

Sponsor TBD Report No.:

AISI/DOE Technology Roadmap Program

Final Report

**PLANT LINE TRIAL EVALUATION OF VIABLE NON-
CHROMIUM PASSIVATION SYSTEMS FOR ELECTROLYTIC
TINPLATE (ETP)**

By

John A. Sinsel

June 2003

**Work Performed under Cooperative Agreement
No. DE-FC07-97ID13554**

**Prepared for
U.S. Department of Energy**

**Prepared by
American Iron and Steel Institute
Technology Roadmap Program Office
Pittsburgh, PA 15222**

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Number of pages in this report: 135

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Executive Summary

Plant trial evaluations have been completed for two zirconium-based, non-chromium passivation systems previously identified as possible alternatives to cathodic dichromate (CDC) passivation for electrolytic tinplate (ETP). These trials were done on a commercial electrolytic tin plating line at Weirton Steel and extensive evaluations of the materials resulting from these trials have been completed. All this was accomplished as a collaborative effort under the AISI Technology Roadmap Program and was executed by seven North American Tin Mill Products producers [Bethlehem Steel {now acquired by International Steel Group (ISG)}, Dofasco Inc., National Steel (now acquired by U.S. Steel), U.S. Steel, USS-Posco, Weirton Steel, and Wheeling-Pittsburgh Steel] with funding partially from the Department of Energy (DOE) and partially on an equal cost sharing basis among project participants.

The initial phases of this project involved optimization of application procedures for the non-chromium systems in the laboratories at Bethlehem Steel and Betz Dearborn followed by extensive testing with various lacquer formulations and food simulants in the laboratories at Valspar and PPG. Work was also completed at Dofasco and Weirton Steel to develop methods to prevent precipitation of insoluble solids as a function of time from the zirconate system. The results of this testing indicated that sulfide staining characteristics for the non-chromium passivation systems could be minimized but not totally eliminated and neither system was found to perform quite as good, in this respect, as the standard CDC system. As for the stability of zirconate treatment, a method was developed to stabilize this system for a sufficient period of time to conduct plant trial evaluations but, working with a major supplier of zirconium orthosulfate, a method for long term stabilization is still under development.

Plant trials were completed for the zirconate and fluorozirconate non-chromium passivation systems using the rinse tank in the chemical treatment section of the Weirton Steel #6 Electrolytic Tin Line (ETL) employing a dip-and-squeegee technique (no current). Line speed trials were completed with each system over the normal commercial operating speeds (600-1800 ft/min.) to ascertain proper zirconium deposition and in order to make final concentration adjustments to the solutions before producing test coils. Four test coils of sufficient quantities were produced with each non-chromium passivation system for extensive evaluations in project participants' and lacquer suppliers' laboratories and for eventual can/end-making trials as well as pack tests for the following applications: sanitary ends, lacquered three-piece cans, plain tin three-piece cans, and D&I food cans.

Tests completed on treatment solution samples taken during the trials with the zirconate and fluorozirconate systems initially indicated significant tin build-up in the solutions as a function of time during the trials. Results of further testing

completed at Bethlehem Steel to address this issue indicated, however, that the major source of tin in the solution samples was probably due to drag-in of plater salts for the plating solution and not dissolution of tin from the as-plated surface of the strip.

Tests completed in participants laboratories on samples of materials produced during the trials consisted of lacquer adhesion tests (dry, wet, screw cap, reverse impact, and mandrel bend), sulfide stain tests, surface oxidation tests, DC polarization tests, atomic force microscopic examinations, and surface oxidation tests utilizing ESCA for measurement of the formation of tin oxide on tinplate surfaces as a function of time. In addition, extensive passivation film characterizations and electrochemical corrosion testing were completed on these materials at Surface Science Western (SSW), University of Western Ontario, London, Ontario under separate contract. Analytical techniques used at SSW included field emission scanning electron microscopy (FESEM) combined with energy dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), linear polarization, and electrochemical impedance spectroscopy (EIS). The results of all this testing indicated that the performances of both the zirconate and fluorozirconate non-chromium passivation systems were very near that of the standard CDC system.

Although extensive evaluations in the laboratories at Valspar, PPG, and ICI with their respective commercial lacquer systems as well as can/end-making trials followed by commercial test pack evaluations on the material resulting from these trials have not been completed, sufficient testing has been completed which lead to the conclusion that both the zirconate and fluorozirconate systems represent viable alternatives to the presently used CDC system. Prior to the commercial utilization of either of these system, however, final optimization of application parameters will have to be completed on specific lines where these systems are to be applied. In addition, work must be completed with suppliers of the zirconate chemistry, such as Southern Ionics, Inc., to finalize a method for the long term stabilization of this system.

1.0 Introduction

In 1998, an American Iron and Steel Institute (AISI) collaborative research project was completed under the guidelines of the Tin Mill Products Collaborative Research Program to identify and evaluate non-chromium alternatives for electrolytic tinplate (ETP). That project was funded and executed by eight North American Tin Mill Products producers and resulted in the identification of three chromium-free passivation systems which, although not performing quite as good as the presently used cathodic dichromate (CDC) treatment, were deemed worthy of taking to the next level of evaluation, namely, commercial line trial evaluations. Two of these systems were based on zirconium (Zr), one being a commercial fluorozirconate treatment and the other consisting of an experimental system based on zirconium sulfate. The third system consisted of a commercial, totally organic treatment, which was found to provide the best protection for surface oxidation but was the worst performer of the three as far as sulfide staining was concerned. The experimental system based on zirconium sulfate, when used in dilute solutions, was also found to exhibit a stability problem, which would have to be rectified before proceeding with a commercial line trial.

In 1999, the present project (Plant Trial Evaluation of Non-Cr Passivations for Electrolytic Tinplate) was established to complete commercial line trials for the three non-Cr passivation systems identified in the previous project and to thoroughly evaluate the products resulting from these trials to determine their commercial viability. Projected benefits of the successful completion of this project were to ensure the continued use of electrolytic tinplate (ETP) as a food packaging material, to ensure continued customer acceptance of tinplate as a food packaging, and to minimize additional costs required to meet impending environmental regulations concerning the presently used cathodic dichromate (CDC) system.

This project was conducted under the AISI/DOE (U.S. Department of Energy) Technology Roadmap Program. Management of the project was done by the opt-in participants with outside resources being utilized only when these resources were otherwise unavailable.

The Plant Trial Evaluation of Non-Cr Passivations for Electrolytic Tinplate project was started in January 1999. The participant and sponsoring companies were:

Bethlehem Steel (now acquired by International Steel Group)
Dofasco, Inc.
LTV Steel (now International Steel Group)
National Steel (now acquired by U.S. Steel)
USS/Posco
U.S. Steel
Weirton Steel

Wheeling-Pittsburgh Steel

Work was performed according to a detailed plan which was included as part of the original project proposal. The project's primary objectives were as follows:

- Complete additional optimization work on non-Cr passivation systems to eliminate or minimize susceptibility to sulfide staining.
- Develop a procedure to stabilize zirconium sulfate.
- Complete plant trial evaluations on optimized non-Cr passivation systems using a commercial tin plating facility.
- Produce test materials treated with the optimized non-Cr passivation systems for evaluations in project participants laboratories and by customers.
- Establish and execute a detailed plan for the evaluation of products resulting from plant trials in participants laboratories as well as in selected customer facilities.
 - ✓ Use the National Food Processors Association/Can Manufacturing Institute//American Iron & Steel Institute (NFPA/CMI/AISI) Container Enhancement Committee in an advisory capacity to plan plant trials and evaluations on resulting materials.
 - ✓ Use NFPA laboratories for evaluation of test packs evaluations on plant trials materials.
- Prepare and issue final report with recommendations.

Following is a description of the management procedures utilized in this project, a summary of the work completed and the results obtained in accordance with the above objectives, conclusions and recommendations based on the results obtained, and a summary financial statement for the project.

2.0 Project Management

Detailed planning necessary for each phase of this project was accomplished by a project team consisting of a Project Manager and technical representatives from each of the participating opt-in companies. The project team, including changes made during the project, was as follows:

John A. Sinsel, Weirton Steel Corporation– Project Manager
Richard N. Steinbicker, Bethlehem Steel Corporation
Ronald G. Herczeg, Sr., Bethlehem Steel Corporation
Terry Jackiw / H. Francis Ng, Dofasco, Inc.
David H. Kah, LTV Steel Company
George R. Eierman, LTV Steel Company
Richard A. Clausius, National Steel Corporation
G.J. Spaeder / Brian Grentz, USS-Posco Industries
Gabriel Osanaiye / Donald Kaufman /
Chyang("C.J.") Wu / Robert B. Leggat, U.S. Steel Corporation
R. Bruce Batdorf, Wheeling-Pittsburgh Steel Corporation

The first meeting of the project team was held on January 22, 1999 to put together detailed work plans for the initial objectives of the project. Periodic meetings were held at various participants facilities to review the progress on the work plans and to develop new action plans based on those results attained. A detailed report concerning each of those meetings was distributed to all members of the project team as well as to the members of the AISI TMP Collaborative Research Board and the AISI Technology Roadmap Program Director.

3.0 Summary of Work Completed and Results Obtained

3.1 Optimization of Non-Cr Passivation Systems Prior to Plant Trials

Additional development and optimization work was done with the commercial totally organic system in the supplier's laboratories in an attempt to eliminate or minimize the sulfide staining characteristics of this treatment. This work involved modifications to the application parameters as well as, in some cases, major formulation changes. The results of testing of materials resulting from this additional work indicated no significant improvement in sulfide staining characteristics as a result of changes made. It was, therefore, decided that no further consideration would be given this treatment at this time.

Optimization work was also completed for the commercial fluorozirconate system in the supplier's laboratories and for the experimental zirconium sulfate-based system in the laboratories at Bethlehem Steel. Samples resulting from these tests were then submitted to PPG for sulfide stain tests with their lacquer systems and to Valspar for a rather extensive testing program in various test media with their lacquer systems.

3.2 Evaluations of Optimized Zirconate and Fluorozirconate Treatments

The results of sulfide stain tests completed at PPG indicated both the zirconate and fluorozirconate performed very near to but not quite as good as the standard CDC treated control material when tested with solvent-based lacquer systems. Neither performed particularly good, however, with the water-based lacquer system tested. The fluorozirconate appeared to perform slightly better than the zirconate system in these tests.

As stated above, the testing program at Valspar on these materials was much more extensive. The testing on lab samples included four Valspar commercial three-piece food can coatings (three internal can lacquers and one external varnish) on panels treated with each of the two zirconium-base, non-Cr passivation systems as well as a CDC treated control material. Formed parts produced from panels coated with the internal lacquers were subjected to test

pack evaluations with various types of food media and various synthetic solutions (food simulants) as well as physical testing of panels coated with the exterior varnish. Food media re-packs consisted of brine solution, barbeque sauce, lard, chicken broth, apple juice, tomato paste, and beef gravy dog food. Packs were stored at 100⁰ F for 12 weeks before opening and evaluating 202 ends for each variable for adhesion in both a formed area and a flat area as well for stain, corrosion, and blush.

Synthetic solution tests were completed to show comparative performances of the lacquers on flat strips packed in media of vastly varying degrees of aggressiveness which were designed to simulate various food types. Synthetic solutions used for these tests were deionized (DI) water, reducing solution (to simulate detinners such as acid fruits & green beans), oxidizing solution (to simulate catalytic or depolarizing residues of sprays, fertilizers, or additives used during growing or storage such as stewed tomatoes + SO₂), Cysteine solution (to simulate sulfur staining products such as potted meat, fish, peas, and corn), sulfur solution (to simulate aggressive products containing brine + acid), cooking salt / acetic acid packs (to simulate brine + acid such as pickles and peppers), and lactic acid solution (to simulate milk products, fruits, and wine). All synthetic solution packs were stored at 100⁰ F for 24 hours before completing evaluations for adhesion & blush, adhesion & blistering, or adhesion, blistering & stain.

Tests completed on the panels coated with external varnish consisted of dry adhesion, water processing, pencil hardness, and wedge bend testing.

The results of the testing completed at Valspar are contained in a report submitted to the project team by Valspar representatives. This report is presented in Appendix 1. As stated in that report, limited amounts of samples were available for testing thus limiting test pieces in generating the data in this report, therefore, reducing the statistical significance of the results. However, there was enough correlation between the data generated and previous test data as well as between related tests in this array to discern trends and draw conclusions with reasonable confidence. Conclusions reached from these data were as follows:

- All treatments performed equivalently in dry tests, in non-aggressive solutions, in reducing solutions, and in oxidizing solutions.
- All treatments performed equivalently in exterior varnish testing.
- Differentiation of performance was observed for the three passivation systems when tested with aggressive and strong media.
- In some instances where differentiation in performance was evident, the non-Cr systems exhibited better performance than the Cr system. However, all results considered, the Cr system offered the best overall performance of the three systems tested.

The above being said, it should be recognized that all commercial lacquer systems and can coatings have been developed to work over CDC or chrome treatment. It would, therefore, appear not unreasonable to believe that some level of coating performance optimization may be possible if specifically designed to work over alternative non-Cr passivation treatments such as those above and that corrections for minor deficiencies of the non-Cr systems could be achieved. The question is, therefore, as follows:

***HOW GOOD DOES A NON-Cr ALTERNATIVE TREATMENT
FOR ETP REALLY HAVE TO BE ?***

3.3 Presentation to NFPA/CMI/AISI Container Enhancement Committee

The above data and question were presented to the NFPA/CMI/AISI Container Enhancement Committee in February 2001. This meeting was attended by representatives of major can-makers/packers (Crown Cork & Seal, Siligan, and Ball), representatives from the major lacquer suppliers (PPG, Valspar, and ICI), the National Food Processors Association (NFPA), and AISI project participants. The results of that meeting were as follows:

- Can-makers and lacquer suppliers agreed that plant line trials were the next steps in the development of the zirconate and fluorozirconate systems.
- Can-makers agreed to serve in an advisory capacity in planning the materials matrix to be produced during plant line trials and testing procedures for the resulting products.
- Lacquer suppliers committed to evaluation programs for materials resulting from plant line trials.
- It was agreed that NFPA would coordinate and monitor test packs associated with these evaluations, if required.

3.4 Stabilization of Dilute Zirconium Sulfate Solutions

The above being accomplished, one other issue involving the stabilization of dilute solutions of zirconium sulfate, the form in which this material would be used for the plant line trials, required resolution. The instability problem for this material was detected during the previous development project. In that study, it was found that the hydrolysis of zirconium sulfate in dilute solutions could be significantly retarded by initially dissolving zirconium sulfate in 0.5M H₂SO₄. This procedure, therefore, represented a short-term solution to the problem, certainly providing sufficient stability to complete plant line trials with this material. A long-term solution for the instability problem, however, will be required.

Experiments were completed in the laboratories at Bethlehem Steel, Dofasco, Inc., and LTV Steel in attempts to identify factors which influenced the stability of zirconium sulfate in dilute solutions and to identify possible additives which could be added to these solutions to provide long-term stability. None of these tests were successful.

At this point, Southern Ionics Inc., Columbus, Mississippi, a supplier of zirconium orthosulfate, in addition to providing materials for our plant line trials, offered to work with us on the development of a long-term solution to the stability problem. During the first meeting with representatives from Southern Ionics, it was apparent that they were quite aware of the instability problem and provided initial recommendations concerning various approaches to resolve this issue. A report on this subject, submitted by Southern Ionic at that first meeting, is presented in Appendix 2.

After the meeting with Southern Ionics, it was apparent that the development of a method for the long-term stabilization of zirconium sulfate would require a rather prolonged effort. It was, therefore, decided to proceed with the plant line trials, using the above described procedure for short-term stabilization and to continue to work on the development of a long term procedure as the project proceeded.

3.5 Plant Line Trials with Non-Cr Passivation Systems

Following the establishment of a detailed trial plan, plant line trials were completed for the non-Cr zirconate and fluorozirconate passivation systems using the rinse tank in the chemical treatment section of the Weirton Steel No. 6 Electro-Tin Plating Line. A schematic of the chemical treatment section, showing the treatment tank as well as the rinse tank for the #6 ETL, is presented in Appendix 3. In preparation for the trials, all deflector and wringer rolls in the chemical treatment section were changed along with the bridle rolls and 3M Billy rolls in the up-pass to the deflector roll to the Oil Box. Due to the configuration of the rinse tank on the #6 ETL, it was possible to fill the tank only to a level of ~ 6 ft. from the bottom with a total volume of ~800 gallons of treatment solution. This was advantageous from the standpoint that the use of much smaller volumes of solution than initially anticipated resulted in lower costs for chemicals. There was concern, however, that the significantly reduced residence or solution contact time when using this smaller volume could be detrimental to proper passivation film deposition. It was, therefore, decided that sprays in the down-pass in the rinse tank would be used, at least when testing the zirconate system, to increase the solution contact time.

Cleaning of the rinse tank was accomplished by first using high pressure sprays to rinse down the sides of the tank followed by scrubbing the side-walls where possible. The side-walls were then rinsed again with high pressure water sprays, concentrated HCl followed by high pressure water sprays, and finally concentrated H₂SO₄ once again followed by high pressure water sprays. Approximately 50 gallons of fluorozirconate concentrate was then added to the tank and the tank was filled to the overflow (~6 ft. off the tank floor) with water. In this manner, fluorozirconate was actually used as a final cleaning agent prior to preparation and addition of the initial passivation treatment to the rinse tank. After ~1 hour, the fluorozirconate/water solution was removed by dumping, the tank was rinsed several times by filling with water and dumping, and the tank was finally filled with water prior to sampling. A sample of water taken at the overflow at this point indicated ~2.5 PPM Cr. Hot water was then circulated through the tank all night prior to beginning the trials the following morning.

3.6 Trials with Fluorozirconate System

The fluorozirconate was the first system tested in the plant line trials. The initial bath for this system was made up by adding 10-12 gallons of fluorozirconate concentrate to ~800 gallons of DI water resulting in a ~1.5% solution. Line speed trials were completed with a passivation solution temperature of ~90° F and an aim tin coating weight of 0.20 lb/BB (pounds per base box) in the plater section of the production line. Passivation film was deposited from the fluorozirconate solution in the rinse tank using a dip-and-squeegee technique with no sprays in the down-pass and no post-rinse before drying. "Pup" coils (i.e., small coils) produced during the speed trials for

fluorozirconate are listed in Table 1 along with line speeds at which they produced as well as resulting passivation film weights in terms of $\mu\text{g Zr/ft}^2$ of surface area.

Table 1

Speed Trial Coils Produced Using Fluorozirconate Passivation

<u>Finished Pup Coil ID</u>	<u>Line Speed (ft/min.)</u>	<u>Resultant Zr ($\mu\text{g/ft}^2$)</u>
K690472	610	72
K690473	950	90
K690474	1250	99
K690475	1500	135
K690476	1740	117

As can be observed in Table 1, results of Zr analyses indicate values ranging from 72 to 135 $\mu\text{g Zr/ft}^2$ with the amounts of Zr generally increasing with increased line speed. This would indicate higher drag-out levels with increased line speed and is believed to be typical of a dried-in-place system (which this system was defined as by the manufacturer). Following addition of 10-12 gallons more of the fluoro-zirconate concentrate to the rinse tank, test coils for extensive evaluations were produced as listed in Table 2.

Table 2

Test Coils Produced with Fluorozirconate for Extensive Evaluations

<u>Finished Test Coil ID</u>	<u>Aim Sn Ctg. Wt.</u>	<u>Base Weight- Temper</u>	<u>Avg. Zr ($\mu\text{g/ft}^2$ T/B)</u>	<u>Intended Application</u>
J542701	0.20lb/BB	75BW, T4	123 / 207	Sanitary Ends
K690479	0.20 lb/BB	60BW, DR8	126 / 159	3-Piece Lacquered Can
K690481	0.75/.20 lb/BB	60BW, DR8	126 / 150	3-Piece Plain Tin Can
K690482	0.25 lb/BB Matte	95BW, T4	162 / 231	D&I Food Can

3.7 Trials with Zirconate System

Following the fluoro-zirconate trials, the rinse tank was dumped and washed several times with DI water and finally with hot DI water prior to re-filling.

Approximately 27 gallons of zirconate solution was made up to ~800 gallons in the clean rinse tank with 0.05 M H₂SO₄* resulting in a solution treatment concentration of ~20 g/l [calculated as Zr(SO₄)₂·4H₂O]. Line speed trials were then completed with this passivation system at a solution temperature of 107⁰ F and an aim tin coating weight of .20 lb/BB in the plating section of the line. Pup coils produced during the speed trials with the zirconate system are listed in Table 3 along with line speeds used to produce the coils as well as passivation film weights deposited in terms of µg Zr/ft² of surface area.

Table 3
Speed Trial Coils Produced Using Zirconate Passivation

<u>Finished Pup Coil ID</u>	<u>Line Speed (ft/min.)</u>	<u>Resultant Zr (µg/ft²)</u>
K690484	675	153
K690485	950	126
K690486	1250	117
K690487	1550	117
K690488	1800	135

As can be observed in Table 3, there is no apparent relationship between the amounts of Zr deposited and line speed indicating that the mechanism of deposition of Zr from the zirconate system may be self-regulating, as was observed in previous laboratory testing, and is quite different than that for the fluorozirconate system.

Following the zirconate speed trials, ~10 more gallons of zirconate concentrate was added to the rinse tank resulting in a final concentration of 20 g/l [again, calculated as Zr(SO₄)₂·4H₂O]. Test coils for extensive evaluations were then produced for the zirconate system as listed in Table 4.

* Very early in this project, it was found that the zirconate system could be stabilized for some period of time by making up the solution in dilute sulfuric acid. Although this is not a permanent solution to the stability issue, it was shown that the stabilization with dilute sulfuric acid would be sufficient to complete the plant line trials before precipitation would occur.

Table 4**Test Coils Produced with Zirconate for Extensive Evaluations**

<u>Finished Test Coil ID</u>	<u>Aim Sn Ctg. Wt.</u>	<u>Base Weight- Temper</u>	<u>Avg. Zr ($\mu\text{g}/\text{ft}^2$ T/B)</u>	<u>Intended Application</u>
K690489	0.20 lb/BB	75BW, T4	108 / 99	Sanitary Ends
K690490	0.20 lb/BB	58BW, DR8	120 / 93	3-Piece Lacquered Can
K690491	0.75/.20 lb/BB	58BW, DR8	126 / 78	3-Piece Plain Tin Can
K690492	0.20 lb/BB Matte	95BW, T4	129 / 60	D&I Food Can

3.8 Evaluation of Materials Produced During Plant Line Trials**3.8.1 Results on Solution Samples Taken During Plant Trials**

The results of analyses completed on solution samples taken during the plant line trials with the fluorozirconate and zirconate systems are presented in Tables 5 and 6.

