proven	2	Variety of Substrates	3
Variable	2	Not Available	2
Available	2		

12. Please list some adjectives to describe these two types of coatings

(Note: Only responses offered more than once are recorded below)

Chemical Treaters

Hot Dip Galvanized		Electrogalvanized	
Good Protection	7	Uniform	5
Rough	4	Smooth	4
Poor Forming	3	Good Forming	3
Poor Painting	3	Paintable	3
Available	2	Less Available	2
Cheaper	2		
Thick	2		

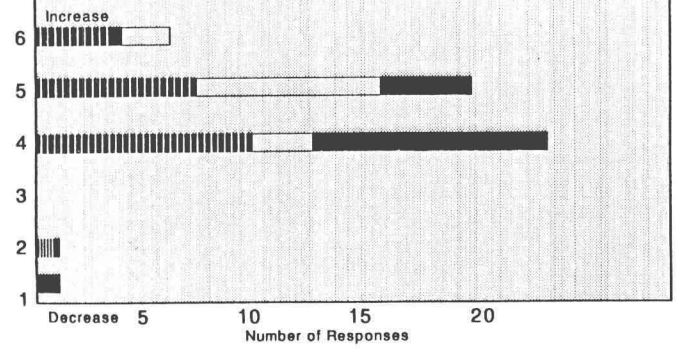
13. There are several important factors in producing a successful corrosion resistant steel auto body. Please rank these in decreasing order of importance; (Most important 1)

Car Makers		Steel Makers		Chemical Treaters	
Design	2.0	Design	1.8	Design	1.9
Coated Steel	2.3	Coated Steel	1.8	Coated Steel	2.8
Phosphate	2.9	Paint System	3.0	Phosphate	2.9
Paint System	3.0	Phosphate	3.1	Paint System	3.4
Rustproofing	4.6	Rustproofing	4.9	Rustproofing	4.6

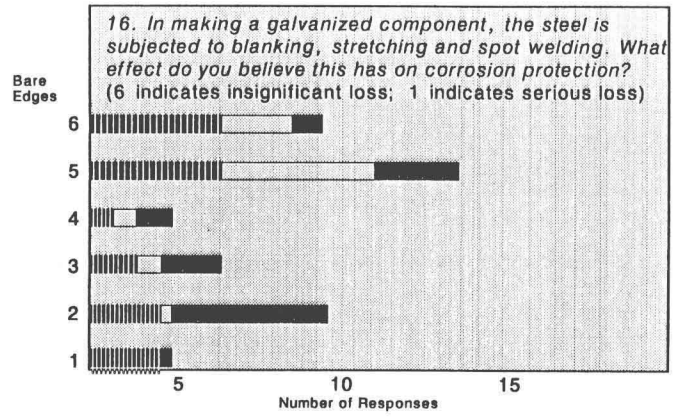
14. If you are associated with accelerated corrosion testing or coated steels and components, what kind of test do you use?

Car Makers (20 Replies)		Steel Makers (10 Replies)		Chemical Treaters (16 Replies)	
Proving Grounds	10	Cyclic	6	Salt Spray	10
Salt Spray	9	Salt Spray	5	Cyclic	7
Cyclic	8	Scab Test	2	Scab Test	4
Scab Tests	3	Proving Grounds	2		

15. Do you believe the portion of coated steels ordered as high strength will increase or decrease?



16. In making a galvanized component, the steel is subjected to blanking, stretching and spot welding. What effect do you believe this has on corrosion protection? (6 indicates insignificant loss; 1 indicates serious loss)



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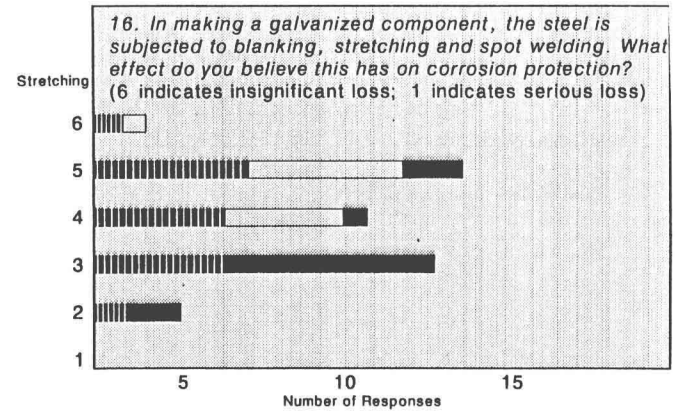