Table 5**Results for Solution Samples Taken During
Production of Fluorozirconate Variables**

<u>Sample</u>	<u>Concentration (PPM)</u>											
	pH	Zr	F	Fe	Sn	Cr	Na	Si	Ti	Al	V	Zn
Fluorozirconate Conc.	0.45	26900	27000	82	N.D.	N.D.	147	93	458	40	N.D.	N.D.
11:45 AM (10/8/01)	2.02	630	657	4	53	3	-	-	-	-	-	-
12:25 PM (10/8/01)	2.08	639	647	5	124	4	-	-	-	-	-	-
2:05 PM (10/8/01)	1.84	1220	1240	20	276	6	-	-	-	-	-	-
2:30 PM (10/8/01)	1.87	1190	1230	20	404	7	-	-	-	-	-	-

Table 6**Results for Solution Samples Taken During
Production of Zirconate Variables**

<u>Sample</u>	<u>Concentration (PPM)</u>											
	pH	Zr	F	Fe	Sn	Cr	Na	Si	Ti	Al	V	Zn
Zirconate Conc.	0.28	183000	-	14	N.D.	N.D.	15	N.D.	N.D.	N.D.	18	39
4:10 PM (10/8/01)	0.81	6330	-	13	72	9	-	-	-	-	-	-
5:50 PM (10/8/01)	0.70	8580	-	44	172	14	-	-	-	-	-	-
6:30 PM (10/8/01)	0.70	8430	-	43	340	14	-	-	-	-	-	-

As can be observed in Tables 5 and 6, significant build-ups of tin in both the fluoro-zirconate and zirconate treatment solutions occurred during the trial which should not be surprising considering the low pH of these solutions. Additional testing was necessary to determine the effect of such tin build-up on Zr deposition and to establish methods for control of such build-up.

3.8.2 Results of Evaluations on Test Coils Produced During Plant Trials

3.8.2.1 Results of Lacquer Adhesion Tests - Lacquer adhesion tests were completed at U.S. Steel on sample panels from the test coils produced during the trials using various ASTM methods. Valspar 6256-046 gold epoxy phenolic coating was applied to panels of each test variable along with panels of 120BW 0.25 lb/BB Reflowed ETP with a standard CDC passivation which was used as a control in all tests.

Dry/wet adhesion tests were completed on coated panels using cross hatch and tape pull before and after retort according to ASTM D3359 (Test Method B). Retort conditions were 250⁰ F & 15 psi for 1 hour with half the sample being exposed to liquid water and the other half to steam in each case. Reverse impact tests were completed using a hemispherical die at 20 and 40 in-lbs. according to ASTM D2794 followed by tape pull and rating again according to ASTM D3359. Mandrel bend tests were completed according to ASTM D522 (Test Method A) using a conical mandrel with a diameter of 1/8" at one end and 1 1/2" at the other. In addition, screw cap adhesion tests were completed on selected samples using in-house methodology at U.S. Steel. The results of all adhesion tests are presented in Table 7.

Table 7**Results of Lacquer Adhesion Tests Completed at U.S. Steel**

Coil # (Passivation System)	<u>Lacquer Adhesion</u>		<u>Screw Cap Adhesion</u>	<u>Reverse Impact</u>	<u>Mandrel Bend</u>
	<u>Dry</u>	<u>Wet</u>			
J542701 (Fluorozirconate)	5B	5B	0 – 1	5B	5B
K690479 (Fluorozirconate)	5B	5B	-	-	5B
K690481 (Fluorozirconate)	5B	5B	-	-	5B
K690482 (Fluorozirconate)	5B	5B	0	5B	5B
K690489 (Zirconate)	5B	5B	0 – 1	5B	5B
K690490 (Zirconate)	5B	5B	-	-	5B
K690491 (Zirconate)	5B	5B	-	-	5B
K690492 (Zirconate)	5B	5B	0	5B	5B
Control (CDC)	5B	5B	2 – 4	5B	5B

As can be observed in Table 7, the results of all dry/wet adhesion, reverse impact, and mandrel bend adhesion tests are listed as 5B indicating no loss of adhesion for any of the samples tested, including the Control sample. The results of the screw cap adhesion tests are interesting and have, in the past, been somewhat erratic, even for standard CDC treated materials. As shown in Table 7, the four non-Cr treated variables tested actually performed better than the CDC Control sample with all samples being rated on a scale of 0 to 10, with 0 = no adhesion loss and 10 = total adhesion loss.

3.8.2.2 Results of Sulfide Stain Tests - Sulfide stain testing was completed at Weirton Steel on samples of each of the test coils produced during the plant line trials using the Cysteine staining test as described by S.C. Britton ("Tin Versus Corrosion", International Tin Research Institute, Fraser Road, Perivale, Greenford, Middlesex, England, 1975, pp. 85-86). The results of these tests along with those of two Control samples (standard CDC-5 tinplate) are contained in Table 8, where a rating of 0 = no observable staining and 10 = total or severe staining.

Table 8**Results of Sulfide Stain Tests Completed at Weirton Steel**

<u>Coil Number (Passivation System)</u>	<u>Sulfide Stain Rating</u>
J542701 (Fluorozirconate)	0
K690479 (Fluorozirconate)	0-1
K690481 (Fluorozirconate)	0
K690482 (Fluorozirconate)	0
K690489 (Zirconate)	0-1
K690490 (Zirconate)	0-1
K690491 (Zirconate)	0
K690492 (Zirconate)	0
Control (CDC) #1	0
Control (CDC) #2	0-1

As shown in Table 8, only four of the samples tested showed any existence of sulfide staining, with one of those samples being one of the Controls. It was, therefore, obvious that the incidence and severity of staining for these non-Cr passivation plant trial materials were much less than observed for the previous laboratory-prepared and pilot trial materials.

3.8.2.3 Results of Surface Oxidation Studies - Surface oxidation studies to determine the relative passivation effectiveness of the two non-Cr passivation systems compared to standard CDC were completed at Weirton Steel on samples of each of the test coils using a previously developed x-ray photoelectron spectroscopy (ESCA) technique. With this technique, the relative amounts of tin metal versus tin oxide were measured as a function of sputter depth down through 375 Å from the surface for each sample both before and after baking at 210⁰ F for one hour in a forced air oven. Plots of percent tin oxide versus sputter depth for the zirconate materials produced during the plant line trials as well as a CDC Control in both the pre- and post-bake conditions are presented as Figures A4-1 and A4-2, respectively, in Appendix 4. Similar plots for the fluorozirconate variables as well as the CDC Control, again in the pre- and post-bake conditions are then presented as Figures A4-3 and A4-4, respectively, in Appendix 4.

The results presented in Appendix 4 indicate that both the zirconate and the fluorozirconate materials are quite effective in retarding surface oxidation and that the zirconate variables appear to prevent oxidation a little better than the fluorozirconate variables. Neither of these treatments is quite as good, however, as the standard CDC system in preventing surface oxidation. The same was found to be true at about the same orders of magnitude during the initial development project for samples produced in the laboratory and on pilot line facilities using these passivation systems.

3.8.2.4 Results of Evaluations Completed at Surface Science Western – Passivation film characterizations and electrochemical corrosion testing were completed under contract at Surface Science Western (SSW), The University of Western Ontario, London, Ontario, Canada, on samples of materials produced during the plant line trials. Analytical techniques used for passivation film characterizations consisted of field emission scanning electron microscopy (FESEM) combined with energy dispersive X-ray (EDX), X-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Electrochemical techniques for corrosion testing consisted of linear polarization and electrochemical impedance spectroscopy. A copy of the final report received from Surface Science Western which contains detailed descriptions of the results obtained from all these tests is presented in Appendix 5.

In summary, the results of film characterizations completed at SSW were as follows:

- Micrographs resulting from SEM analyses and results of XPS analyses indicated very low levels or thin films of zirconium on the tin surfaces .
- Results of ToF-SIMS once again indicated very low levels of zirconium on the tin surface being in the order of 1 nm in thickness or less.
- Results using ToF-SIMS also indicated that the zirconium layers present on these samples are relatively non-uniform compared to what is normally observed for the passivation layer on standard CDC-5 tinplate.
- In addition, ToF-SIMS images also showed that zirconium was present in the surface films as zirconium oxide.

Results of the electrochemical corrosion testing completed at SSW were as follows:

- The open circuit potential did not vary much between different Zr passivated samples ranging from - 580 to - 595 mV_{sec}.
- The solution resistance (R_s) values were quite similar for all samples ranging from 0.038 to 0.050 Ohm.cm².
- The polarization resistance (R_p), coating resistance (R_c), and charge transfer resistance (R_{ct}) values for all samples tested are quite similar in magnitude and indicate that fluorozirconate, zirconate, and CDC all have very similar corrosion resistance.
- Although the coating capacitance (Q_c) values indicate relatively non-uniform passivation films for the fluorozirconate and zirconate systems compared to CDC (confirming previous surface analysis results), the extent of surface coverage for these samples do not appear to significantly affect their corrosion behavior.

3.8.2.5 Surface Testing Completed at Dofasco, Inc. – Linear polarization and electrochemical impedance spectroscopy measurements were also completed at Dofasco, Inc. on selected samples from the plant line trials along with atomic force microscope (AFM) determinations. Details of this testing are presented in Appendix 6. No significant differences were found between the AFM images for the various materials tested. It is significant to note, however, that results of electrochemical testing suggested that the corrosion rate was not dependent on the quantity of zirconium on the tinplate surfaces which compares well with the above SSW results.

3.8.2.6 Additional Testing – As stated previously, significant amounts of tin build-up were observed in the passivation treatment solutions during the relatively short duration of the trials (Tables 5 & 6). Tests were completed in the laboratories at Bethlehem Steel to determine the effect, of any, of dissolved tin on zirconium deposition from zirconate and fluorozirconate solutions. In initial tests, dissolution rates for tin were, therefore, determined for the two electrolytes. In the laboratory, zirconate solution, when in contact with granular tin with agitation, was found to dissolve tin at a rate of ~ 28 PPM tin / hour and

fluorozirconate was found to exhibit a tin dissolution rate of ~ 20 PPM tin / hour. These values are significantly less than what was observed during the plant trials which lead to the conclusion that much of the tin in the trial solutions was the result of drag-in of plater chemicals adhering to the strip during line stoppages. It was further concluded that the relatively low tin dissolution rates observed in the laboratory would not be sufficient to detrimentally affect Zr deposition from the treatment solutions.

4.0 Conclusions and Recommendations

From the results of those test that were completed, it is certainly apparent that the zirconate and fluoro-zirconate systems represent viable alternatives for the electrolytically deposited dichromate system presently used. Some evaluations are still going at Valspar, PPG, and ICI on those variables designated for sanitary end and 3-piece lacquered can applications using their respective, commercial lacquer systems. Also not completed were evaluations of plant trial variables designated for 3-piece plain tin and D&I food can applications by producing cans in commercial can-making facilities followed by evaluation of resulting cans by test packs prepared in commercial packing facilities and monitored in the laboratories at NFPA.

It was not the intent of the project to totally optimize the commercial application parameters for the zirconate and fluoro-zirconate and that must be left to those who implement these systems in the future. It was the intent, however, to develop a method to totally stabilize the zirconate system and that, unfortunately, was not accomplished. It is believed, however, that continued work with suppliers such as Southern Ionics will result in such a method or technique. Finally, although direct work with potential customers to evaluate these products was not done, in reality, final customer acceptance of these types systems must eventually be done through direct interaction between those customers with each individual TPM producer.

5.0 List of Appendices

Appendix 1 – Valspar Report Entitled “Laboratory Investigation into the Comparative Performance, in Conjunction with Typical Food Can Coatings, of Two Types of Non-Chrome Treated Tinplate Versus Standard Treated Tinplate”

Annexure A1-1: AISI Committee Correspondence

Annexure A1-2: Chromium Passivation of Tinplate Surfaces and Strategy for Alternatives

Appendix 2 – Southern Ionics Report Entitled “Zirconium Orthosulfate Stability”

Appendix 3 – Schematic of Chemical Treatment Section of Weirton Steel #6 ETL

Appendix 4 – XPS Tin Oxide Versus Sputter Depth Plots of Zirconate, Fluorozirconate, and Standard CDC Before and After Baking

Appendix 5 – Surface Science Western Report Entitled “A Report on the Surface Analysis and Electrochemical Testing of Zirconium-Passivated Tinplate Samples

Annexure A5-I: SEM Micrographs Collected from the Tinplate Samples

Annexure A5-II: XPS Survey Scan Spectra Collected from the Tinplate Samples

Annexure A5-III: Positive Ion ToF-SIMS Images Collected from The Tinplate Samples

Annexure A5-IV: Overlay of Positive Ion ToF-SIMS Images Collected from the Tinplate Samples

Annexure A5-V: Linear Polarization Curves Obtained in As-Prepared and Deaerated Synthetic Pear Juice

Annexure A5-VI: Electrochemical Impedance Spectra Obtained in As-prepared and Deaerated Synthetic Pear Juice

Appendix 6 – Dofasco Report Entitled “Atomic Force Microscopy (AFM) Images of AISI Passivation Trial Materials”

6.0 References

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Appendix 1



The Valspar Corporation

*Packaging Coatings Group
2001 Tracy Street
Pittsburgh, PA 15233
Phone 412-766-9300
FAX 412-766-4517*

Laboratory Investigation into the Comparative Performance, in Conjunction with Typical Food Can Coatings, of Two Types of Non-Chrome Treated Tinplate Versus Standard Chrome Treated Tinplate

Introduction:

In an attempt to investigate the comparative performance of two types of non-chrome treated tinplate, in comparison with standard chrome treated tinplate, panels of each were coated with different food can coatings and subjected to a series of laboratory tests typically used by Valspar for their assessment and development.

Background:

The American Iron and Steel Institute (AISI) has a program to investigate the potential use of non-chrome passivation systems, due to environmental concerns over the use of the standard chrome systems. As part of this program, Valspar agreed to carry out test work with possible candidate technologies, and was provided with samples of two alternative treatments; a zirconium based treatment and a fluoro-zirconate treatment. Details of the samples provided are summarized in the AISI Committee correspondence from J. Sinsel, Project Manager – Non-Cr Passivation Commercial Line Trial, attached as Annexure A1-1.

Method:

Metal: 0.25 # tin weight, 75 # basis weight, tinplate:

1. Commercially available Cr treated – Weirton Steel
2. Zirconium-base treatment – applied in Bethlehem Steel laboratory
3. Fluoro-zirconate treatment – applied by a commercial supplier of the treatment in the supplier's laboratory.

Three Piece Food Can Coatings:

1. Commercial solvent based epoxy phenolic gold sanitary interior
2. Commercial water based epoxy phenolic gold sanitary interior

3. Commercial solvent based modified epoxy white sanitary interior
4. Commercial solvent based modified epoxy clear exterior varnish.

Laboratory Tests:

Sample panels were coated at typical specified film weights by means of wire wound bars and then baked for the specified time at peak metal temperature. The interior coatings were then subjected to two sets of resistance testing and the exterior to a simple array of comparative tests:

1. Media Testing of Interior Coatings: Conventional 202 ends were fabricated from the panels and packed and processed in the media listed below. The media used are repacks of packed product and hence are not expected to give the same result as a fresh commercial pack but are used to indicate comparative performance. The packed ends were stored at 100⁰ F for 12 weeks to accelerate failure and then each test piece was rated for adhesion in the flat and finished area and for stain/corrosion/blush.
 - i. Brine Solution
 - ii. Barbeque Sauce
 - iii. Lard
 - iv. Chicken Broth
 - v. Apple Juice
 - vi. Tomato Paste
 - vii. Beef Gravy Dog Food
2. Synthetic Solution Testing of Interior Coatings: Strips were cut from the coated panels and processed in a series of synthetic solutions as listed below. The synthetic solutions are used to show comparative performance in environments of varying aggressiveness and give a quick indication of positive and negative properties. Each test piece was rated immediately after process, for blister and stain as is appropriate.
 - i. Dry Adhesion
 - ii. Water Process
 - iii. Deionized Water Process
 - iv. Reducing Solution – Used to screen reducing products / detinners, eg. Acid fruits and green beans
 - v. Oxidizing Solution – Used to screen oxidizing packs especially where catalytic or depolarizing residues of sprays, fertilizers, or additives are present, eg. Stewed tomatoes with added sulphur dioxide

- vi. Cysteine Solution – Used to screen sulphur staining packs, eg. Potted meat, fish, peas, and corn. Less aggressive than Sulphur Solution for blistering
- vii. Sulphur Solution – Used to screen aggressive packs containing sulphur, brine, and acid
- viii. Cooking Salt/Acetic Acid Solution – Used to screen packs with brine and acid, eg. Pickles and peppers
- ix. Lactic Acid Solution – Used to screen lactic acid containing packs, eg. Milk products, fruits, and wines

3. Exterior Varnish Testing:

- i. Dry Adhesion
- ii. Water Process
- iii. Pencil Hardness
- iv. Wedge Bend

Results:

Results for all testing described above are summarized in the following:

Table A1-1 shows the Media test results.

Table A1-2 shows the Solution test results.

Table A1-3 shows the exterior varnish results.

Each test piece has been rated on a scale of 0-10, where 0 shows gross failure and 10 indicates zero deterioration during test.

Significance of Results:

Due to a limitation in the amount of test plate available, the number of test pieces in each test was limited, reducing the statistical significance of the results.

Furthermore, the treatment application on the test plate was not generally of commercial quality appearance, especially the fluoro-zirconate treated plate, and test pieces had to be sorted prior to test to remove those worst in appearance and to establish a baseline for comparison for those used in test. There is however enough correlation between the data and previous test data and between related tests in this array, to discern trends and draw conclusions with reasonable confidence.

Table A1-1

Results of Food Media Testing At Valspar

<u>Food Media</u>	<u>Rating</u>								
	<u>Internal Lacquer*/ Passivation**</u>			<u>Internal Lacquer*/ Passivation**</u>			<u>Internal Lacquer*/ Passivation**</u>		
	<u>A/CDC</u>	<u>A/Zr</u>	<u>A/Zr-F</u>	<u>B/CDC</u>	<u>B/Zr</u>	<u>B/Zr-F</u>	<u>C/CDC</u>	<u>C/Zr</u>	<u>C/Zr-F</u>
Brine Process									
Adhesion (fab/flat)	10/10	10/10	10/10	10/10	10/10	7/8	10/10	7/9+	4/4
Stain/Corrosion/Blush	6/6	9/9	5/5	9+/9+	10/10	4/4	10/10	10/10	10/10
Barbeque Sauce									
Adhesion (fab/flat)	8/10	9+/10	10/10	10/10	10/10	10/10	8/10	10/10	10/10
Stain/Corrosion/Blush	10/10	10/10	10/10	10/10	10/10	6/6	10/10	10/10	10/10
Lard									
Adhesion (fab/flat)	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10
Stain/Corrosion/Blush	10/10	10/10	8/8	10/10	8/8	7/7	10/10	10/10	10/10
Chicken Broth									
Adhesion (fab/flat)	10/10	10/10	10/10	10/10	10/10	10/10	10/10	4/5	7/7
Stain/Corrosion/Blush	10/10	8/8	8/8	9/9	9/9	5/5	10/10	10/10	10/10
Apple Juice									
Adhesion (fab/flat)	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10
Stain/Corrosion/Blush	9+/9+	10/10	7/7	10/10	10/10	8/8	10/10	10/10	10/10
Tomato Paste									
Adhesion (fab/flat)	10/10	10/10	10/10	10/10	10/10	10/10	10/10	9+/9+	9+/9+
Stain/Corrosion/Blush	9+/9+	9+/9+	9+/9+	9+/9+	9+/9+	9/9+	8/8	8/8	8/8
Beef Gravy Dog Food									
Adhesion (fab/flat)	10/10	10/10	10/10	10/10	9+/10	10/10	9+/9+	4/1	5/2
Stain/Corrosion/Blush	5/10	4/5	3/3	5/10	4/4	4/4	9/9	10/10	9/9

* Internal Lacquer A = Solvent-Base Epoxy Phenolic Gold @ 3.5-4.5 msi
Internal Lacquer B = Water-Base Epoxy Phenolic Gold @ 4.0-5.0 msi
Internal Lacquer C = Solvent-Base Epoxy White @ 7.0-9.0 msi

** CDC = Cathodic Dichromate, Zr = Zirconate, & Zr-F = Fluorozirconate

Table A1-2

Results of Synthetic Solution Testing at Valspar

<u>Synthetic Solution</u>	<u>Rating</u>								
	<u>Internal Lacquer*/ Passivation**</u>			<u>Internal Lacquer*/ Passivation**</u>			<u>Internal Lacquer*/ Passivation**</u>		
	<u>A/CDC</u>	<u>A/Zr</u>	<u>A/Zr-F</u>	<u>B/CDC</u>	<u>B/Zr</u>	<u>B/Zr-F</u>	<u>C/CDC</u>	<u>C/Zr</u>	<u>C/Zr-F</u>
Dry Adhesion	10	10	10	10	10	10	10	10	10
Water Process									
Adhesion (Liq./Vap.)	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10
Blush (Liq./Vap.)	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10	10/10
Deionized Water									
Adhesion	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/9/8
Blister	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/9/9	7/6/5	6/5/4
Reducing Solution									
Adhesion	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/9
Blister	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10
Oxidizing Solution									
Adhesion	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10
Blister	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10
Cystein Solution									
Adhesion	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	9/9/9	3/3/2	2/2/1
Blister	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	10/10/10	9/9/9	3/3/3	2/2/2
Stain	10/10/10	8/7/7	9/9/8	8/8/8	8/7/7	7/5/5	7/7/7	9/9/9	9/9/9
Sulfur Solution									
Adhesion	10/10/10	10/10/10	10/10/10	8/5/2	10/10/8	10/10/10	10/10/9	7/6/5	8/7/6
Blister	10/10/10	10/10/10	6/6/6	10/10/10	10/10/10	10/10/10	9/9/8	7/6/3	9/9/8
Stain	10/10/10	10/10/10	10/10/10	5/5/4	5/5/5	3/3/2	8/8/8	7/7/7	7/7/7
Salt/Acetic Acid									
Adhesion	10/10/10	10/10/10	10/10/10	6/6/6	8/7/6	10/10/10	10/10/10	10/10/10	6/6/6
Blister	9/9/9	9/9/9	5/5/5	3/3/3	3/3/2	2/2/2	3/3/3	5/5/4	2/2/2
Lactic Acid									
Adhesion	10/10/10	10/10/10	10/10/10	10/10/10	5/3/2	7/7/5	9/7/7	8/6/5	4/4/3
Blister	3/3/3	2/2/2	3/3/3	0/0/0	0/0/0	0/0/0	0/0/0	0/0/0	0/0/0

* Internal Lacquer A = Solvent-Base Epoxy Phenolic Gold @ 3.5-4.5 msi
 Internal Lacquer B = Water-Base Epoxy Phenolic Gold @ 4.0-5.0 msi
 Internal Lacquer C = Solvent-Base Epoxy White @ 7.0-9.0 msi

** CDC = Cathodic Dichromate, Zr = Zirconate, & Zr-F = Fluorozirconate

Table A1-3**Results of External Varnish Testing at Valspar**

<u>Test</u>	<u>Rating</u>		
	Modified Epoxy External Varnish @ 3.5-4.5 msi (CDC)	Modified Epoxy External Varnish @ 3.5-4.5 msi (Zirconate)	Modified Epoxy External Varnish @ 3.5-4.5 msi (Fluorozirconate)
Dry Adhesion	10	10	10
Water Process - 90' @ 250⁰ F			
Adhesion (Liquid/Vapor)	10/10	10/10	10/10
Blush (Liquid/Vapor)	10/10	10/10	10/10
Pencil Hardness	2H	2H	2H
Wedge Bend	8/8/8	8/8/8	8/8/8

Discussion:

A simple scan of the test results shows that both non-chrome treatments are generally deficient compared with the performance of the chrome standard. The fluoro-zirconate treatment performed worse than the zirconium treatment. There were however a few instances where the test treatment gave a better result than the standard, depending on the coating chemistry.