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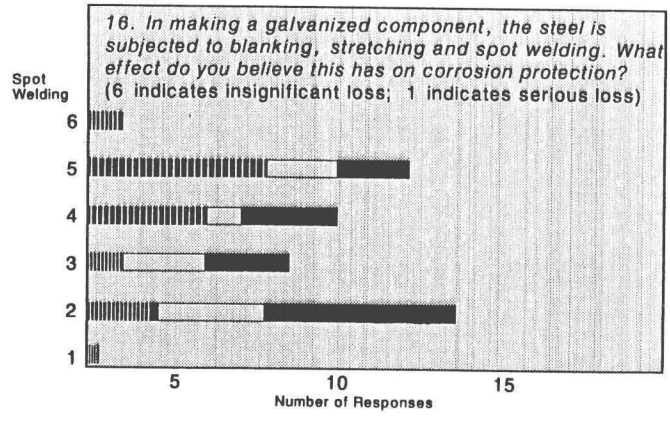
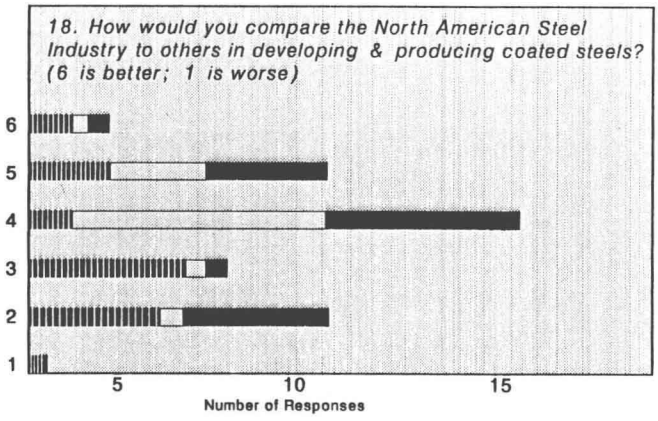


17. Are you concerned about the domestic availability of any of the coated steels?

	Yes	No	Products
Car Makers	83%	17%	Galvanized, Electrogalv.
Steel Makers	71%	29%	Electrogalv., HD Exposed Galv.
Chemical Treaters	31%	69%	Electrogalv., One Side Galv.



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The task force appreciates the time and input from the 60 respondents who contributed to this survey.

850209

Improving the Galvanic Properties of Zinc-Rich Organic Coatings by Corona Discharge Treatment

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ABSTRACT

Zinc-rich organic precoated steel sheet is an attractive product for corrosion-resistant automotive applications due to its formability, weldability, availability and cost. A disadvantage of this product is an inability of the coating to provide a significant level of cathodic protection to areas of the steel base exposed to the environment at sites of damage to the coating. To gain increased understanding of this behavior, we studied the galvanic properties of zinc-rich organic coatings with electrochemical, microscopic and electronic methods. We observed high electrical resistances within these coatings that preclude effective galvanic protection of steel by the zinc in the coating. Based on these studies, we discovered that corona-discharge treatment, an inexpensive electric discharge treatment, significantly increases the coating's conductivity and galvanic activity. Compared to untreated coatings, corona-discharge treated coatings show significantly higher levels of galvanic protection in electrochemical and accelerated corrosion tests.

INTRODUCTION

Increasing use of road deicing salts, a trend toward design of lighter vehicles with thinner, higher-strength steels for greater fuel efficiency, and increased consumer awareness have contributed to a growing interest in more corrosion-resistant automobiles (1-5). Precoated steel sheet, that is, steel sheet supplied by a steelmaker with a uniform coating applied, is a cost-effective material with a favorable combination of the required properties, namely, high strength and toughness, formability, weldability, paintability and corrosion resistance. The variety of precoated sheet steel products available has been reported previously (6).