All treatments performed equivalently in dry and non-aggressive solutions as in the exterior varnish performance testing and water, Reducing and Oxidizing solutions. There was however some level of differentiation of the performance of the treatments in all of the aggressive and staining media, which is consistent with what is expected with the change in treatment type. See the discussion document "Chromium Passivation of Tinplate Surfaces and Strategy for Alternatives" by John Weir of the Valspar Corporation, which is attached as Annexure A1-2.

Considering that all coatings tested have been developed to work over chrome treatment it is reasonable to assume that some level of coating performance optimization may be possible if specifically designed to work over an alternative treatment. Alternatively, the use of higher film weights may be a means of overcoming the deficiencies in pack performance due to the treatment.

Conclusion:

While there are some instances where the non-chrome treatments show better results than the chrome treatment, it is clear that the chrome treatment offers the

best overall performance. On balance, the zirconium treatment performs better than the fluoro-zirconium treatment, which shows more deficiencies in both corrosive and staining media. Rating is then summarized as: chrome > zirconium > fluoro-zirconate.

Recommendations:

1. Present current results to the can industry. A larger application trial be carried out with the zirconium treatment to validate application and subsequently provide a greater quantity of substrate for testing.
2. An expanded array of laboratory performance testing be undertaken to increase statistical significance and assess performance with other technologies.
3. Determine the potential for current coating technology to be optimized for use with the non-chrome treatment.
4. Assess whether higher coating film weights could be used to improve performance of current technology over non-chrome treatment.
5. Initiate a set of commercial pack tests to confirm the performance of the zirconium treatment.

Grant Schutte

Sub-notes:

1. This report's intended readers are all involved in the Rigid Packaging industry, as metal or coating suppliers, can makers or can fillers; it is therefore assumed that everyone involved is familiar with the fundamental terminology and technology of the industry.
2. Certain of the test methods used are considered to be of a proprietary nature and hence specific information on the test methodology has not been included in this report. Customers or technology partners that have secrecy agreements with Valspar, will be provided with specific details on request.

Annexure A1-1

American Iron and Steel Institute

COMMITTEE CORRESPONDENCE

March 1, 2000

John R. Weir
The Valspar Corporation
Packaging Coatings Group
2001 Tracy Street
Pittsburgh, PA 15233

Dear John:

Panels treated with two of our non-Cr passivation systems are **FINALLY** available for your coating optimization work to minimize sulfide staining. Enclosed please find approximately 108 panels treated with a zirconium-base treatment in the laboratories at Bethlehem Steel and approximately 90 panels treated with a fluoro-zirconate treatment in a commercial suppliers laboratory. Descriptions of these materials are as follows:

Zirconium Treated Panels

Panels are ~ 18" x 6" treated on one side using a rotating cathode assembly to approximately 4.5" to 5.0" with the demarcation between treated and untreated areas clearly visible. Individual panels are marked in the untreated area (but on the treated side) with the date of production followed by a code ranging from 01 to 136. Selected codes having been retained from the initial sample set produced for other testing. Any portion of the treated area for each panel should be applicable for testing purposes.

Fluoro-Zirconate Treated Panels

Panels are ~ 4" x 7" treated on both sides using a dip-and-squeegee technique followed by drying. Individual panels are not marked or coded.

As you indicated in our last communication, your evaluation/development work should take approximately 2 months. I will, therefore, be in contact with you sometime in April to determine the status of your work and to schedule a time in early May for you to review your results with our project team.

During our last meeting, you may remember that there was a third non-Cr passivation system that we were also considering. For your information, this

system did not fair well in our laboratory optimization work and the system is presently undergoing additional development in a commercial suppliers laboratory. At this point, I don't know whether or not this system will be available in the near future for your testing (or, for that matter, inclusion in our commercial line trials). I will keep you informed as information concerning this third system is received but I certainly would not hold up your work at this point on the two systems included in this submission.

Good luck !

Sincerely,

John A. Sinsel
Project Manager
Non-Cr Passivation Commercial

Line Trial

c: Bill Balutanski, Valspar
Bob Fatzinger, AISI

Annexure A1-2

CHROMIUM PASSIVATION OF TINPLATE SURFACES AND STRATEGY FOR ALTERNATIVES

Corrosion mechanism of coated metal substrates. Analyses of electrochemical impedance spectroscopy data as well as measurements of the diffusion of water and oxygen through organic coatings indicate that the organic coating applied over a metal or conversion coating substrate is not a significant barrier to transport of these species through the organic coating. An increase in coating thickness will increase the time required for saturation of the organic coating with water and oxygen but will not reduce the amount of these species that will reach the interface between substrate and organic coating. Furthermore, some analyses indicate that this diffusion rate is not the rate limiting step in corrosion under the organic coating. The result is that the substrate/organic coating interface will be exposed to a highly corrosive water and oxygen environment.

The typical metal substrate under the organic coating, whether coated by a native oxide layer or an artificially created protective layer will contain sites of differing electrochemical potential due to local differences in composition. This difference in potential will result in electrical current flow if a conductive pathway is available. Areas of differing potential will act as anode or cathode in the resultant electrochemical cell and corrosion will occur. The anodic reaction will be oxidation of the substrate while the cathodic reactions will be reduction of water to molecular hydrogen and hydroxide ion. Molecular oxygen will be reduced to hydroxide ion. Water at the organic coating/metal interface without molecular oxygen is sufficient to initiate the corrosion reaction (1).

The accumulation of hydroxide under the organic coating results in an extremely alkaline environment that may dissolve an oxide or conversion coating and prevent formation of any subsequent protective layer. The volume increase as a result of hydroxide ion and corrosion product formation under the coating results in blistering of the coating (2). Molecular hydrogen will diffuse through the organic coating without difficulty but hydroxide ion will not. As the substrate oxides dissolve by formation of metal hydroxide complexes, more metal surface is exposed which will in turn oxidize and form metal oxides that will then dissolve as the corrosion process continues. For the corrosion protection mechanism to be effective, the corrosion process must be interrupted by preventing water from reaching the metal/organic coating interface, by preventing dissolution of the existing inorganic layer covering the metal surface, or by precipitation of an insoluble protective layer as a result of the corrosion reaction.

An additional consideration in assessing the corrosion or degradation of coated metal substrates is the effect of water uptake on the organic coating. In the case of epoxy coatings, water uptake by the coating was observed by electrochemical impedance spectroscopy and was shown to swell the epoxy coating (3). Such a

change in organic coating geometry has the effect of changing the diffusion coefficient of the coating for water as well as subjecting the coating to additional mechanical stress.

Corrosion protection mechanism of chromium/chromium oxide (CDC) passivated tinplate. Assuming a typical corrosion cell environment as described previously, the chromium/chromium oxide layer will be exposed to an extremely alkaline environment. As the pH increases due to chromium metal oxidation with concurrent water and oxygen reduction, the reaction of hydroxide ion produced by the reduction of water and chromium(III) ion from the oxidized chromium metal results in a precipitate of chromium(III) oxide. This precipitate forms a protective layer over the corroding areas in the corrosion cell and thus slows the corrosion reaction. Eventually, the corrosion reaction will stop as no additional area is exposed.

CHROMIUM REPLACEMENT STRATEGY

Alternate Passivation Systems. The strategy for alternate conversion coatings has to a large extent been designed to duplicate the critical characteristics of the chromium/chromium oxide layer. Ideally, an alternate passivation treatment should exhibit high resistance to dissolution in alkaline environments when a can or end is forming exposing a fresh tin/iron surface. To duplicate the corrosion protection mechanism of chromium/chromium oxide, the non-chromium passivation treatment should be capable of forming insoluble reaction products from the hydroxide and the dissolved passivation treatment.

Alkaline Resistance. A common approach is to create an initial protective oxide layer that is insoluble in alkaline environments. Examination of the Pourbaix diagrams for metal oxides (4) shows that the approximate pH stability limits are as follows; chromium(III) oxide – 15, zirconium(IV) oxide – 12.5, titanium(IV) oxide – 12, silicon(IV) oxide – 10.5, and aluminum(III) oxide – 9. The preponderance of alternate conversion coatings that are currently in use or are being tested are titanium and zirconium oxide based systems for aluminum substrates (5-15), both conventional spray/rinse and no-rinse applications, systems which exhibit the most alkaline resistant oxides after chromium.

The lack of solubility of the conversion coating in the titanium and zirconium oxide based systems, while imparting initial corrosion resistance, provides no opportunity for formation of a protective layer of corrosion products. Even if the initial conversion coating has no porosity preventing the initiation of corrosion, the forming operation will expose fresh tin/iron surface that has no protective layer other than tin and iron oxides. Attempts to impart additional corrosion protection to these areas have been based on phosphate rinses to take advantage of the capability of phosphate to inhibit hydration of metal oxides (16).

Oxidation/Reduction Reactions. An important factor that is lacking in this strategy for chromium/chromium oxide replacement is the oxidation of the tin/iron surface that occurs on reaction with chromium(III) when the chromium/chromium oxide passivation layer is initially created. The high oxidizing potential of the chromate passivation solution will result in an initial corrosion. Reaction of these sites will reduce the electrochemical potential below that of surrounding areas of the surface which thus become the higher potential areas and react with the chromium(VI). With infinite time all surface sites would react eliminating any preferential corrosion sites.

Since an oxidizing agent is lacking in the titanium and zirconium based passivation treatments, the properties of the deposited conversion coating as well as the mechanism of formation of this passivation layer will depend on the initial oxide surface with which the passivating solution will react. A passivation formulation should be designed to either remove an oxide layer prior to formation of a passivation layer or incorporate the oxide as a component of the passivation layer. In either case the choice of cleaning method will constrain the passivation layer composition and process. The use of acidic or alkaline cleaners will result in an oxide of very different thickness and properties. Since the passivation layer is formed by precipitation due to the surface pH change on dissolution of the oxide, the amount of conversion coating that is obtained will be dependent on the amount and reactivity of the residual tin and iron oxides. Acidic cleaners result in very thin air formed oxide and low levels of passivation layer while alkaline cleaners result in moderate to high levels of oxide and generally higher levels of passivation layer.

For the no-rinse versions of titanium and zirconium oxide passivation treatments, little or no reaction of the oxide remaining after the cleaning process will occur and the reaction products, if any, will be incorporated into the conversion coating. In this type of system, the corrosion resistance of the passivated substrate will depend on the properties of the tin and iron oxides as well as the applied passivation layer. One advantage of this system is that the level of passivation is independent of the amount of initial oxide since the deposition is not determined by dissolution of existing oxides.

CONCLUSIONS

It is apparent that the chromium/chromium oxide passivation layer system embodies a unique combination of physiochemical characteristics. At best, alternate systems can only duplicate individual characteristics of this system with the resultant diminution of resistance to service environments. However, the lower level of resistance of the alternate systems is adequate for many service environments, even if less than that afforded by the CDC process. In terms of process control, this lower level of corrosion resistance is reflected in tighter tolerances for process parameters and a less forgiving product.

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Appendix 2



ZIRCONIUM ORTHOSULFATE STABILITY

Interim Report

Joe c. Steelhammer, Ph.D.
8/8/99

Objective

The objective of this project is to define the variables that control the stability of zirconium orthosulfate solutions (ZOS).

Discussion

Background

An earlier interim report (6/23/99) presented data showing that samples of ZOS made in the laboratory demonstrated excellent stability when compared to production batches of ZOS. At ambient temperatures ($\sim 72^{\circ}\text{f}$), laboratory samples would show no signs of deposits even after 1 year, whereas a small amount of deposit would be visible in the production sample within 30 days. This report also reported that the rate of deposit formation and the amount of deposit formed in the production sample significantly increased if the storage temperature was 140 of instead of ambient, whereas the laboratory sample still remained deposit free. This is demonstrated in figure 1 which shows the deposit formed in a production sample of ZOS after 7 days of storage at 140°f compared to a deposit free laboratory sample that had been stored for 14 days at 140°f .



FIGURE I: Laboratory ZOS (left) and Production ZOS (right) solutions stored at 140°F for 14 and 7 days, respectively. Both samples are unfiltered. The laboratory sample showed no signs of deposits.

The 140° F storage temperature represents the upper temperature limit (120-140° F) that ZOS solutions are stored in SII storage tanks and shipped to customers now that ZOS is made from zirconium basic sulfate and sulfuric acid.

Effect of Seed Crystals on ZOS Stability

Recently it has been demonstrated that deposits in laboratory samples of ZOS could be induced if seed crystals, in the form of deposits (scale) taken from a ZOS storage tank, were added. Figure 2 demonstrates that the addition of scale from a ZOS storage tank (to be referred to as ZOS scale) at a level of ~0.1-0.2% results in deposits in laboratory samples stored at 140° F for only 2 days. The higher the zirconium concentration, the greater the deposit. Additionally Figure 2 shows that laboratory samples with no seed crystals are deposit free after 8 days.



FIGURE 2: Laboratory ZOS samples with and without ZOS scale present as seed crystals and stored at 140° F. Left 3 samples (no seed) are 14.5, 17.5, and 20% ZrO₂. Right three samples (with seed) for 14.5, 17.5, and 20% ZrO₂.

Sand, dirt, calcium sulfate, titanium dioxide, aluminum trihydrate, and zirconium hydroxide were also evaluated as seed crystals at storage temperatures of 140 °F. Only zirconium hydroxide was found to induce significant deposition in ZOS solutions. This suggests the seed crystal must be zirconium-based in order to promote deposit formation.

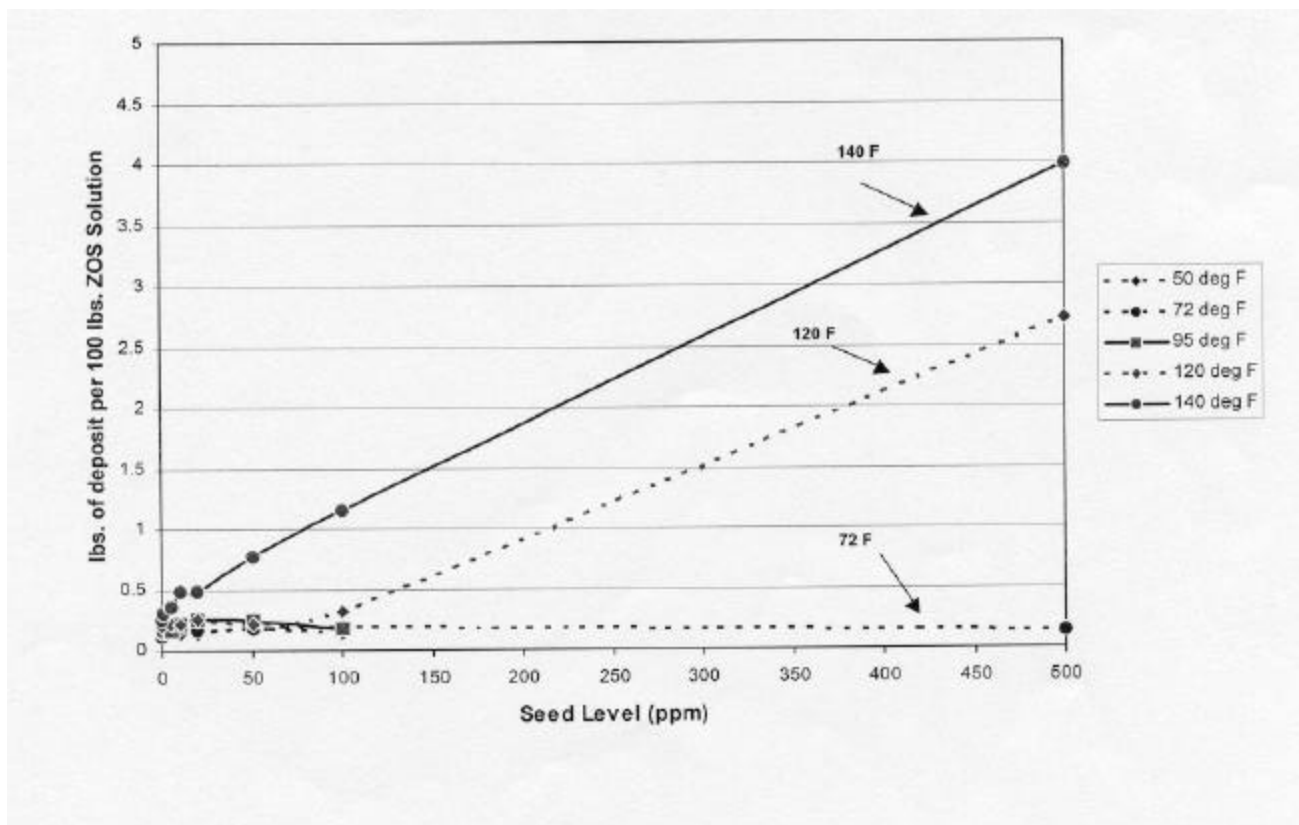
Deposits/scale taken from customer and plant ZOS storage tanks and laboratory stability studies have been found to be a zirconium hydroxy sulfate (a basic zirconium sulfate) with a S/Zr ratio of 1.0.

Effect of Temperature and Seed Crystal Concentration on ZOS Stability

A set of experiments aimed at quantitatively defining the dependence of deposit formation in ZOS solutions on seed crystal concentration and temperature have recently been initiated. These studies used a production batch of ZOS (17.0% ZrO₂) that was filtered in the laboratory through a 1.4 µ filter prior to addition of the seed crystals. The seed crystals used were obtained from ZOS storage tank deposits. Seed crystal concentrations ranged from 1 ppm to 500 ppm and storage temperatures studied were 32,50,72,95,120 and 140 °F.

Figure 3 shows the weight of deposit formed in the ZOS solutions after 6 days storage at the indicated temperature as a function of the seed crystal concentration.

FIGURE 3: ZOS SCALING: Seed Level (0-500 ppm) vs. Weight of Deposit
Production Batch ZOS. 6 days storage time.

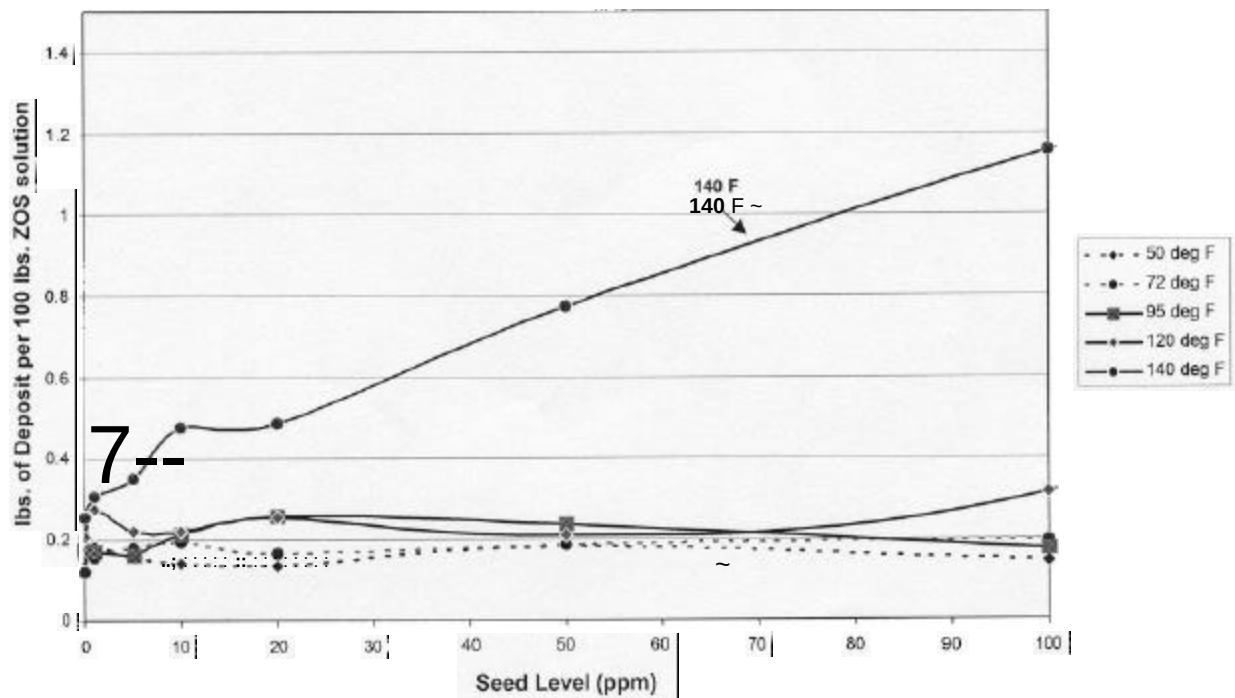


As can be seen in Figure 3, at a given seed level, there is a threshold temperature for rapid (6 days) deposit build-up. Below this temperature, the insoluble content, as zirconium seed crystals, is not a major factor in rapid scaling.

Figure 3 also shows that above the threshold temperature, the weight of deposit formed after 6 days is linear with the seed level concentration.