A precoated sheet product which has been utilized extensively for automobiles is Zincrometal[R], which has a two-layer, zinc-rich coating usually applied to only one side of steel sheet by coil-coating techniques (7, 8). Since its introduction in 1971, over 8 million tons of Zincrometal have been produced in the United States (9). Although known to provide an excellent barrier to corrodents, the Zincrometal coating provides a much lower level of galvanic, or sacrificial, protection than does a metallic zinc coating (10-13). Low galvanic activity permits rusting of the steel base to occur when exposed to a corrosive environment at sites of damage to the coating.

This paper presents the results of studies to characterize and explain the galvanic properties of Zincrometal. It also describes our discovery of a treatment for Zincrometal which significantly increases its galvanic activity through alteration of the coating's conductive properties.

[R] Zincrometal, Zincromet, and Dacromet are tradenames registered to Diamond Shamrock Chemicals Co.

Description of Zincrometal

Zincrometal is the tradename licensed by Diamond Shamrock Chemicals Co. to steel sheet producers for a weldable, corrosion-resistant, two-layer zinc-rich coating applied to steel by coil-coating techniques (Figure 1). The base layer, called Dacromet®, is a proprietary mixture comprised primarily of zinc dust in a water-based chromic acid solution. The top layer, called Zincromet®, is a zinc-filled phenoxy resin containing approximately 85%, by weight, 50%, by volume, zinc dust. The product typically used by the automobile industry is coated on one side and has a minimum dry film thickness of 13 microns (0.5 mil) and contains approximately 0.3 g/m^2 of chromium in the Dacromet layer.

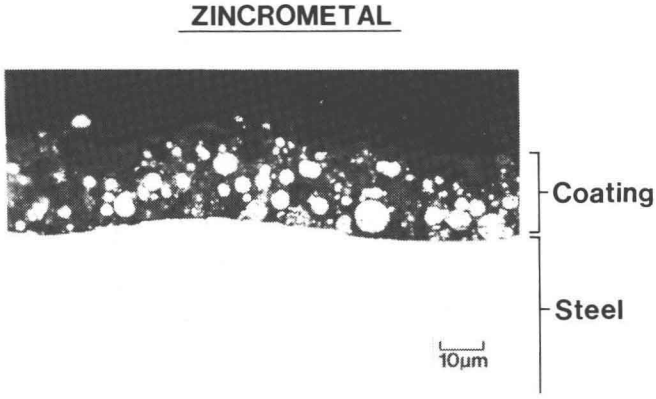

FIGURE 1. ZINCROMETAL CROSS-SECTION

Galvanic Corrosion Protection

When two dissimilar metals are electrically connected and exposed to an electrolyte (ion-conducting medium, e.g., saltwater), the metal of lower (more negative) electrochemical potential will give up ions to the solution while the metal of higher electrochemical potential will be protected from corrosion. These reactions are illustrated in Figure 2 for the zinc-iron system. To determine the rate of galvanic corrosion, the current of electrons flowing between the metals can be measured with a zero-resistance ammeter. If the electronically conducting circuit between the two metals is broken, current cannot flow and the galvanic reactions do not occur and both metals react with the solution at their individual self-corrosion rates.

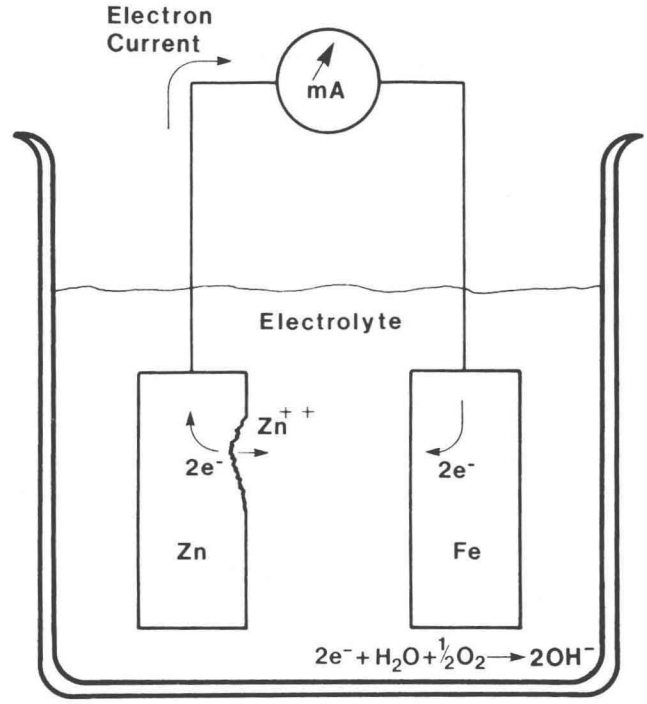

FIGURE 2. ELECTROCHEMICAL REACTIONS FOR ZINC CONNECTED TO IRON IN AN ELECTROLYTE

EXPERIMENTAL

Materials

Test materials include low carbon cold-rolled steel (drawing quality aluminum killed), Zincrometal from different coil-coaters with and without an internal lubricant and electroplated 20 g/m^2 zinc-coated sheet.

Laboratory Tests

Galvanic currents flowing between a bare steel sample and a coating were measured with the apparatus shown in Figure 3. The potentiostat was set to maintain zero potential difference between the electrodes of the galvanic couple to measure true short circuit galvanic current. Recordings were made of galvanic current and electrochemical potential vs time. Electrode sample holders were used which confined 1 cm^2 of the coated specimen surface and 5 cm^2 of bare steel to be in contact with the aerated pH 6, 0.5N NaCl electrolyte solution.

The electrical resistance through coatings was measured with the apparatus shown in Figure 4. Large area, flat contacts were used with light pressure to prevent puncturing through the coating and a low voltage digital ohmmeter was used to avoid electrical arcing through the coating.