Figure 4 is the same data shown in Figure 3, but is restricted to seed crystal concentrations less than 100 ppm (0.01 %). This figure shows that at 140 F, significant deposit formation occurs at seed crystal

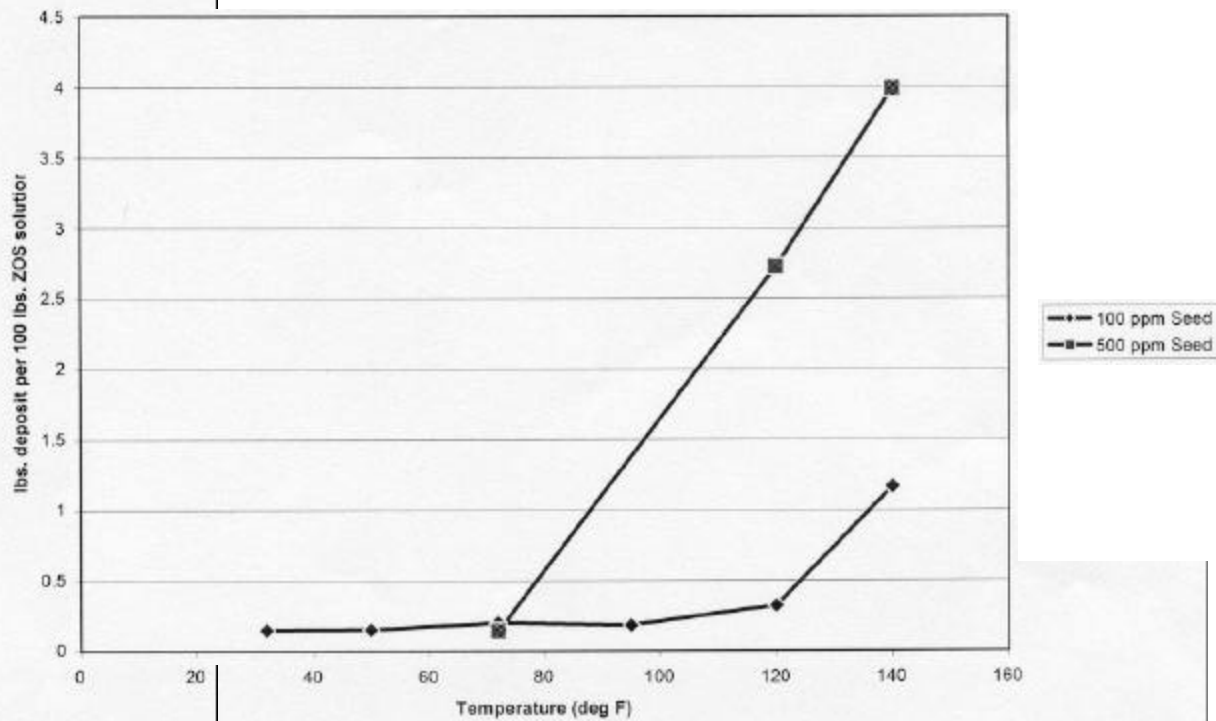
FIGURE 4: ZQS SCALING: Seed Level (0-100 ppm) vs. Weight of Deposit
Production Batch ZOS. 6 days storage time.



concentrations as low as 10-20 ppm. Figure 4 also shows that some deposition in ZOS solutions occur even at seed crystal concentrations of zero and storage temperatures of 50 °F. Although not shown in figure 4, the amount of deposit formed at 0 ppm seed crystal concentration and 32 °F is comparable to that at 50 °F .

Figure 5 shows the amount of deposit formation after 6 days as a function of temperature. As can be

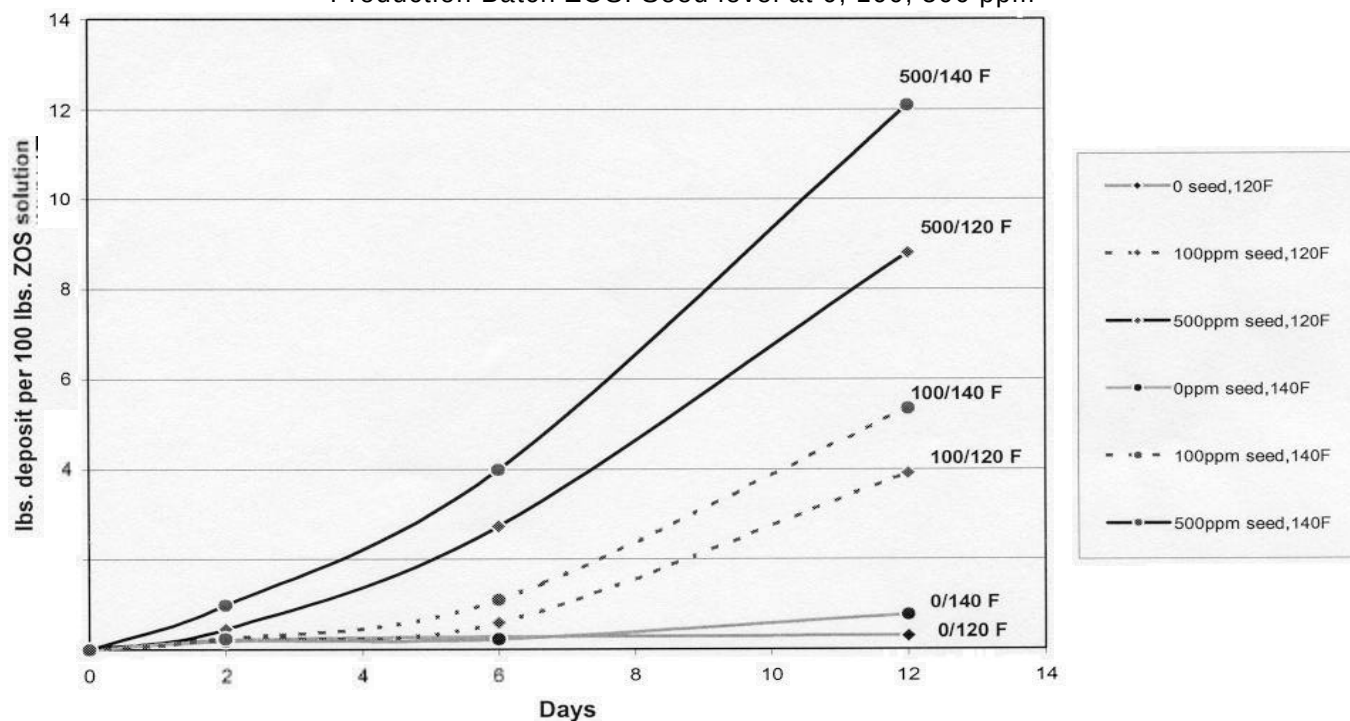
FIGURE 5: ZOS SCALING: Weight of Deposit vs. Temperature
Production Batch ZOS. 6 days storage time. 100 & 500 ppm seed.



seen, significant scaling occurs down to ambient temperatures (75-85 °F) for seed crystal concentrations of 500 ppm or more. At a seed crystal concentration of 100 ppm, significant scaling ceases at temperatures of 120 or less.

figure 6, shown on the next page, shows the rate of deposit formation as a function of time for seed crystal concentrations of 0, 100, and 500 ppm and storage temperatures of 72, 120, and 140 of. The rate of scale formation was found to fit a polynomial equation at temperatures greater than the threshold temperature and at a given temperature decrease as the seed concentration decreased.

FIGURE 6: ZOS SCALING: Weight of Deposit vs. Time
Production Batch ZOS. Seed level at 0, 100, 500 ppm

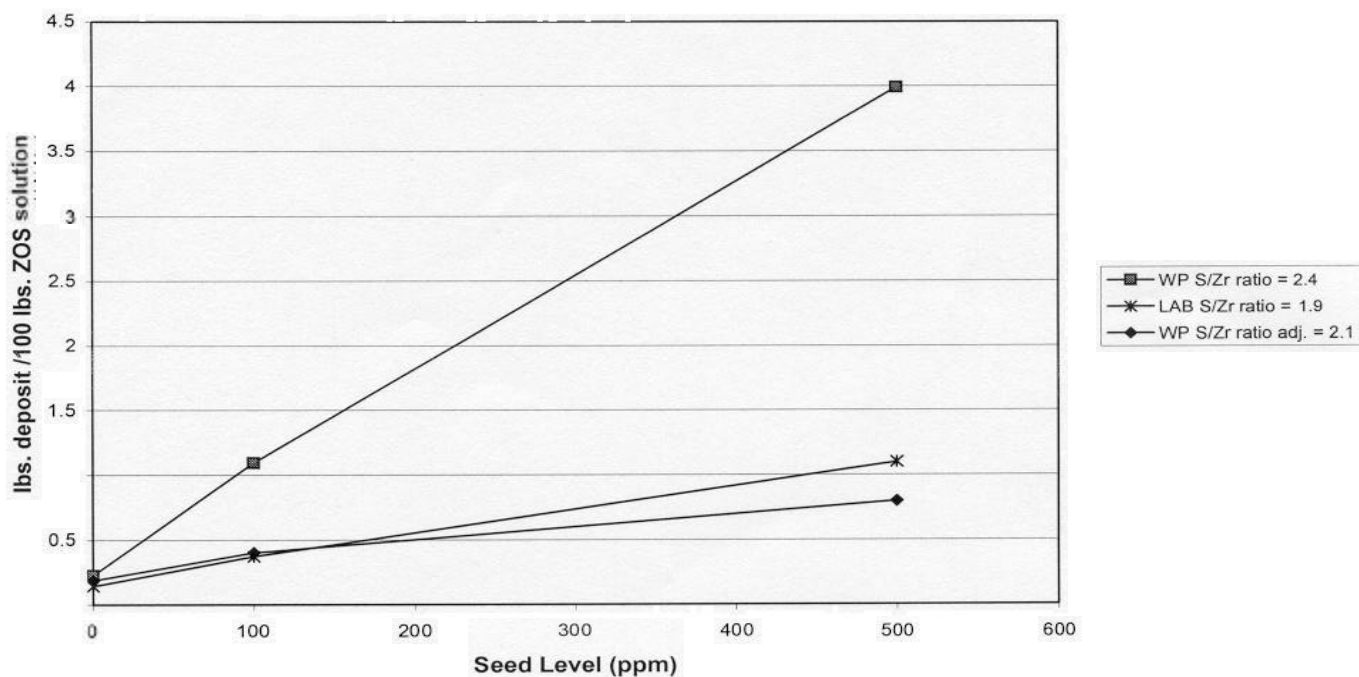


Effect of Sulfate to Zirconium Ratio on Deposit Formation in ZQS solutions

The quantitative results presented in Figures 3-6 of this report were based on the use of one common production batch of ZOS. Although there are no specific ranges of sulfate as there is for %ZrO₂, the desired SO₄/Zr ratio is around 2.0 ± 0.1. For the production batch used in this study, the SO₄/Zr ratio was 2.4. To determine if the SO₄/Zr ratio was an important parameter, the SO₄/Zr ratio of this production batch was adjusted to 2.1 while maintaining the ZrO₂ level at 17.0%, and compared to a laboratory prepared ZOS solution having a ratio of 1.9.

Figure 7, shown on the next page, shows the results of these studies for seed concentrations of 0, 100, and 500 ppm and temperatures of 140 °F. As can be seen in figure 7, there were little differences in the amount of deposit formation for the adjusted production sample and laboratory sample having SO₄/Zr ratios of approximately 2.0. However, the original production sample with a ratio of 2.4 resulted in about 4 times the amount of deposit formed. This clearly demonstrates that the SO₄/Zr ratio can be an important factor in deposit formation and should be controlled as close to 2 as possible.

Figure 7: ZOS SCALING: Effect of SO_4/Zr Ratio on Deposition



Conclusions

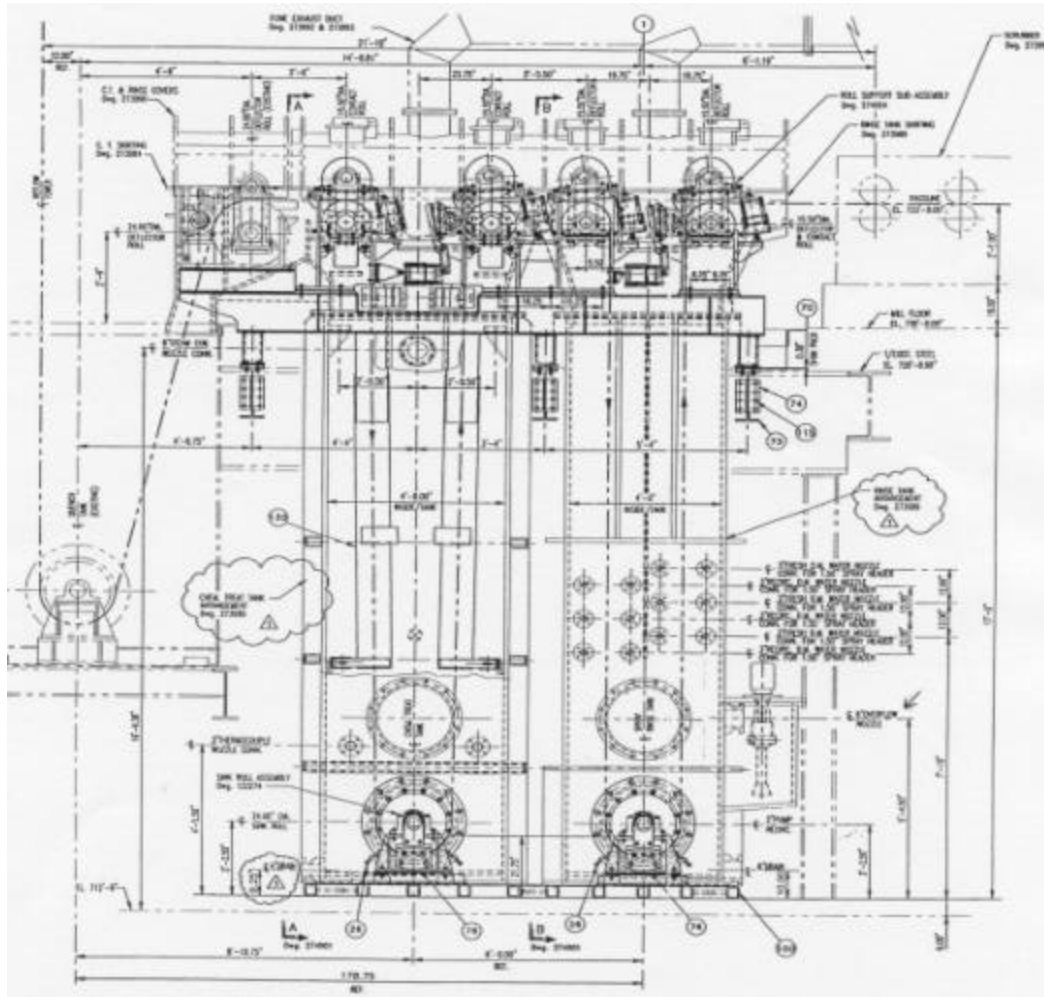
Three factors have been found to be important in the deposit formation that occurs in ZOS storage tanks. These are:

1. The quantity of zirconium-based insolubles that can act as seed crystals and promote rapid deposit formation.
2. The storage temperature. For a given seed level concentration, there is a threshold temperature above which rapid deposit formation will occur.
3. The SO_4/Zr sulfate ratio in the ZOS product.

It has also been found that a much smaller quantity of deposit still forms, even in the absence of seed crystals and high temperatures. Thus, while controlling the above variables will significantly reduce the amount of deposits formed, they can not be totally eliminated.

Appendix 3

Chemical Treatment Section on Weirton Steel #6 ETL



Appendix 4

Figure A4-1. Tin Oxide Fraction (Pre-Bake Condition – Zirconate Variables)

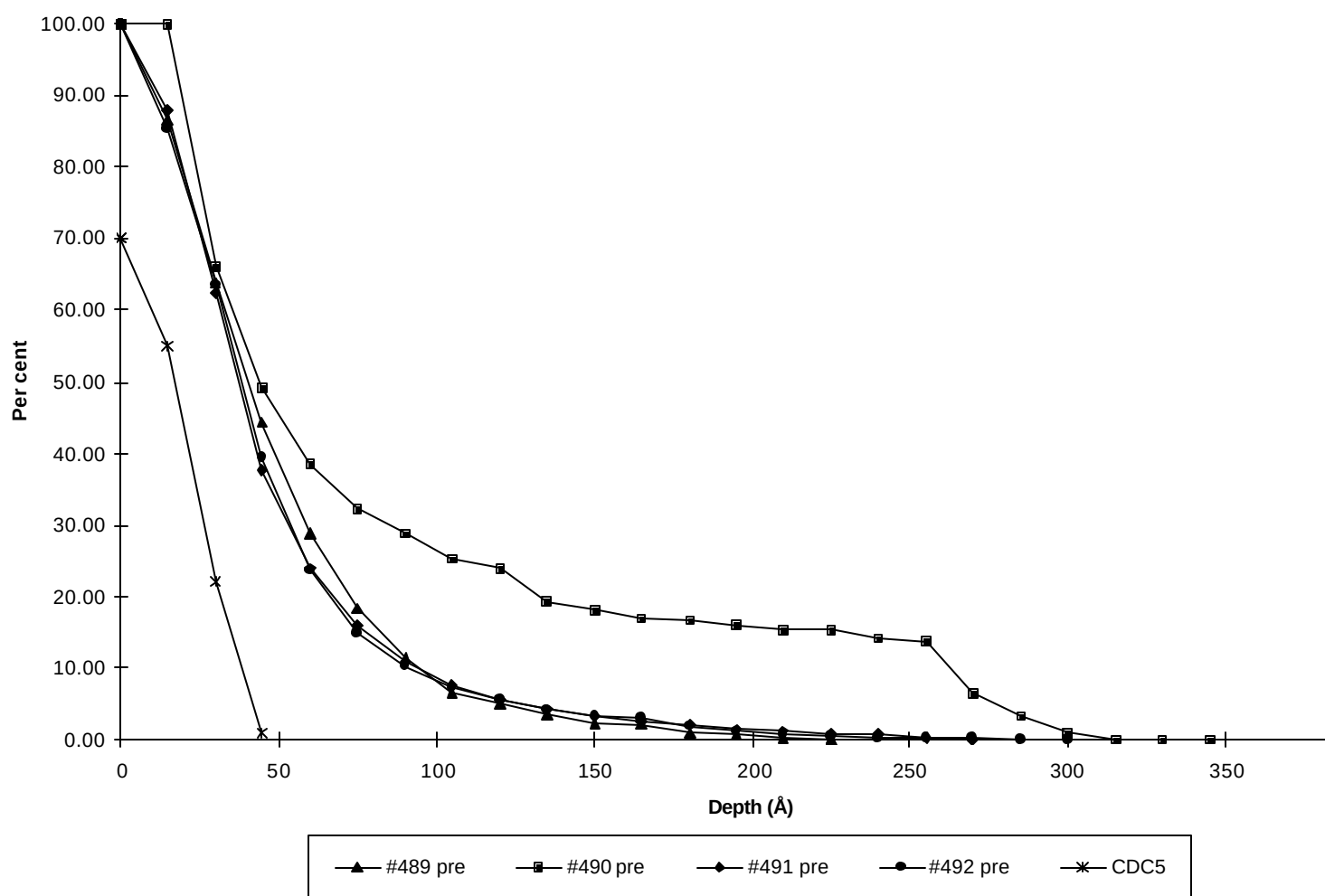


Figure A4-2. Tin Oxide Fraction (Post-Bake Condition – Zirconate Variables)