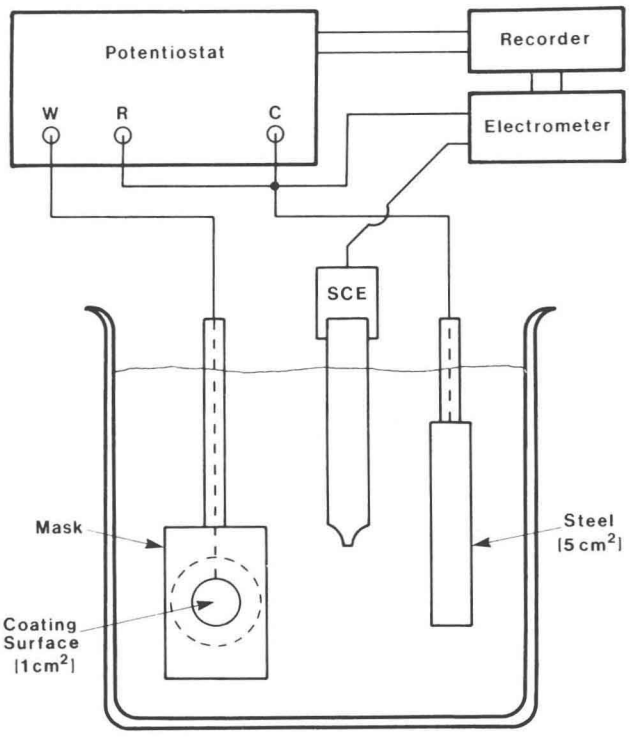

FIGURE 3. INSTRUMENTATION USED TO MEASURE GALVANIC CURRENT AND ELECTROCHEMICAL POTENTIAL

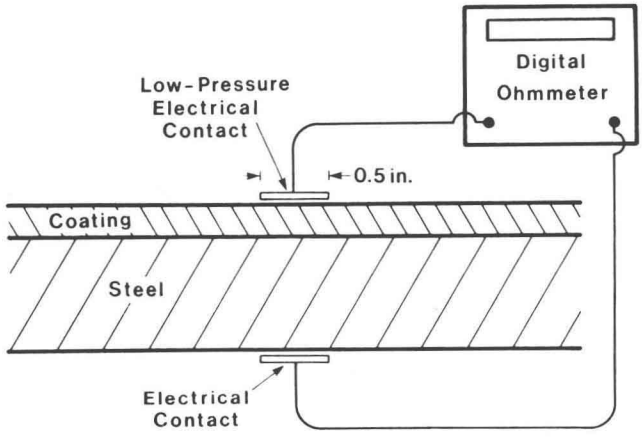

FIGURE 4. COATING RESISTANCE MEASUREMENT APPARATUS

The accelerated corrosion test used in the study was the salt-spray test conducted according to ASTM B117.

Corona Discharge Treater

Samples were treated with a corona-discharge surface treater, comprising a 15 cm diameter x 30 cm long dielectric-covered treater roll, a 2 kW, 0-9.6 kHz high voltage corona discharge generator and a device for translating sample panels beneath the treater (Figure 5). Corona Discharge input energy densities used were in the range of 1-2 Joules/cm^2. Reviews of the corona discharge technique and its uses have been published (14, 15).

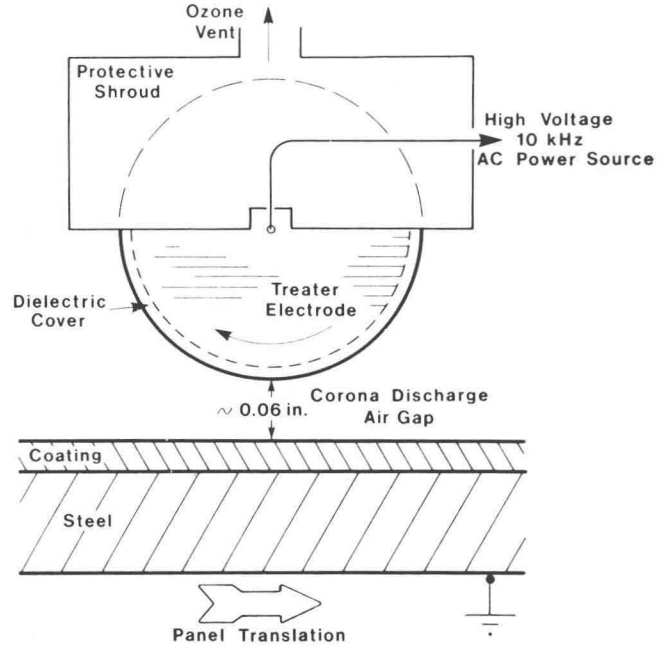

FIGURE 5. CORONA DISCHARGE TREATER

RESULTS AND DISCUSSION

Galvanic Current Measurements

Comparison of traces of galvanic current and electrochemical potential vs time for Zincrometal and a metallic zinc coating (Figure 6) show that Zincrometal provides negligible galvanic current while the zinc electroplate provides a high level of current until the coating is consumed. Without zinc dissolution providing current, the electrochemical potential of the couple rises to the corrosion potential of steel allowing the steel electrode to corrode. The lack of significant galvanic current offered by Zincrometal is unexpected since the Zincrometal coating contains approximately twice the mass of zinc per unit surface area as does the electroplated coating (~40 g/m^2 for Zincrometal, 20 g/m^2 for the electroplate).

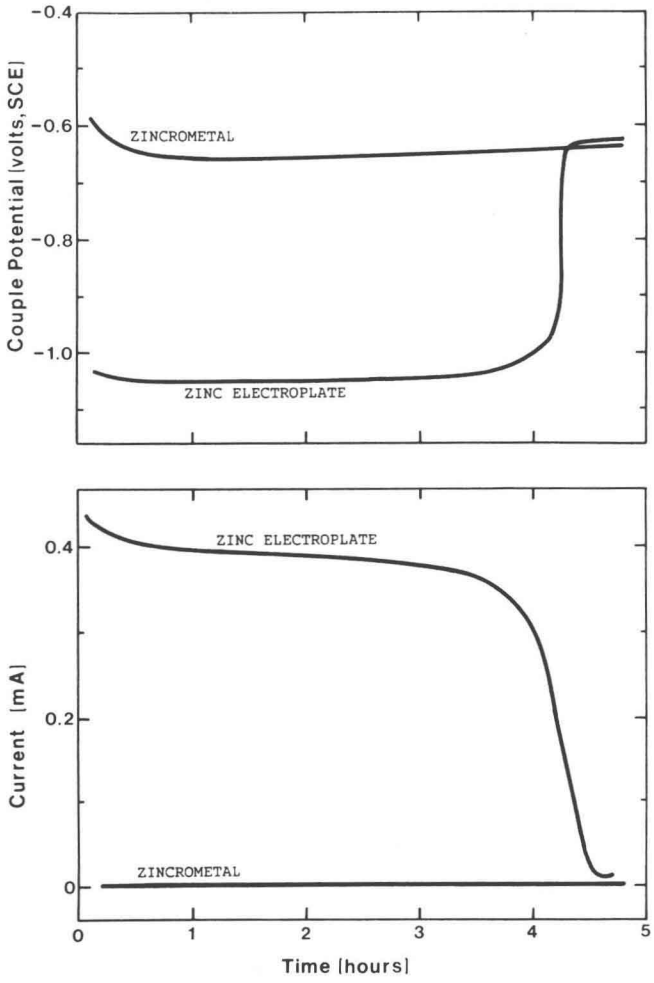

FIGURE 6. CURRENT AND ELECTROCHEMICAL POTENTIAL FOR A GALVANIC COUPLE OF 1 cm^2 COATED STEEL AND 5 cm^2 BARE STEEL IN 0.5N NaCl SOLUTION

Electrical Resistance of Coatings

In order for a coating to provide galvanic protection to steel sheet, electrical contact must exist between zinc in the coating and the steel base. A means of measuring the degree of electrical contact is to measure the electrical resistance between the surface of the coating and the steel substrate.

The resistance measurements (Table 1) show that the Zincrometal and Dacromet coatings have very high electrical resistance compared to a metallic coating. These findings are evidence of the presence of insulating phases between zinc in the Zincrometal coating and the steel substrate. This lack of continuous electrical connection prevents zinc in the Zincrometal coating from being galvanically useful.

TABLE 1. ELECTRICAL RESISTANCE MEASUREMENTS

Coating	Measured Resistance (ohms)
Cathodic E-Coat	infinite
Electroplated Zinc	<0.1
Zincrometal	$\sim 10^6$
Dacromet	$\sim 10^6$

Previous studies of zinc-filled organic coatings have also found high electrical resistances (16, 17). One author explains that, in order to have a cohesive organic coating with low porosity and good formability characteristics, it is necessary to have complete wetting of the pigment particles by the resin and, thus, metal-metal contact in the coating is not possible (16).

The high resistivities measured here seem inconsistent with the excellent resistance weldability of Zincrometal. However, unlike the present measurement conditions, spot-welding involves deformation of the coating by the high electrode pressure and heating due to passage of high currents through the coating.

Effect of Electric Discharge Treatment on Zincrometal

When dielectric materials (non-conductors of direct current) are subjected to electric fields exceeding their dielectric strength, a phenomenon called dielectric breakdown occurs. This breakdown is characterized by a sudden flow of current arising from ionization of molecules of the dielectric. In electronic devices such as capacitors, the occurrence of this phenomenon can permanently "short-out" the capacitor by creating a conducting path between the capacitor plates.

We have found that this dielectric breakdown effect can be used advantageously to interconnect zinc particles imbedded in the organic matrix of Zincromet and electrically connect these particles through the insulating Dacromet layer to the steel base (Figure 7). The establishment of these conductive paths allows some of the zinc in the Zincromet layer to galvanically protect the steel base.