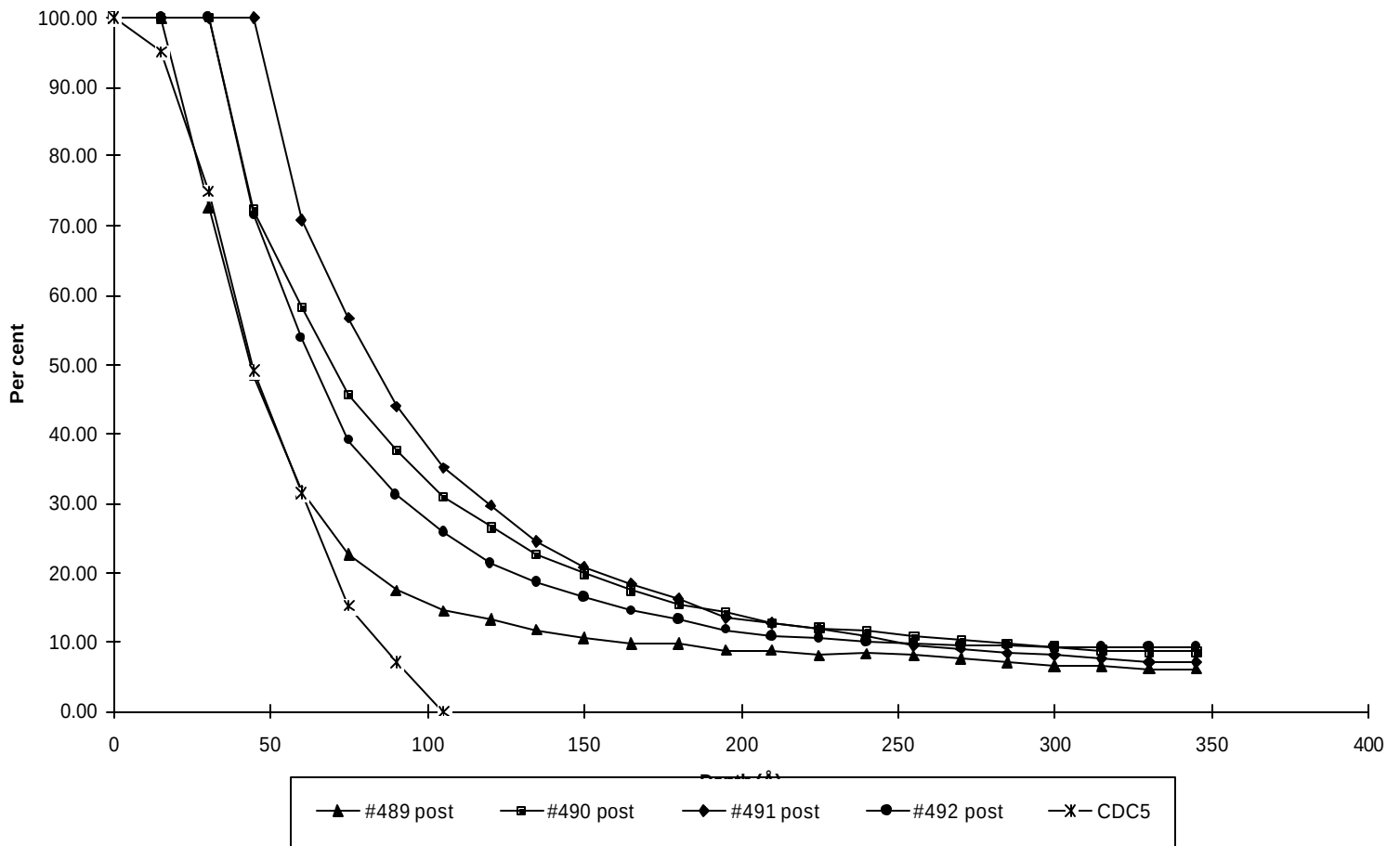
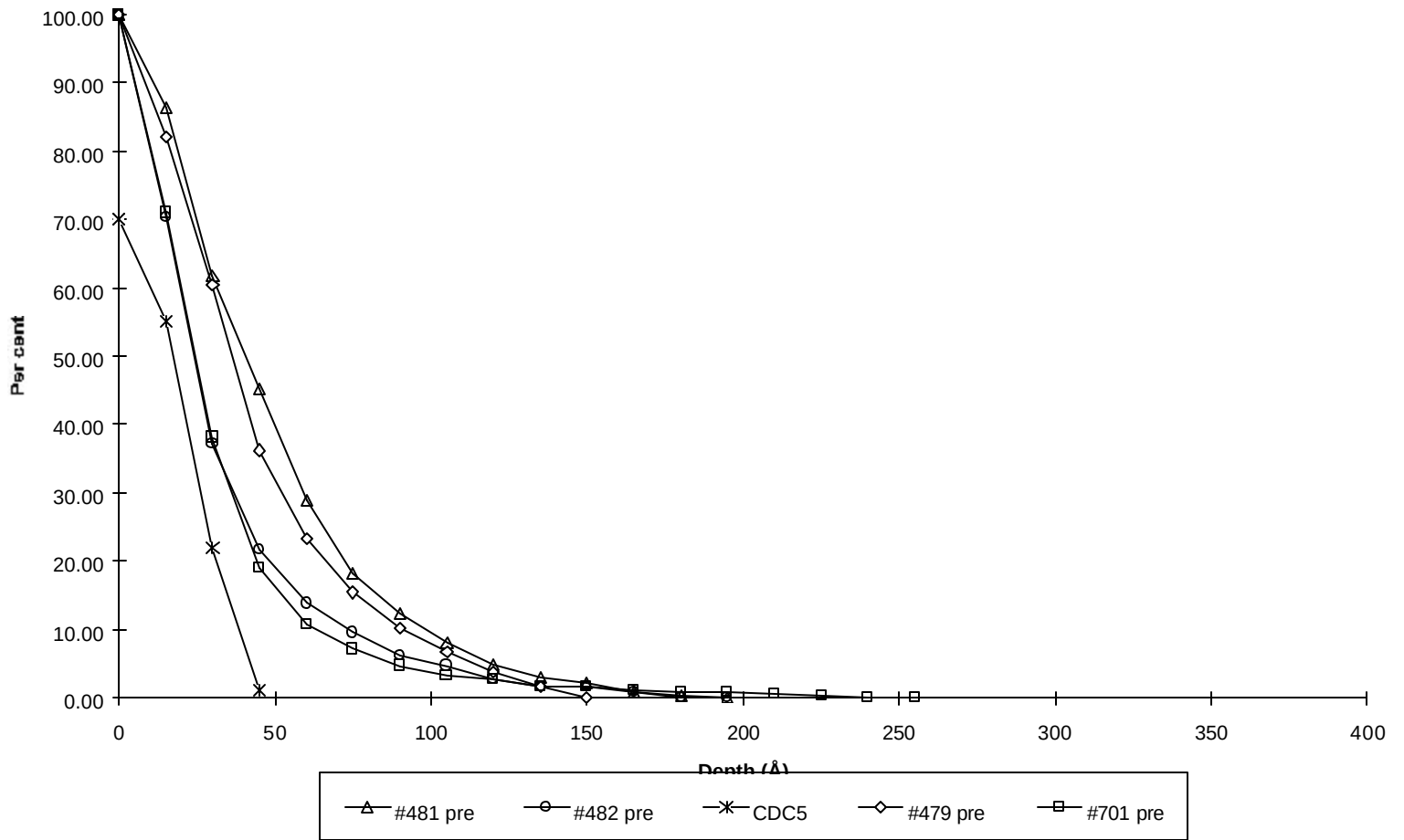
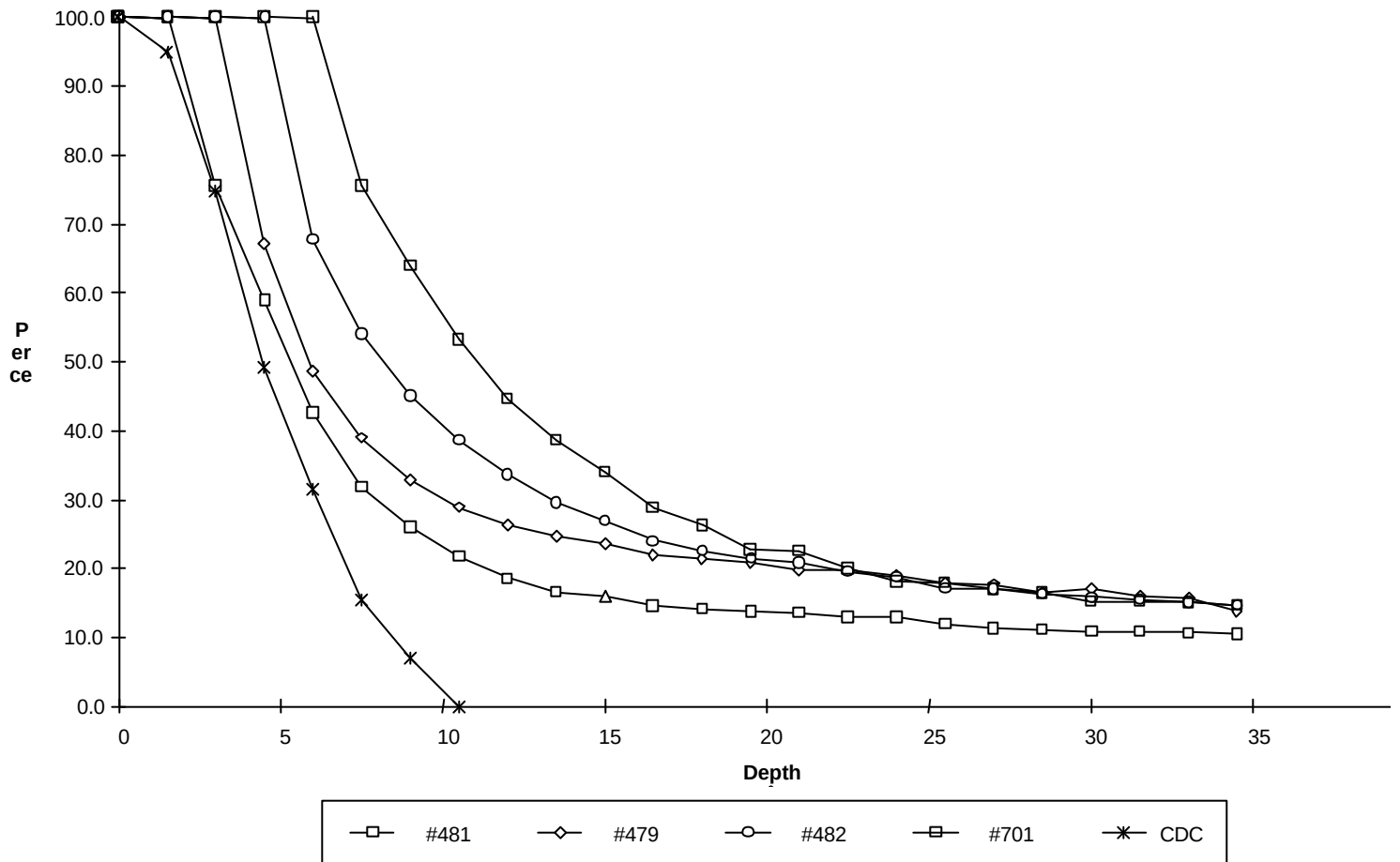


Figure A4-3. Tin Oxide Fraction (Pre-Bake Condition) – Fluorozirconate Variables



**Figure A4-4. Tin Oxide Fraction (Post-Bake Condition) –
Fluorozirconate Variables**



Appendix 5

**A REPORT ON THE SURFACE ANALYSIS
AND ELECTROCHEMICAL TESTING OF
ZIRCONIUM-PASSIVATED
TINPLATE SAMPLES**

For

**Mr. John Sinsel, AISI Project Manager
Commercial Line Trail Evaluation of Non-Cr Passivations for ETP
Weirton Steel Corporation
3006 Birch Drive
Weirton, West Virginia, WV 26062 UNITED STATES OF AMERICA**

By

**Surface Science Western
Room G-1, Western Science Centre
The University of Western Ontario
London, Ontario N6A 5B7 CANADA**

September 13, 2002

Prepared by: Sridhar Ramamurthy, Ph.D.

1.0 INTRODUCTION

Eight tinplate samples, in a trial run, were passivated with a non-chromate passive treatment. This treatment, based on either a fluorozirconate or a zirconium orthosulfate compound, had been applied in a commercial line. Determination of the passive film characteristics, such as film morphology, composition and its chemistry, and the extent of surface coverage, is of major interest. This was determined using surface analytical techniques such as field emission scanning electron microscopy (FESEM) combined with energy dispersive X-ray (EDX) spectroscopy, X-ray photoelectron spectroscopy (XPS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Evaluation of the corrosion behaviour, especially the extent of corrosion protection provided by each treatment, is another topic of interest. Corrosion behaviour of these samples was determined using electrochemical techniques such as linear polarisation and electrochemical impedance spectroscopy (EIS).

2.0 SAMPLE MATRIX

Nine samples were examined in this study. Of these, four contained a fluorozirconate passive film while another four were subjected to a zirconium orthosulfate treatment. A CDC-treated tinplate sample was also examined for comparison purposes. A detailed description of these samples is presented in Table A5-1.

Table A5-1. Description of the tinplate samples.

Treatment	Coil #	Description	Coating Weight
BetzDearborn Permatreat 1001 (Fluorozirconate) Variables	J542701	75BW, T-4, Reflowed ETP	0.20 lb/BB
	K690479	60BW, DR-8, Reflowed ETP	0.20 lb/BB
	K690481	60BW, DR-8, Reflowed ETP (line marked on .75 lb/BB side)	0.75/0.20 lb/BB
	K690482	95BW, T-4, Matte ETP	0.20 lb/BB
Zr Orthosulfate (Zirconate) Variables	K690489	75BW, T-4, Reflowed ETP	0.20 lb/BB
	K690490	58BW, DR-8, Reflowed ETP	0.20 lb/BB
	K690491	58BW, DR-8, Reflowed ETP (line marked on .75 lb/BB side)	0.75/0.20 lb/BB
	K690492	95BW, T-4, Matte ETP	0.20 lb/BB
Standard Cathodic Dichromate Treatment (CDC)	CDC-tinplate	Standard Cathodic Dichromate Treated Material (CDC-5)	0.20 lb/BB

3.0 EXPERIMENTAL METHODOLOGY

High-resolution secondary electron micrographs were collected using an Hitachi S-4500 field emission SEM (FESEM). A beam voltage of 1.0 keV was used for imaging so that the near surface morphology of the tinplate samples could be determined. Secondary electron micrographs were obtained from a representative area at four different magnifications: 500 X, 1500 X, 10000 X and 50000 X.

The X-ray photoelectron spectroscopy (XPS) measurements were performed to determine the outer surface composition. XPS provides elemental information from a depth of approximately 3 – 5 nm, and it can detect all elements except hydrogen and helium. The minimum detection limit is approximately 0.5 atomic %, for most elements. XPS analyses were performed using a Kratos Axis Ultra X-ray photoelectron spectrometer. An Al- K_{α} X-ray beam focused over an area 700 x 300 μm^2 in size was used for this examination.

The time-of-flight secondary ion mass spectrometry (ToF-SIMS) analyses were performed using an ION-TOF ToF-SIMS IVTM instrument. A pulsed 25 keV Ga^+ ion beam was rastered across a 500 x 500 μm^2 region encompassing the area of interest. The positively charged secondary ions were extracted and mass analysed using a time-of-flight analyser. The mode used to acquire these data results in a beam diameter and a lateral resolution of 1 μm , with a mass resolution greater than 10000 (amu) above $m/z = 200$.

Two types of electrochemical measurements were carried out in this study. The first one is known as linear polarisation, in which the applied potential is swept from 10 mV more negative than the open circuit potential (E_{corr}) to 10 mV more positive than E_{corr} at a sweep rate of 1 mV/s. The resulting current density was measured as a function of the applied potential using a potentiostat and plotted on a linear scale against the difference between the applied potential and E_{corr} . The polarisation resistance, R_p , is the slope of the current density-potential difference plot; polarisation resistance is inversely proportional to corrosion rate.

The second type of electrochemical measurement, known as electrochemical impedance spectroscopy (EIS), was also performed on all of the tinplate samples. In this technique, a small sinusoidal AC potential is superimposed on the DC potential applied to the tinplate sample. Amplitude and phase shift of the resultant current signal is then measured. The impedance value is obtained by dividing the AC potential amplitude with the AC current amplitude. In a typical EIS experiment, the frequency of the AC potential is varied over a wide range (100 kHz to 10 mHz) in discrete steps, and the impedance and phase shift values are determined as a function of the frequency of the AC potential. After the experiment, the impedance and phase shift values are plotted against the frequency of the AC potential; this is known as the Bode plot. The impedance data are then modelled using an equivalent circuit

consisting of a series of resistors and capacitors representing the corrosion reactions occurring during the EIS measurements. This helps to identify the nature and magnitude of the reactions that are occurring at the coating surface, as well as the coating/metal interface.

The equivalent circuit used in this study is based on a $R_s[Q_c\{R_c(R_{ct}Q_{dl})\}]$ model. This model has been extensively used in the analysis of EIS data from the coated metals and has been used recently in tinplate corrosion studies. This model consists of a solution resistance (R_s), a coating resistance (R_c), a coating capacitance (Q_c), a charge transfer resistance associated with the corrosion rate of the substrate (R_{ct}), and a constant phase element associated with the dielectric layer on the substrate (Q_{dl}). Higher values of R_c and R_{ct} indicate a more corrosion resistant coating and the substrate, respectively. The coating capacitance, Q_c , is a measure of the permeability or porosity of the tin coating; lower values of Q_c represent a less porous/permeable tin coating.

Electrochemical experiments were performed using a Solartron 1287 potentiostat and a Solartron 1255 frequency response analyser. Experiments were performed in a deaerated synthetic pear juice. The use of synthetic pear juice has eliminated the variations in corrosivity that have been observed in real fruit juices. The individual components in mass % (mg/kg) were: fructose 5%, sucrose 3%, glucose 3%, sorbitol 0.9%, malic acid 0.07%, citric acid 0.12%, chloride ion (KCl) 60 ppm, phosphate ion ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$) 100 ppm, sulphate ion (K_2SO_4) 280 ppm, and stannous ion ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) 85 ppm.

Fresh solutions were prepared prior to each series of tests. Typical pH values of the test solution ranged between 2.6 to 2.8. Samples were immersed for a period of three hours in the deaerated solution and the open circuit potential was monitored during that period. Experiments were performed after three-hour immersion; the open circuit potential was found to reach a stable value by that time. Five linear polarisation measurements were performed first. The corrosion potential was allowed to stabilize for five minutes in between each linear polarisation measurement. E_{corr} values were noted prior to each linear polarisation measurement. At the end of five measurements, the corrosion potential was allowed to stabilize for five minutes, its value documented, and an electrochemical impedance spectroscopy measurement performed.

Electrochemical measurements were also performed in pear juice solutions that had been boiled and cooled down to room temperature. The solution was constantly purged with nitrogen gas during the boiling and subsequent cooling down period, and the nitrogen purging continued until the solution had been completely used up. This procedure is similar to that employed for the grapefruit juice used in the Alloy Tin Couple Test (refer to ASTM Standard #A623). Apparently, this procedure of boiling and cooling the solution removes most of the dissolved oxygen and extends the life of the solution. Electrochemical measurements were performed in this solution to determine the differences in the electrochemical behaviour between the as-prepared and boiled and cooled down solutions.

4.0 RESULTS AND DISCUSSION

4.1 SEM Analysis

As mentioned in Section 3.0, secondary electron micrographs were collected at four different magnifications using a primary electron beam voltage of 1.0 keV. It was expected that this low beam voltage would be helpful in determining the outer surface morphology.

Despite imaging at 1 keV, the micrographs presented in Annexure A5-I show the morphology of the outer surface of the tin coating, and not the morphology of the zirconium passive layer. This suggests that the zirconium passive layer is very thin. The SEM micrographs presented in Annexure A5-I also exhibit the following features:

1. Exposed iron-tin alloy regions can be seen on several of the samples examined in this study. This is due to the lower coating weight of 0.20 lb/BB found on these samples. As expected, the samples containing a coating weight of 0.75 lb/BB did not exhibit this behaviour.
2. Differences in the surface morphology between the matte-finish and reflowed samples can be clearly seen in these micrographs. The coating thickness also appears to be somewhat non-uniform on the matte-finished samples.
3. In general, the tinplate samples subjected to BetzDearborn Permatreat 1001 (fluorozirconate) exhibit greater amounts of micro-precipitates on the outer surface. Moreover, these precipitates appear to be randomly distributed.

4.2 XPS Analysis

XPS analysis was conducted on all zirconium-passivated tinplate samples as well as the CDC-treated tinplate. The results from the XPS analyses are presented in Annexure A5-II. The composition data (atomic %), determined from the survey scan spectra, are summarised in Table A5-2.

For the samples containing the zirconium-based passive layer, the results presented in this table indicate that very low levels of zirconium were found on the tinplate surface; the concentration of zirconium varied from 0.3 to 1.2 at.%. Due to the low zirconium concentrations observed on these samples, high resolution zirconium spectra could not be collected. Hence, the chemical state of zirconium could not be identified from the XPS measurements.

Table A5-2. Elemental composition (atomic %) as determined by XPS analysis.

Treatment	Sample Number	Elements Detected (Atomic %)									
		C	Ca	Cl	F	N	O	S	Sn	Zr	Cr
BetzDearborn Permatreat 1001 (Fluorozirconate) Variables	J542701	40.	0.6	1.5	3.8	1.4	38.	-	14.	0.3	-
	K690479	41.	0.4	0.8	1.9	0.5	40.	-	15.	0.6	-
	K690481	40.	0.8	0.7	3.4	0.6	39.	-	15.	0.5	-
	K690482	42.	0.7	0.4	7.1	2.1	33.	-	15.	0.6	-
Zr Orthosulfate (Zirconate) Variables	K690489	40.	-	-	-	1.4	43.	1.4	13.	0.9	-
	K690490	44.	0.7	-	-	0.6	40.	1.1	13.	0.6	-
	K690491	39.	-	0.8	-	1.4	43.	1.0	15.	1.0	-
	K690492	42.	1.2	0.0	-	-	41.	1.4	13.	1.2	-
Standard Cathodic Dichromate Treated Material (CDC-5)	CDC-Tinplate	34.	-	-	-	-	46.	-	9.2	-	10.

The orthosulfate treatment samples exhibited slightly greater amounts of zirconium compared to the fluoro-zirconate treatment samples. This is also reflected in the tin concentrations; lower levels of tin were observed for the orthosulfate treatment samples compared to those for the fluoro-zirconate-treated samples. In addition, within each passivation treatment, the matte-finished samples exhibited greater amounts of zirconium compared to other processing conditions. XPS analyses also indicated that, depending on the processing condition, either sulfur or fluorine was also found on the sample surface.

The CDC-tinplate sample exhibited a much greater concentration of chromium on the outer surface. The chromium concentration was approximately 10 at.%, which is 10 times greater than the zirconium concentration found on the zirconium-passivated samples. Because chromium was detected in significant quantities, a high resolution Cr(2p) spectrum was collected; this is also presented in Annexure A5-II. The binding energies of the chromium peaks indicate that chromium is mostly present as a chromite or chromium hydroxide species. A small contribution from hexavalent chromium (Cr^{+6}) species was also observed in the Cr(2p) high resolution spectrum.

4.3 ToF-SIMS Analysis

ToF-SIMS analyses were performed on all nine samples. For each sample, ToF-SIMS analyses were performed on three different areas $500 \times 500 \mu\text{m}^2$ in size. Both positive and negative secondary ions were collected from each area.

During the data analysis, positive ion images were found to provide the most useful information, thus only the results from the positive ion images will be presented and discussed.

Annexure A5-III presents the positive ion ToF-SIMS images collected from the three areas on each sample. The colours in the images are based on a thermal scale ranging between 0 to 255 units. Black represents 0 intensity, while white represents an intensity of 255. Brighter regions in the image qualitatively indicate the presence of greater quantities of the ion of interest, while the darker regions qualitatively represent lower concentrations or the absence of the ionic species.

Please note that the ion image identified as ZrO_2 actually corresponds to ^{122}Sn mass number. Similarities between this image and those for Sn and SnO can be clearly seen in the ToF-SIMS images presented in Annexure A5-III.

The results presented in Annexure A5-III indicate that the zirconium coating is patchy and non-uniform in appearance. Islands of zirconium-rich regions can be seen in the ToF-SIMS images. The trends exhibited by the Zr and ZrO ion images suggest that zirconium could be present as zirconium oxide on the sample surface. In addition to the patches of zirconium, tin and iron species were also detected on the outer surface. Tin appears to be present mostly as a continuous layer, while iron can be seen at selected locations within the area analysed, perhaps corresponding to the rolling marks.

The fact that the tin layer present underneath the zirconium coating can be detected, suggests that the zirconium coating may be three monolayers or less in thickness. This corresponds to a thickness of approximately 1 nm. Detection of iron suggests that the tin coating is also non-uniform, perhaps due to the low coating weight employed in this study. The iron-containing regions are fewer on the heavily coated tinplates (0.75 lb/BB) compared to the 0.20 lb/BB coating weight samples.

ToF-SIMS images from the CDC-tinplate sample indicate that the chromate passive layer was distributed much more uniformly than the zirconium-based passive layer. The chromate layer was so thick at some locations that the tin coating underneath was not detected. The uniformly distributed chromate layer also prevented the detection of the iron-enriched regions exposed through the tin coating. Moreover, the ToF-SIMS images for chromium are quite intense in brightness, indicating the presence of greater amounts of chromium on the sample surface. This observation is similar to that seen from the XPS analysis, where chromium concentrations of approximately 10 at.% were observed.

Qualitative comparison of the ToF-SIMS images from the eight tinplate samples indicates that the orthosulfate treatment samples, in general, appeared to exhibit a greater surface coverage of zirconium than the fluorozirconate treatment samples. In addition, the matte-finished samples (K690482 and K690492) appeared to exhibit a much more uniform surface coverage than the

other samples. These observations are consistent with the XPS results, which indicate that, in general, the orthosulfate treatment samples exhibited slightly greater amounts of zirconium than the fluorozirconate treatment samples, and greater amounts of zirconium were found on the matte-finished samples.

Using the intensity scale employed for displaying ToF-SIMS images, it is possible to determine the extent of surface coverage for each species of interest. In this study, the percentage of pixels exhibiting intensity values between 71 and 246 units within the area analysed was determined for FeO, ZrO, and SnO species. These oxide species were used instead of the metallic species, because the metallic species tend to saturate the detector and both the oxide and metallic species exhibited a similar distribution. Because three areas were examined for each sample, the surface coverage values were averaged over these three areas; the resulting data are summarised in Table A5-3. This type of data analysis provides a semi-quantitative measure of the extent of surface coverage, and can be useful in determining the changes in the surface coverage as a result of changes in the processing conditions.

Table A5-3. Extent of surface coverage determined from ToF-SIMS images.

Treatment	Sample #	Mean Surface Coverage (%)			
		FeO	ZrO	CrO	SnO
BetzDearborn Permatreat 1001 (Fluorozirconate) Variables	J542701	7.8	5.5	–	86.7
	K690479	3.4	15.5	–	81.1
	K690481	1.0	10.7	–	88.3
	K690482	2.8	22.3	–	75.0
Zr Orthosulfate (Zirconate) Variables	K690489	5.6	19.8	–	74.6
	K690490	5.0	14.7	–	80.3
	K690491	2.3	14.0	–	83.8
	K690492	8.0	16.0	–	76.0
Standard Cathodic Dichromate Treated Material (CDC-5)	CDC- Tinplate	11.4	–	67.8	20.7

The results presented in Table A5-3 indicate that the tinplate samples from orthosulfate treatment, on average, exhibited more surface coverage than the samples from fluorozirconate treatment. Moreover, all four orthosulfate treatment samples exhibited a similar surface coverage, while wide variations in surface coverage are seen on the fluorozirconate treatment samples. Finally, the matte-finished samples exhibited better surface coverage than the

other samples. As expected, the CDC-tinplate sample exhibited much greater surface coverage of the passive layer than that exhibited by the zirconium-passivated samples; 68% for the CDC-tinplate sample compared to approximately 15% for zirconium-passivated samples. These results suggest that there is a direct correlation between the extent of surface coverage and the concentration of the passivating element (zirconium or chromium) determined from XPS measurements.

ToF-SIMS images can be superimposed on each other to produce an overlay of images. These overlays can be useful in identifying the distribution of two or three species in an area of interest. Overlay is created by assigning a specific colour to each ion image. For example, FeO was assigned the colour green in this analysis, ZrO was represented by the colour blue, and the colour red was assigned to SnO. When two species co-exist in a region, the colour of that region will change to the combination of the colours of both species; for example if FeO (green) and SnO (red) co-exist, then that region will be yellow in colour, produced by the combination of red and green colours. Similarly, if ZrO and SnO co-exist, that region will be purple in colour, and if ZrO and FeO co-exist, then the region will be orange in colour. Thus, the overlay images can sometimes be useful in determining which species co-exist in a region of interest.

The overlay images, presented in Annexure A5-IV, were produced from ToF-SIMS images for all of the samples and all of the areas analysed. ToF-SIMS images for FeO, ZrO, and SnO are also presented in this annexure. Please note that the colour scheme is different for the CDC-tinplate samples. These overlay images indicate that, for the zirconium-passivated samples, the sample surface was mostly covered with a tin oxide (SnO) layer. Regions enriched in FeO can also be seen in these images, however some of these iron-rich regions also appeared to contain an SnO layer (indicated by the yellow colour). ZrO appears to be present in patches and is associated with SnO in most of the regions. There are some regions where ZrO is the dominant species; however, such regions are fairly small in size. Finally, the overlay images from the CDC-tinplate sample indicate that the CrO species is dominant on the sample surface. Smaller SnO-enriched regions were found in the areas where the CrO species were not present.

4.4 Electrochemical Measurements

Electrochemical experiments were performed on a minimum of three different specimens from each sample of interest. For each specimen, five linear polarisation experiments were performed, followed by an EIS measurement. Thus, the average polarisation resistance values were calculated from a minimum of 15 measurements, and EIS results were averaged from a minimum of three different experiments.

The results from the linear polarisation measurements performed in the as-prepared synthetic pear juice solution are presented in Table A5-4. Representative linear polarisation plots are presented in Annexure A5-V. Table A5-4 lists the mean open circuit potential and the average polarisation resistance (R_p) values determined from the linear polarisation measurements. The results presented in this table indicate that the open circuit potential did not vary significantly among different zirconium-passivated samples; the open circuit potential varied from -581 to -593 mV_{sce}. The matte-finished samples appeared to exhibit the lowest open circuit potential. The CDC-tinplate sample exhibited a mean open circuit potential of -576 mV_{sce}.

Table A5-4. Results from the linear polarisation measurements performed in the as-prepared synthetic pear juice.

Treatment	Sample #	Mean Open Circuit Potential, E_{corr} (V _{sce})	Mean Polarisation Resistance, R_p (Ohm.m ²)
BetzDearborn Permatreat 1001 (Fluorozirconate) Variables	J542701	-0.584	0.528 ± 0.262
	K690479	-0.583	0.650 ± 0.273
	K690481	-0.587	0.400 ± 0.089
	K690482	-0.593	0.651 ± 0.269
Zr Orthosulfate (Zirconate) Variables	K690489	-0.582	0.448 ± 0.125
	K690490	-0.588	0.497 ± 0.130
	K690491	-0.581	0.388 ± 0.133
	K690492	-0.591	0.503 ± 0.207
Standard Cathodic Dichromate Treated Material (CDC-5)	CDC-Tinplate	-0.576	0.715 ± 0.143

The polarisation resistance values indicate that, for a similar processing condition, the fluoro-zirconate treatment samples exhibited slightly better corrosion resistance than those subjected to orthosulfate treatment. This is surprising, considering that the fluoro-zirconate treatment samples exhibited lower zirconium levels and poor coverage compared to the orthosulfate treatment samples. The results presented in Table A5-4 also indicate that the matte-finished sample exhibited the greatest corrosion resistance, while, surprisingly, the 0.75 lb/BB samples exhibited the least corrosion resistance. It is not presently known why the heavily coated tinplate samples are the most susceptible to corrosion. Finally, the polarisation resistance values indicate that the CDC-treated tinplate sample exhibited slightly better corrosion resistance compared to the samples containing the zirconium-based passivation layer.

Table A5-5 presents the results from the linear polarisation measurements performed in synthetic pear juice solutions that had been boiled and cooled down to room temperature. The results presented in Table A5-5 indicate that the open circuit potential was slightly more negative (-589 to -598 mVsce) compared to those measurements performed in the as-prepared solution. The polarisation resistance values also appear to be slightly greater for the measurements performed in the boiled and cooled down pear juice. The trends in the open circuit potential and the polarisation resistance could perhaps be due to much reduced levels of oxygen present in the boiled and cooled down pear juice solutions; the pear juice solution was constantly deaerated during boiling, subsequent cooling, and during electrochemical experimentation. This could have significantly reduced the dissolved oxygen levels, leading to greater corrosion resistances observed in this study.

Table A5-5. Results from the linear polarisation measurements performed in the boiled and cooled down synthetic pear juice.

Treatment	Sample #	Mean Open Circuit Potential, E_{corr} (V_{sce})	Mean Polarisation Resistance, R_p ($\Omega \cdot m^2$)
BetzDearborn Permatreat 1001 (Fluorozirconate) Variables	J542701	-0.589	1.040 ± 0.303
	K690479	-0.593	1.310 ± 0.334
	K690481	-0.590	0.646 ± 0.179
	K690482	-0.595	0.913 ± 0.268
Zr Orthosulfate (Zirconate) Variables	K690489	-0.597	0.893 ± 0.104
	K690490	-0.598	0.964 ± 0.196
	K690491	-0.596	0.822 ± 0.160
	K690492	-0.590	0.572 ± 0.087
Standard Cathodic Dichromate Treated Material (CDC-5)	CDC-Tinplate	-0.581	1.080 ± 0.395

Despite the differences in the magnitude of the polarisation resistance values between the as-prepared and boiled and cooled down solutions, the trends in the R_p values are similar for both sets of solutions. For example, the fluoro-zirconate treatment samples exhibited greater R_p values compared to those from the orthosulfate treatment. The R_p values for the CDC-tinplate samples were, on average, greater than those exhibited by the zirconium-passivated samples.

Thus, the effect of boiling synthetic pear juice appears to reduce the levels of dissolved oxygen in the solution. However, the results presented in Tables A5-

4 and A5-5 also indicate that the corrosion behaviour is similar for both solutions. Boiling and cooling down synthetic pear juice may also kill any bacteria present in the solution, thus perhaps extending its shelf life.

As mentioned in Section 3.0, EIS measurements were also performed in both solutions. Annexure A5-VI presents the representative EIS spectra collected in the as-prepared and deaerated synthetic pear juice solutions. The results from the equivalent circuit modelling are presented in Tables A5-6 and A5-7 for the as-prepared, and boiled and cooled down solutions, respectively.

Table A5-6. Results from the equivalent circuit modelling performed on the EIS data collected from tinplate samples immersed in the as-prepared synthetic pear juice.

<u>Treatment</u>	<u>Sample #</u>	<u>Solution Resistance, R_s (Ohm.m²)</u>	<u>Mean Coating Resistance, R_c (Ohm.m²)</u>	<u>Mean Charge Transfer Resistance, R_{ct} (Ohm.m²)</u>	<u>Mean Coating Capacitance, Q_c (mF/cm²)</u>
BetzDearborn Permatreat 1001 (Fluorozirconate) Variables	J542701	0.042 ± 0.006	0.141 ± 0.045	0.242 ± 0.139	1000 ± 100
	K690479	0.044 ± 0.004	0.427 ± 0.095	0.171 ± 0.140	800 ± 200
	K690481	0.040 ± 0.001	0.143 ± 0.067	0.166 ± 0.145	1200 ± 100
	K690482	0.047 ± 0.008	0.564 ± 0.303	0.165 ± 0.047	800 ± 100
Zr Orthosulfate (Zirconate) Variables	K690489	0.040 ± 0.009	0.199 ± 0.076	0.143 ± 0.076	1200 ± 300
	K690490	0.047 ± 0.004	0.246 ± 0.096	0.213 ± 0.096	1200 ± 100
	K690491	0.043 ± 0.003	0.137 ± 0.099	0.208 ± 0.164	1100 ± 300
	K690492	0.048 ± 0.006	0.080 ± 0.016	0.502 ± 0.267	900 ± 200
Standard Cathodic Dichromate Treated Material (CDC-5)	CDC-Tinplate	0.046 ± 0.013	0.415 ± 0.034	0.173 ± 0.150	400 ± 50

The results of the equivalent circuit modelling indicate that the solution resistance (R_s) values are quite similar for the EIS measurements in both solutions. This is to be expected, as the solution composition was the same for all measurements. The fact that the solution resistance is not varying over a wide range – such as an order of magnitude – and that the scatter in the R_s values is very small, improves the confidence in the results from the EIS measurements in general, and, in particular, the equivalent circuit modelling of the EIS data.

Another observation that can be made from the electrochemical results presented in Tables A5-4 to A5-7 is that the polarisation resistance (R_p), coating resistance (R_c) and the charge transfer resistance (R_{ct}) values were quite similar in magnitude. This, again, adds validity to the electrochemical data, especially for the results from the equivalent circuit modelling.

Table A5-7. Results from the equivalent circuit modelling performed on the EIS data collected from tinplate samples immersed in the boiled and cooled down synthetic pear juice.

Treatment	Sample #	Solution Resistance, R_s (Ohm.m ²)	Mean Coating Resistance, R_c (Ohm.m ²)	Mean Charge Transfer Resistance, R_{ct} (Ohm.m ²)	Mean Coating Capacitance, Q_c (mF/cm ²)
BetzDearborn Permatreat 1001 (Fluorozirconate) Variables	J542701	0.047 ± 0.001	0.571 ± 0.237	0.267 ± 0.094	600 ± 100
	K690479	0.048 ± 0.008	0.190 ± 0.148	0.503 ± 0.356	700 ± 100
	K690481	0.044 ± 0.008	0.370 ± 0.201	0.335 ± 0.311	1000 ± 300
	K690482	0.040 ± 0.009	0.505 ± 0.060	0.391 ± 0.202	500 ± 50
Zr Orthosulfate (Zirconate) Variables	K690489	0.047 ± 0.005	0.337 ± 0.167	0.302 ± 0.147	700 ± 100
	K690490	0.047 ± 0.006	0.407 ± 0.109	0.262 ± 0.068	700 ± 200
	K690491	0.046 ± 0.012	0.294 ± 0.028	0.432 ± 0.035	600 ± 100
	K690492	0.046 ± 0.041	0.145 ± 0.058	0.375 ± 0.075	800 ± 100
Standard Cathodic Dichromate Treated Material (CDC-5)	CDC-Tinplate	0.054 ± 0.016	0.583 ± 0.234	0.106 ± 0.064	400 ± 100

The results from the EIS measurements (Tables A5-6 and A5-7) exhibit trends similar to those observed from the linear polarisation measurements (Tables A5-4 and A5-5). The coating resistance (R_c) values for the fluoro-zirconate treatment samples were slightly greater than those observed for the orthosulfate treatment samples. The CDC-tinplate samples also exhibited greater R_c values. The heavily coated tinplate samples exhibited the lowest coating resistances, an observation consistent with that from the linear polarisation measurements.

Examination of the coating capacitance (Q_c) values yields some interesting trends. The coating capacitance for the matte-finished sample, in general, was the lowest among the zirconium-passivated samples. This indicates a less

porous coating or a more uniform surface coverage; an observation consistent with the results from the surface analytical measurements. Also, the CDC-treated tinplate sample exhibited the lowest Q_c values among the samples analysed. This sample is the least porous of all the samples when ranked in terms of the coating coverage, an observation, again, consistent with the ToF-IMS results, which indicated a much more uniform chromate coverage on the tinplate surface. Also, the coating capacitance (Q_c) values are similar for both zirconium passivation treatments; this is surprising considering that the fluorozirconate treatment samples exhibited poor coverage, and would be expected to exhibit greater coating capacitance values. Finally, these results also indicate that the extent of surface coverage does not appear to significantly affect the corrosion behaviour of the tinplate samples; all of the tinplate samples examined in this study exhibited more or less similar corrosion resistance values.

5.0 SUMMARY

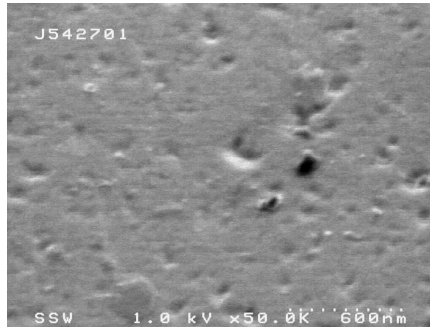
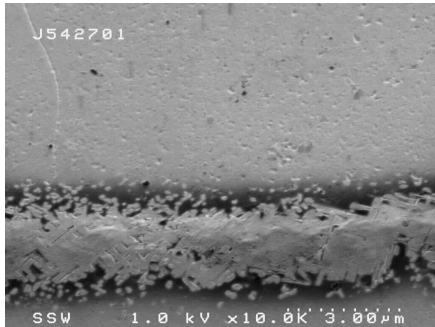
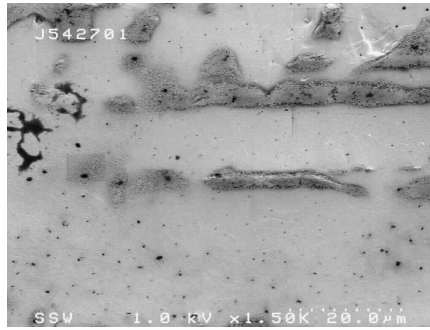
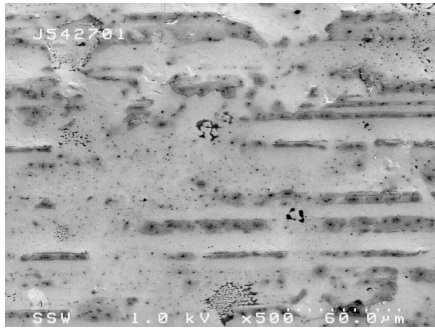
Extensive surface analytical and electrochemical measurements were performed on nine tinplate samples subjected to either a zirconium-based or a dichromate passivation treatment. The results indicate that:

1. Despite imaging at 1 keV, only the outer surface morphology of the tin coating could be detected using field emission SEM analysis; this suggests that the zirconium passive layer is very thin.
2. XPS survey scan spectra indicated that very low levels of zirconium were found on the tinplate surface; the concentration of zirconium varied from 0.3 to 1.2 at.%. In contrast, the CDC-tinplate sample exhibited a much greater concentration of chromium (~ 10 at.%).
3. XPS analyses indicated that the orthosulfate treatment samples exhibited slightly greater amounts of zirconium compared to those from the fluorozirconate treatment.
4. ToF-SIMS analyses and subsequent data processing indicated that the chromate layer on the CDC-tinplate sample exhibited much more uniform coverage than the zirconium-based passive layers.
5. Among the samples containing a zirconium-based passive layer, the tinplate samples from the orthosulfate treatment, in general, appeared to exhibit greater surface coverage than the fluorozirconate treatment samples.
6. Both linear polarisation and EIS measurements indicated that these differences in the zirconium concentration and its surface coverage did not appear to significantly affect the corrosion behaviour of the samples.
7. Electrochemical measurements indicated that fluorozirconate treatment samples exhibited slightly better corrosion resistance than orthosulfate treatment samples.

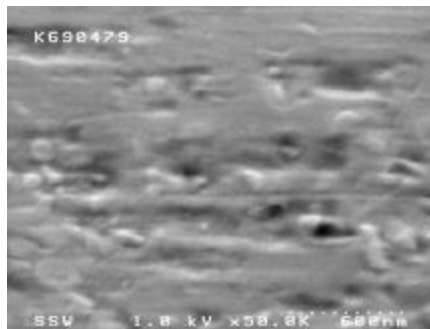
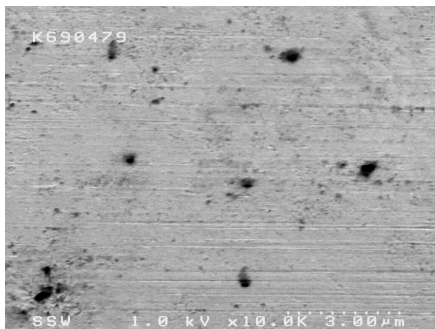
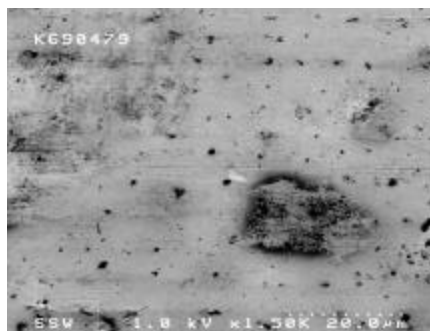
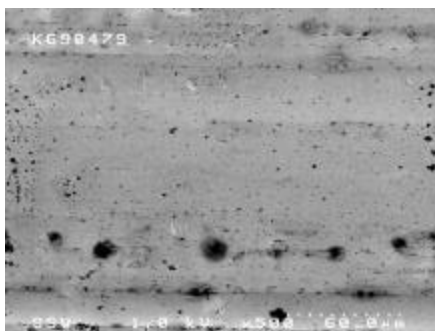
8. The CDC-treated tinplate sample appeared to be slightly more corrosion resistant compared to those containing the zirconium passivation layer.
9. Similar electrochemical behaviour was observed in both the as-prepared and boiled and cooled down synthetic pear juice solutions. However, the experiments in boiled and cooled down synthetic pear juice solution yielded slightly greater corrosion resistances and more negative corrosion potentials, perhaps as a result of greater removal of the dissolved oxygen in the boiled and cooled down synthetic pear juice solutions.

Annexure A5-I

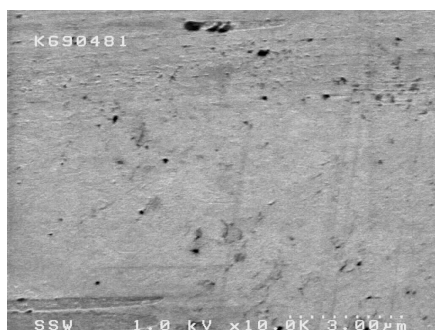
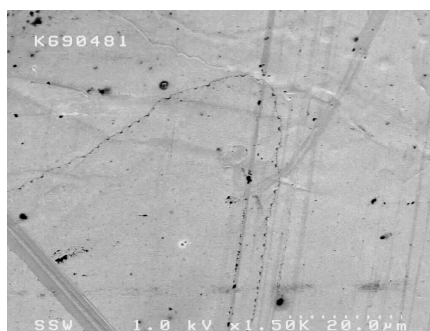
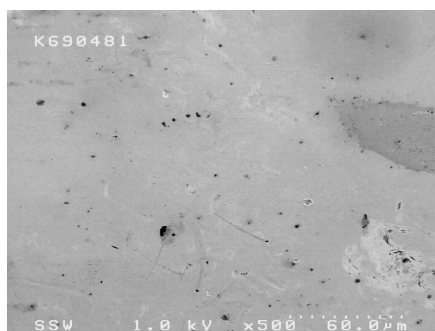
**SEM MICROGRAPHS COLLECTED
FROM THE TINPLATE SAMPLES**