A convenient method found for applying such a high-voltage treatment is corona-discharge (CD) treatment, a commonly used technique in plastic, paper and foil processing for altering surface energy (14, 15). In this technique, the material to be

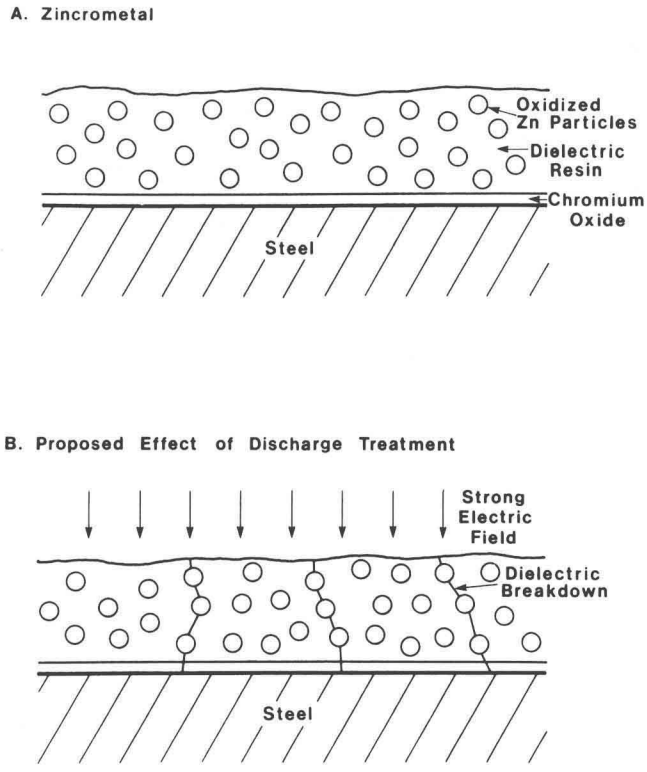

FIGURE 7. SCHEMATIC DIAGRAM OF ZINCROMETAL STRUCTURE, A, AND PROPOSED EFFECT OF HIGH VOLTAGE TREATMENT, B.

treated becomes one of the electrodes in an atmospheric pressure, gas-discharge cell (Figure 4).

Corona discharge treatment has a striking effect on the conductivity and galvanic activity of Zincrometal. Electrical resistance measurements (Table 2) show that the treatment effects decreases in resistance of over five orders of magnitude for Dacromet and Zincrometal coatings. Electrochemical measurements (Figure 8) show that, in contrast to an untreated coating, CD-treated Zincrometal provides a significant level of galvanic protection.

The amount of zinc available for galvanic protection was determined by anodic polarization of the coatings at -0.8V vs SCE, to dissolve zinc, measuring current passed and integrating the current-time trace to obtain total charge passed. These results (Table 3) shows that the discharge treatment causes a significant fraction of the zinc in Zincrometal to be galvanically useful. We believe that the incomplete activation of all of the approximately 40 gm/m^2 of zinc in Zincrometal is primarily due to the insoluble nature of the Zincromet organic resin preventing contact of the electrolyte with underlying zinc particles.

TABLE 2. ELECTRICAL RESISTANCE MEASUREMENTS

Coating	Measured Resistance (ohms) As-Produced	After CD Treatment*
Cathodic E-Coat	infinite	infinite
Electroplated Zinc	< 0.1	< 0.1
Zincrometal	$\sim 10^6$	~ 1
Dacromet	$\sim 10^6$	~ 1