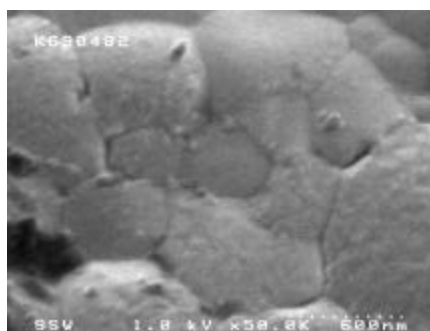
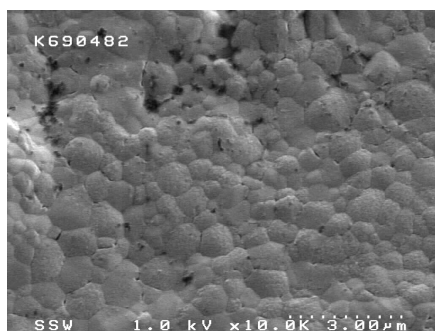
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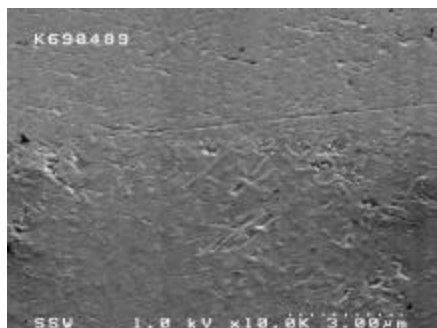
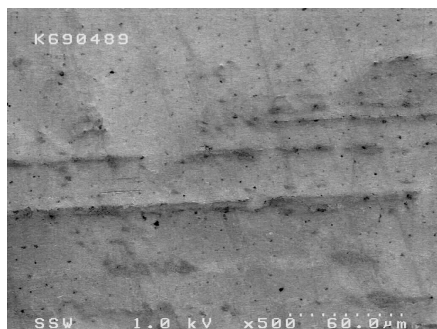
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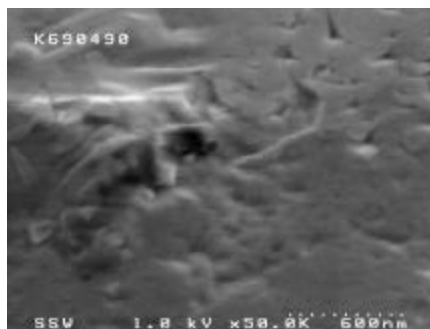
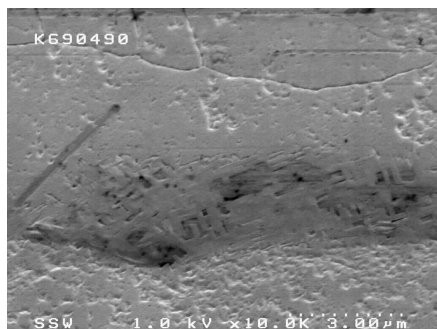
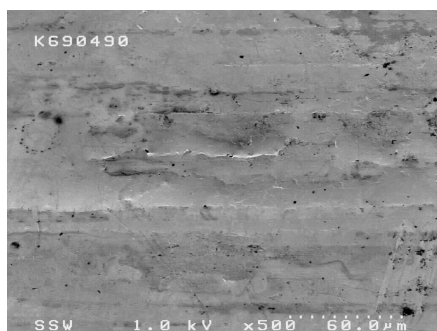
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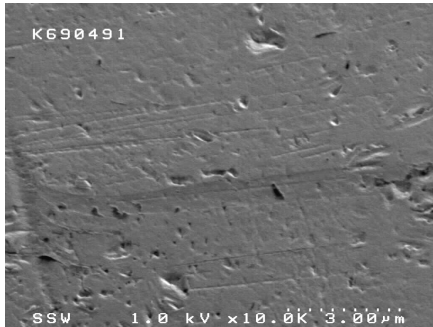
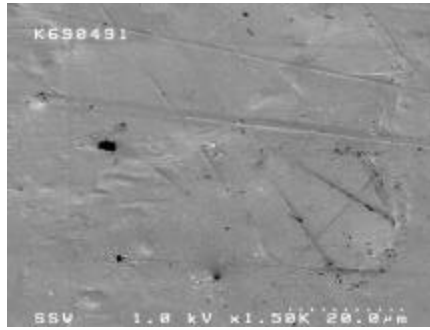
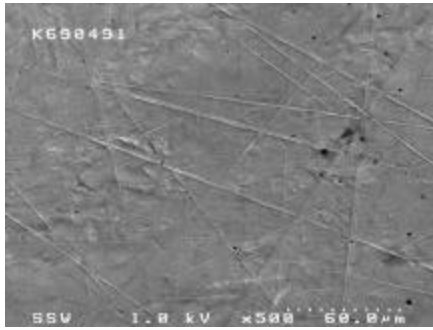
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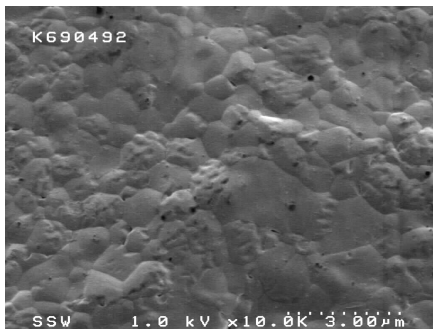
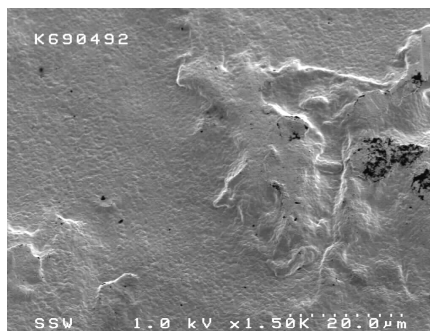
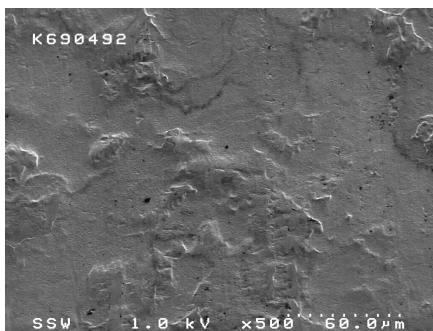
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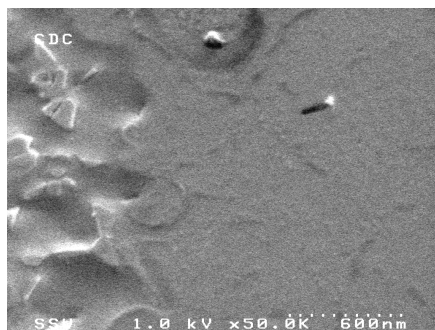
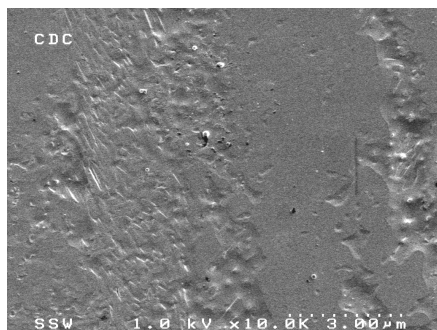
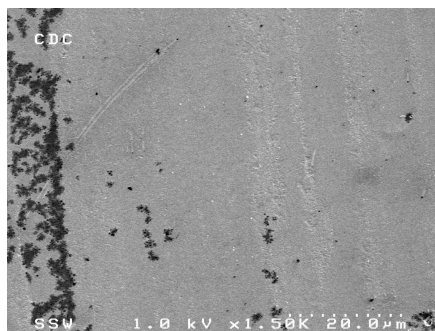
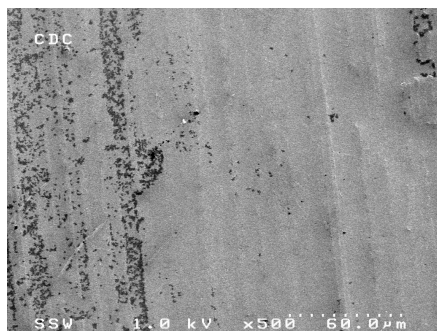
Secondary Electron micrographs collected from sample # K690490



Secondary Electron micrographs collected from sample # K690491



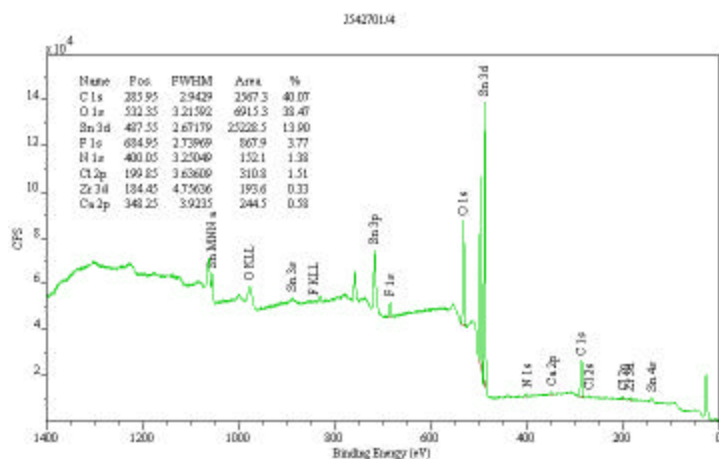
Secondary Electron micrographs collected from sample # K690492



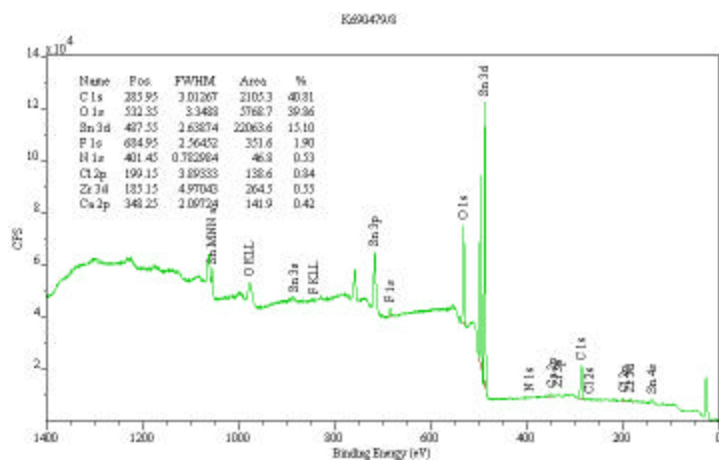
Secondary Electron micrographs collected from sample # CDC-Tinplate

Annexure A5-II

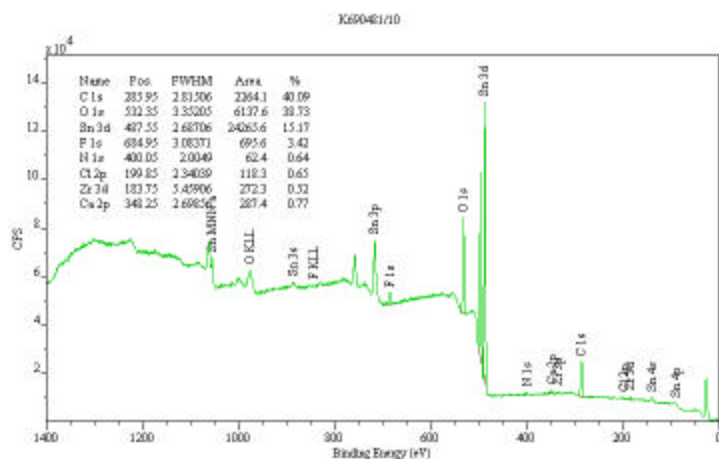
**XPS SURVEY SCAN SPECTRA COLLECTED
FROM THE TINPLATE SAMPLES**



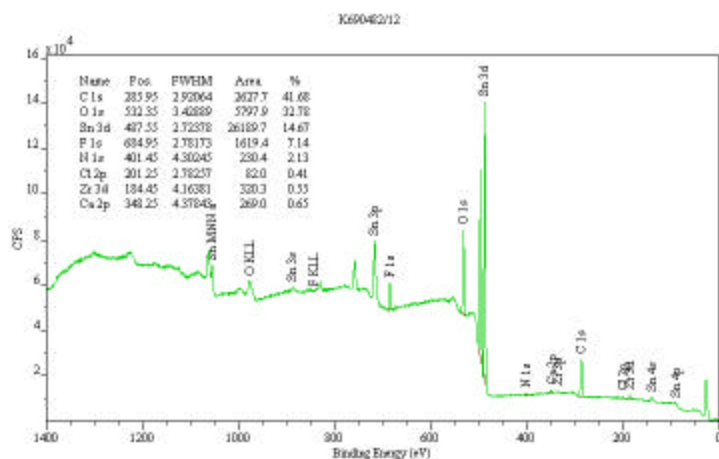
XPS survey scan spectra collected from sample #J542701



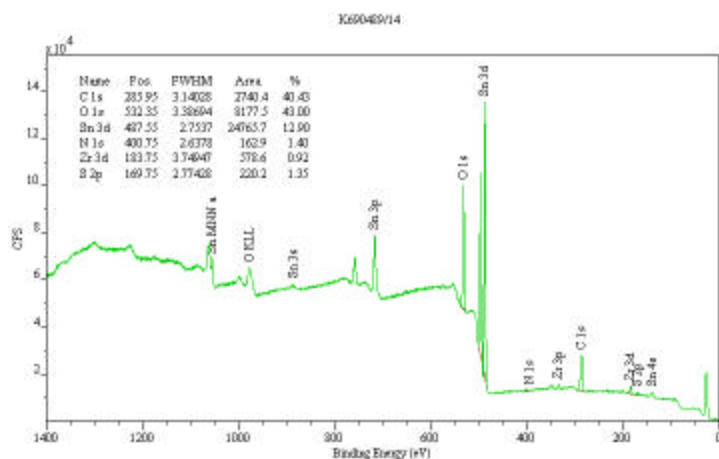
XPS survey scan spectra collected from sample #K690479



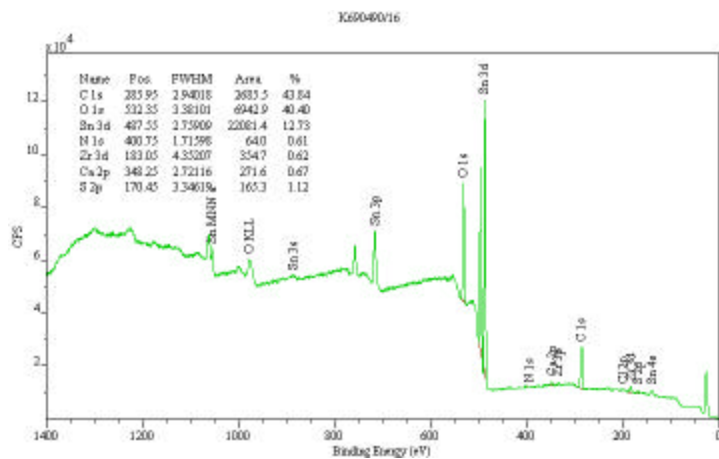
XPS survey scan spectra collected from sample #K690481



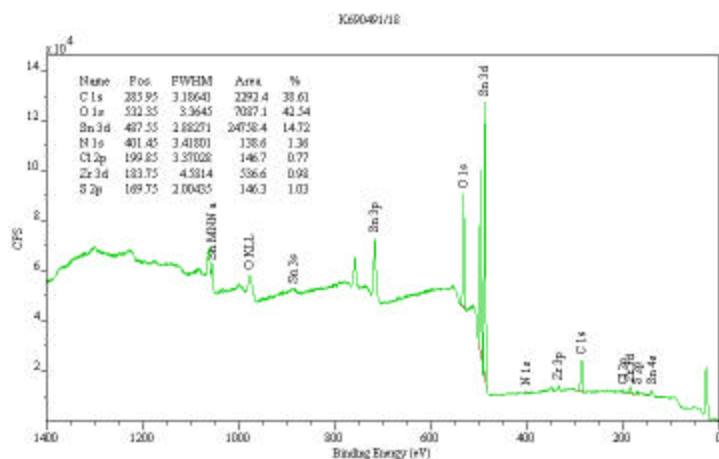
XPS survey scan spectra collected from sample #K690482



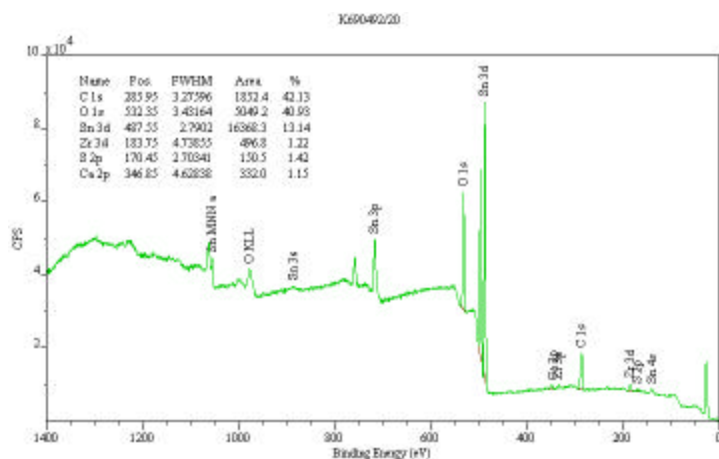
XPS survey scan spectra collected from sample #K690489



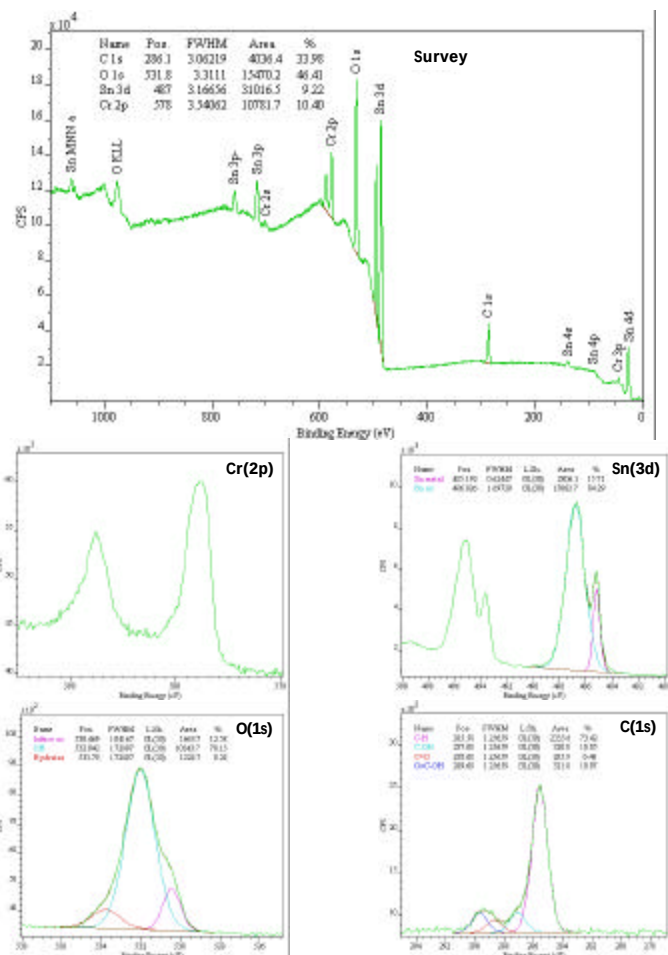
XPS survey scan spectra collected from sample #K690490



XPS survey scan spectra collected from sample #K690491



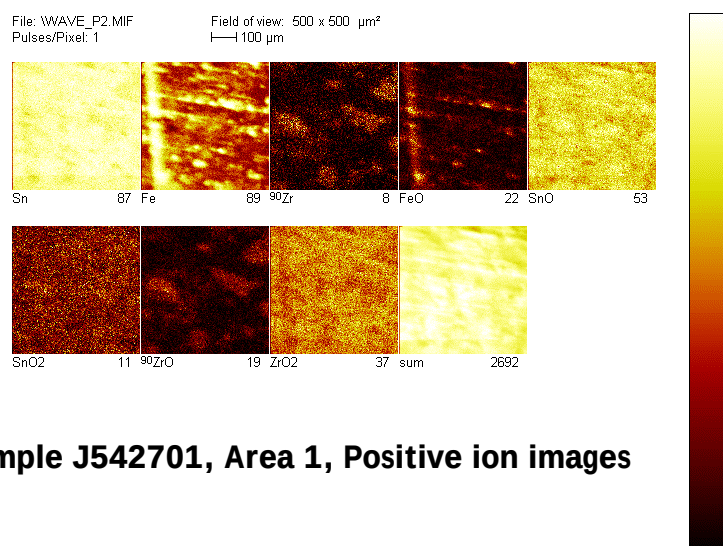
XPS survey scan spectra collected from sample #K690492



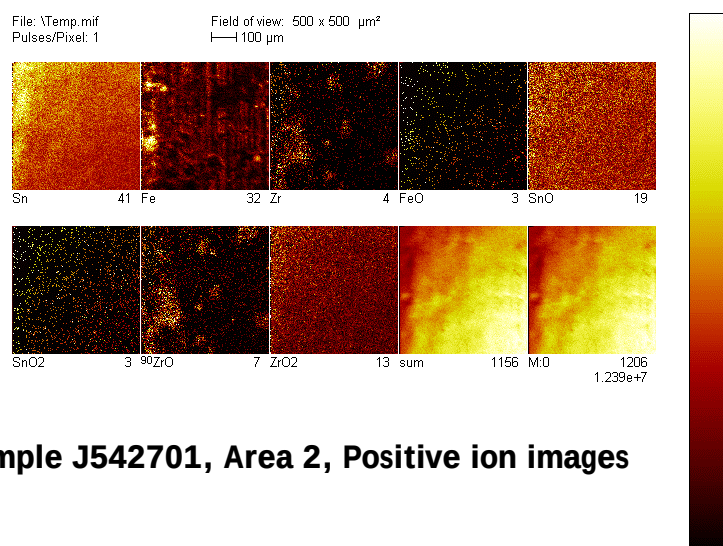
XPS spectra collected from sample #CDC-Tinplate

Annexure A5-III

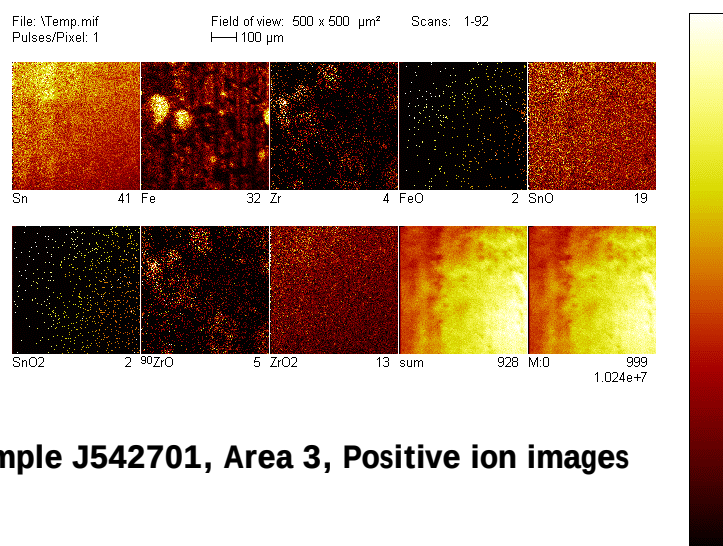
**POSITIVE ION ToF-SIMS IMAGES COLLECTED
FROM THE TINPLATE SAMPLES**



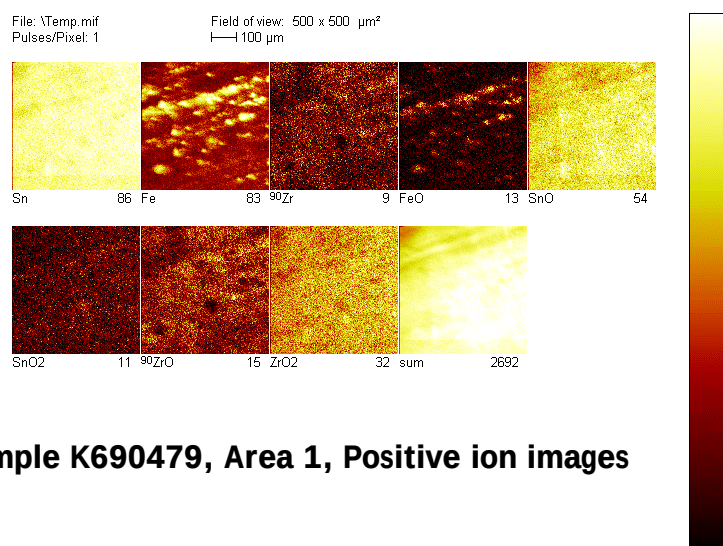
Sample J542701, Area 1, Positive ion images



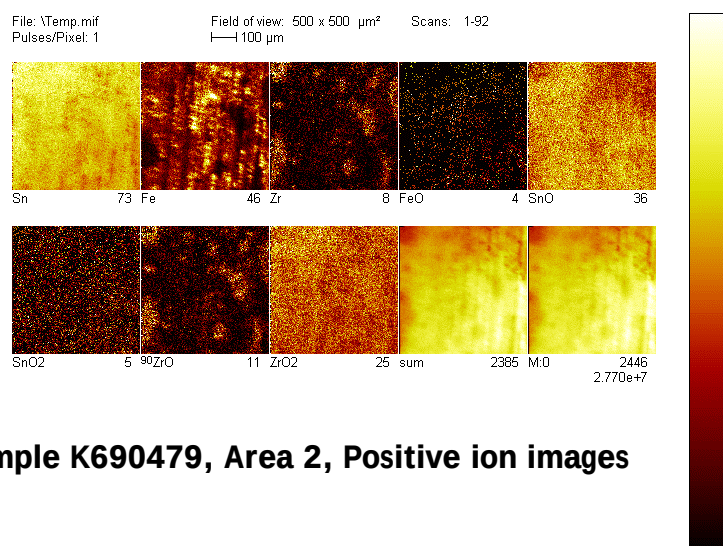
Sample J542701, Area 2, Positive ion images