* A corona-discharge treatment energy density of 1 Joule/cm^2

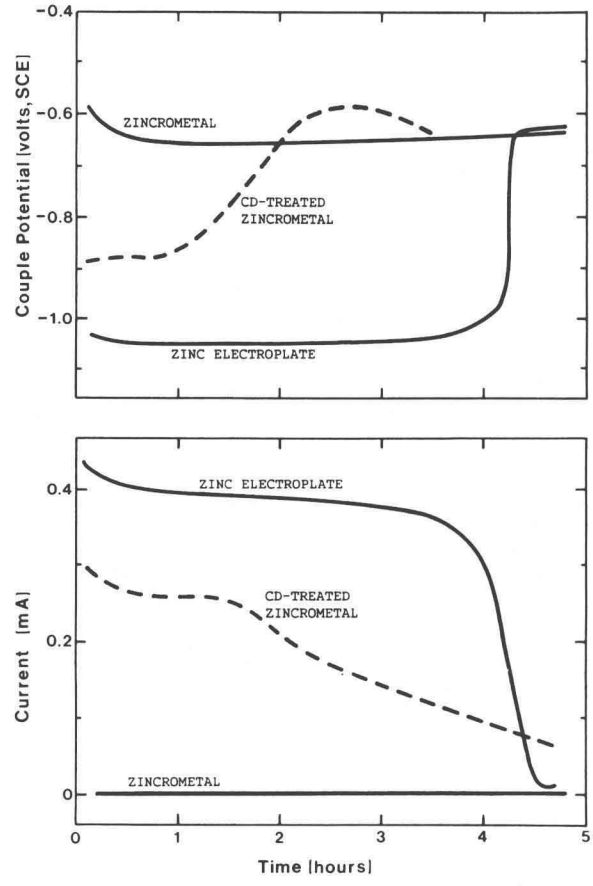

FIGURE 8. CURRENT AND ELECTROCHEMICAL POTENTIAL FOR A GALVANIC COUPLE OF 1 cm^2 COATED STEEL AND 5 cm^2 BARE STEEL IN 0.5N NaCl SOLUTION

TABLE 3. TOTAL ZINC AVAILABLE FOR GALVANIC PROTECTION

Coating	Total Charge Passed* Coulombs/cm²	Zinc Equivalent (g/m²)
Electroplated Zinc	5.7	19
Zincrometal	0.0	0
CD-Treated Zincrometal	1.5-3.0	5-10

* Anodic Polarization at -0.8V, SCE, for 15 minutes

Accelerated salt-spray testing of CD-treated and untreated Zincrometal panels, scribed before testing (Figure 9), shows that, for untreated Zincrometal, steel exposed at scribes through the coating corrodes with red-rust staining the panel surfaces. In contrast, CD treated Zincrometal protects the exposed steel from rusting. At long test durations, once the electrically connected zinc that is in contact with the environment has been consumed, the coating reverts to normal Zincrometal behavior, providing excellent barrier protection.

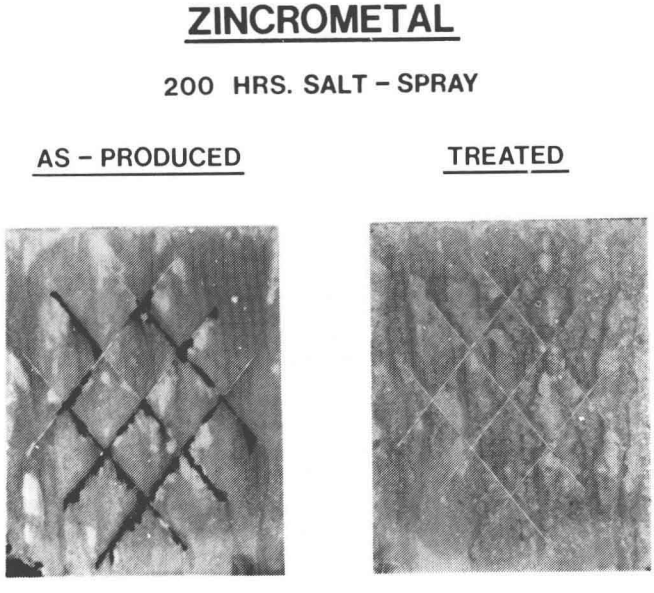

FIGURE 9. EFFECT OF CORONA-DISCHARGE TREATING ZINCROMETAL ON CORROSION PERFORMANCE, (PANELS SCRIBED TO STEEL BEFORE TESTING)

SUMMARY

In summary, the low level of galvanic activity displayed by Zincrometal is shown to result from high electrical resistances between zinc in the coating and the steel base. Without an electronically conducting path between zinc and steel, galvanic protection reactions cannot occur.

Treating Zincrometal with an electric discharge results in electrical interconnection of zinc in the coating to the steel base, completing the circuit required for galvanic reactions. The electrical conductance and galvanic activity of treated Zincrometal is shown to be significantly higher than untreated Zincrometal.

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