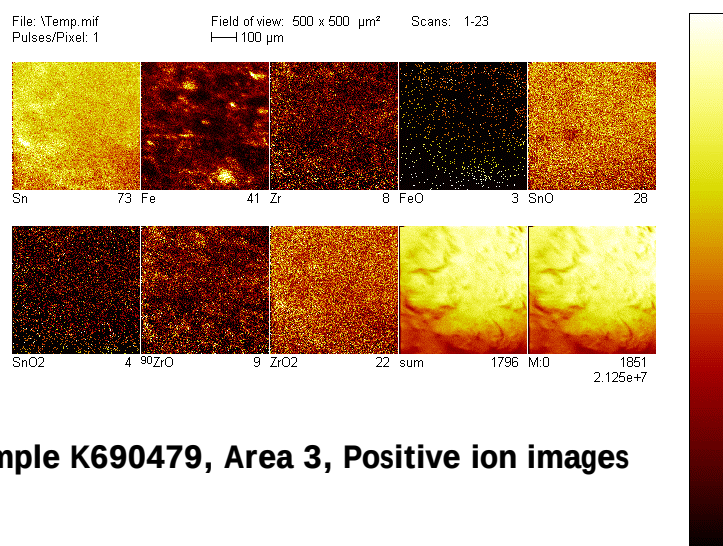
Sample J542701, Area 3, Positive ion images



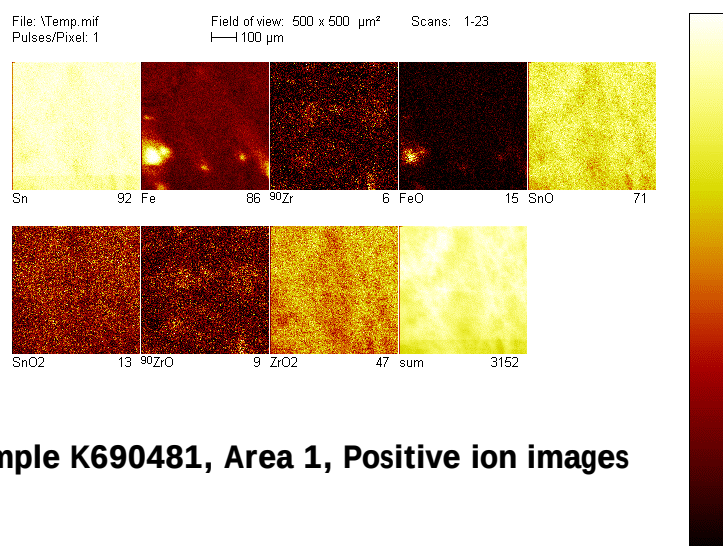
Sample K690479, Area 1, Positive ion images



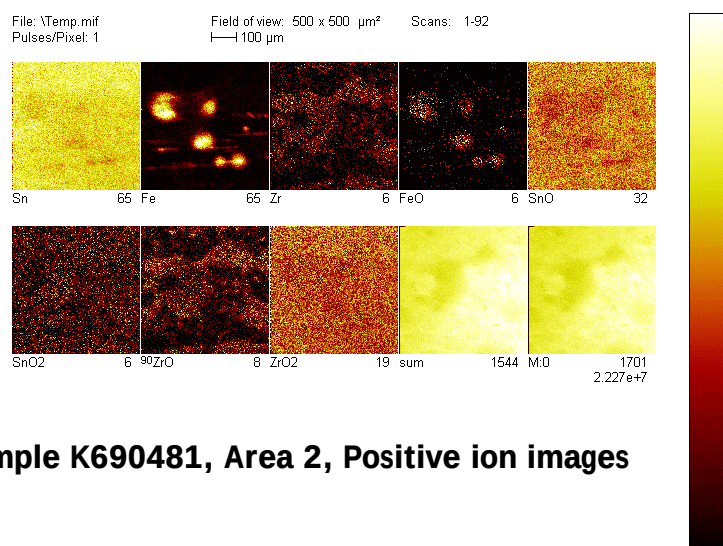
Sample K690479, Area 2, Positive ion images



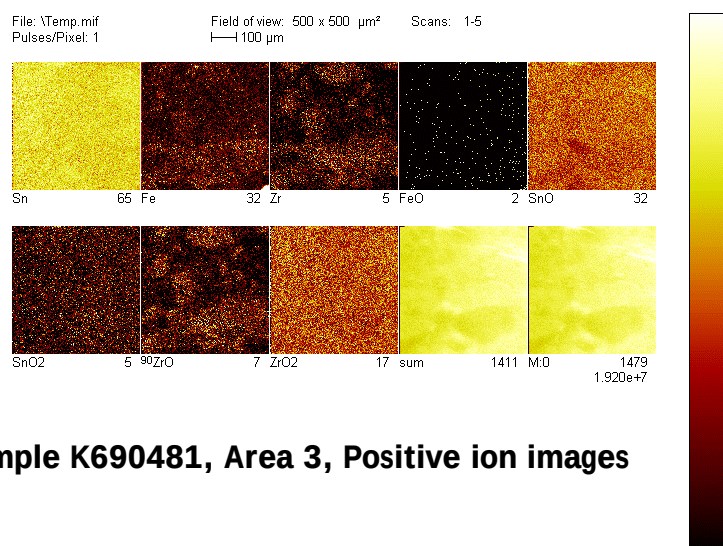
Sample K690479, Area 3, Positive ion images



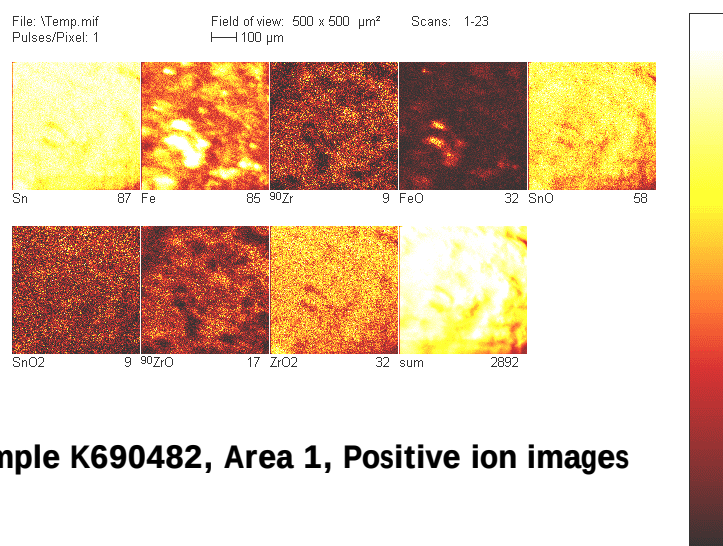
Sample K690481, Area 1, Positive ion images



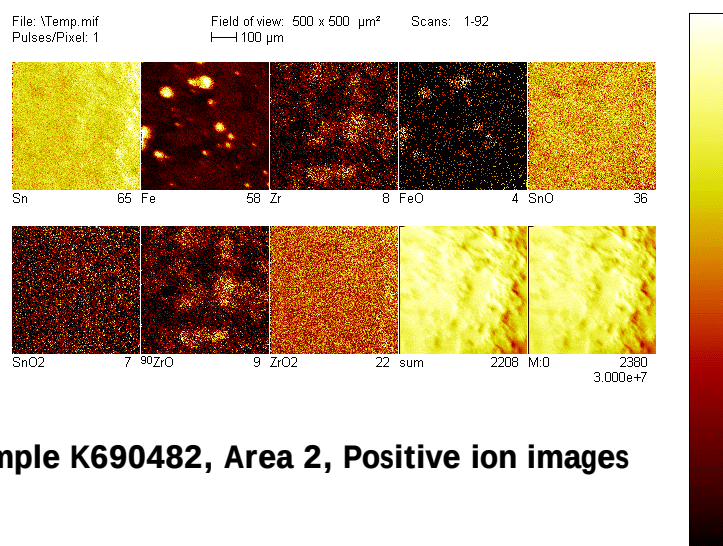
Sample K690481, Area 2, Positive ion images



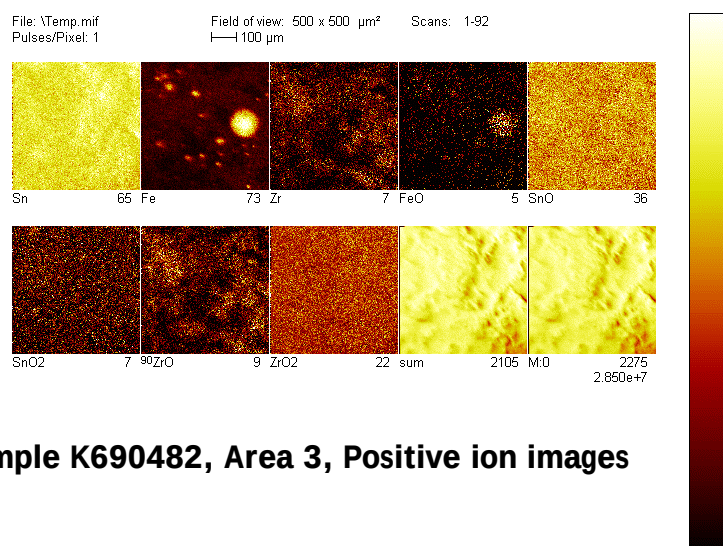
Sample K690481, Area 3, Positive ion images



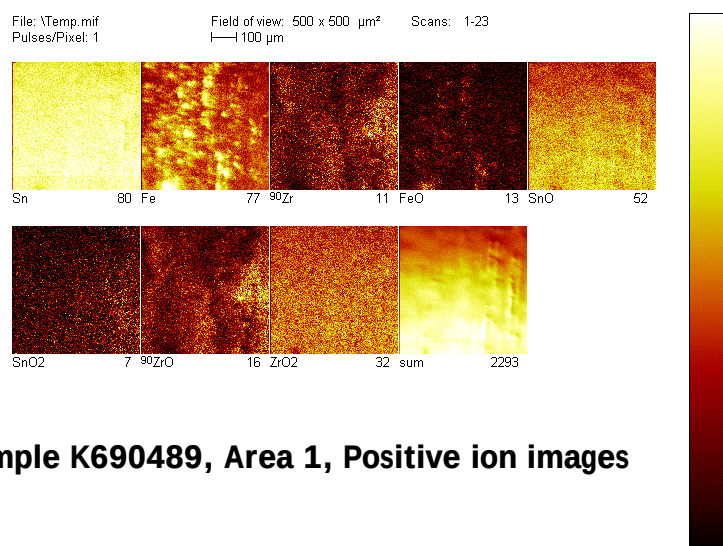
Sample K690482, Area 1, Positive ion images



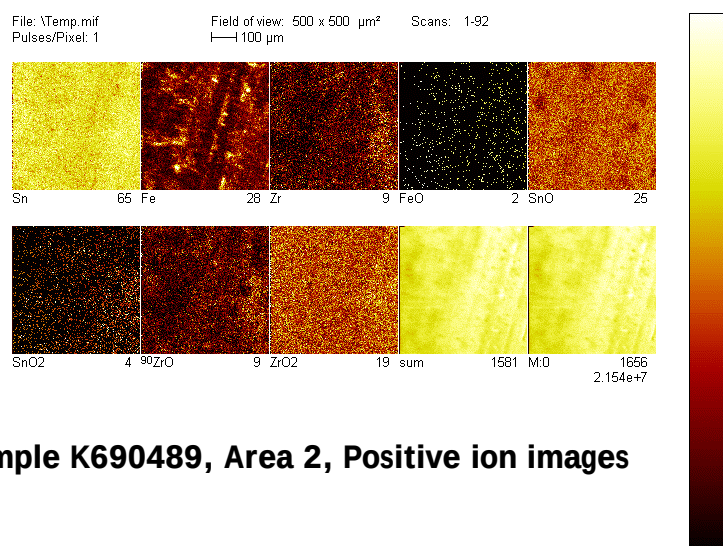
Sample K690482, Area 2, Positive ion images



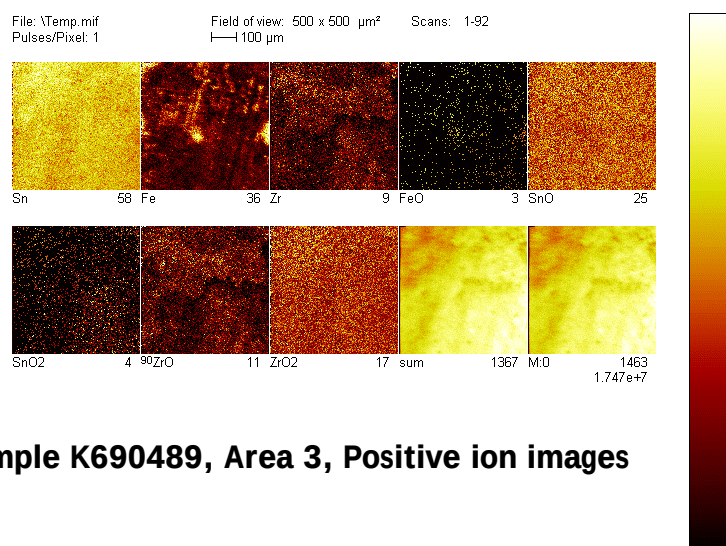
Sample K690482, Area 3, Positive ion images



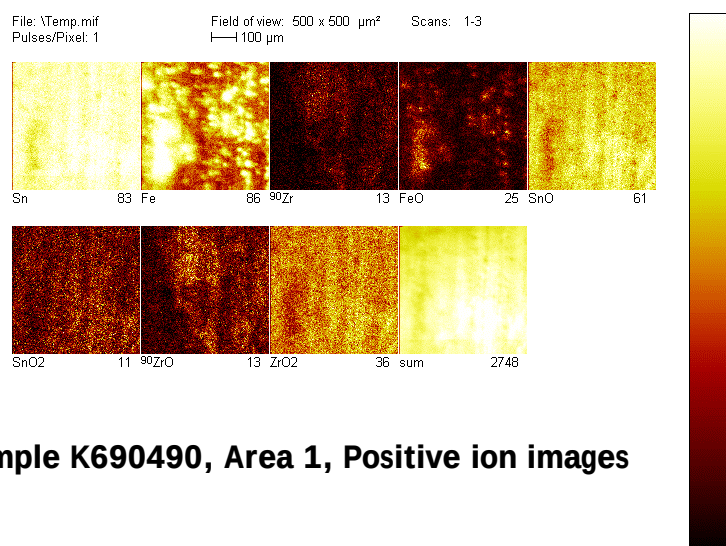
Sample K690489, Area 1, Positive ion images



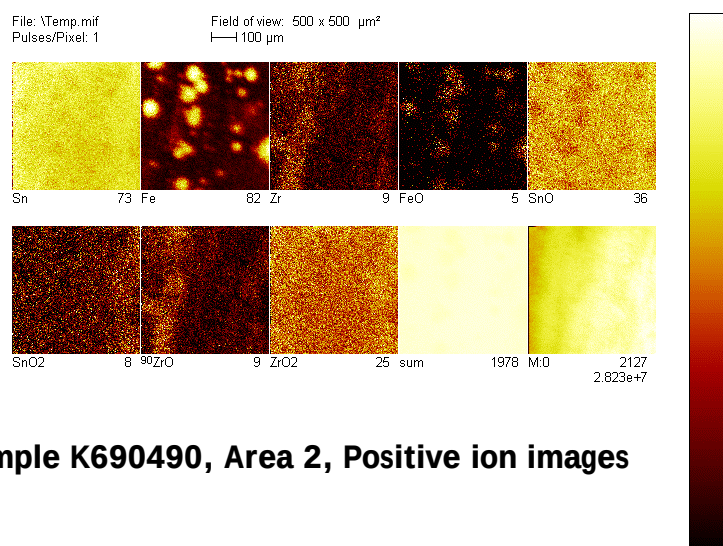
Sample K690489, Area 2, Positive ion images



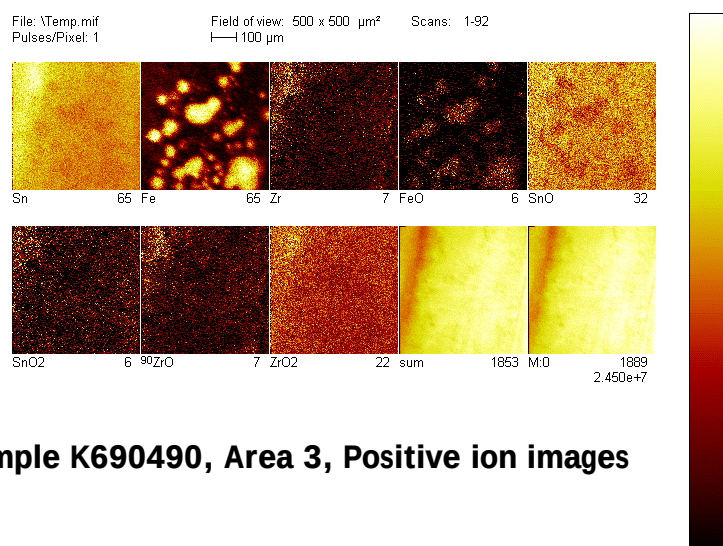
Sample K690489, Area 3, Positive ion images



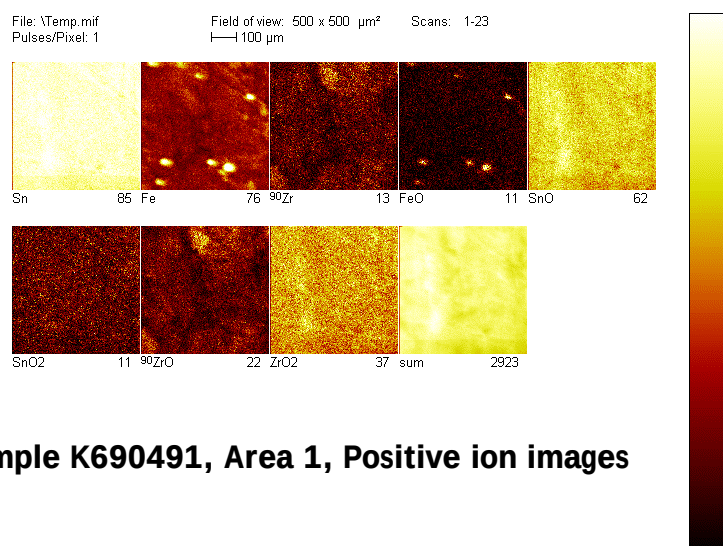
Sample K690490, Area 1, Positive ion images



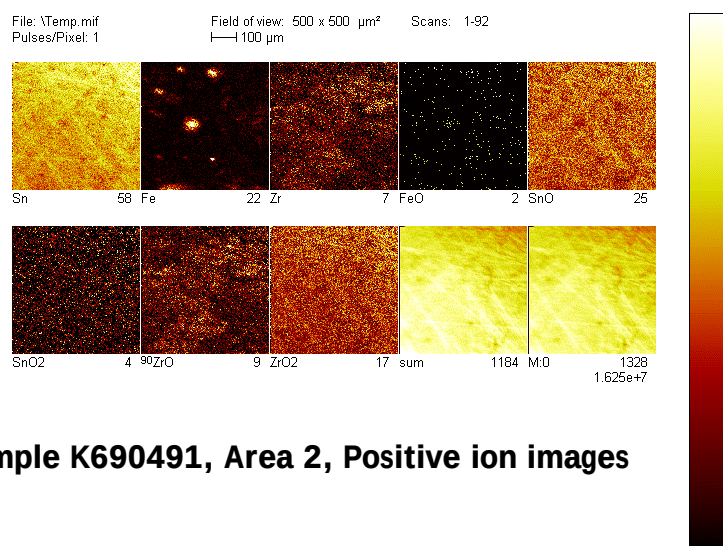
Sample K690490, Area 2, Positive ion images



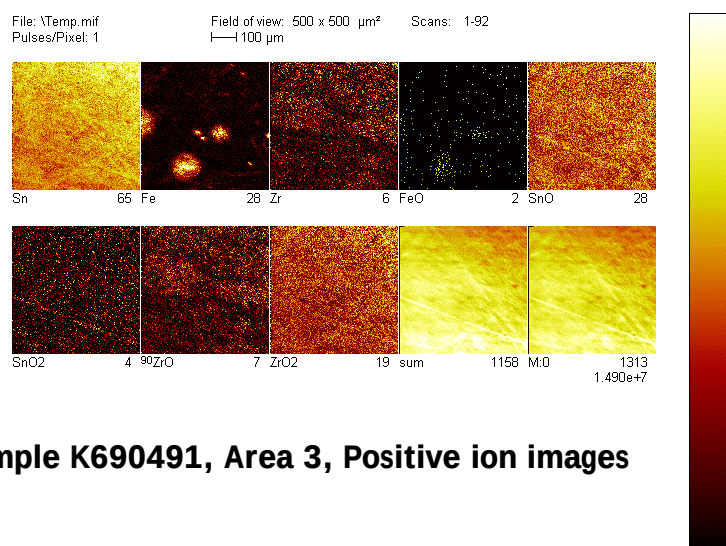
Sample K690490, Area 3, Positive ion images



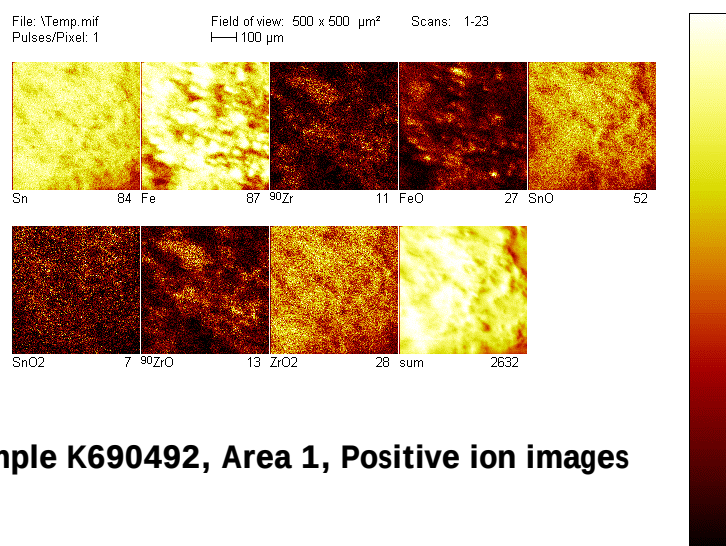
Sample K690491, Area 1, Positive ion images



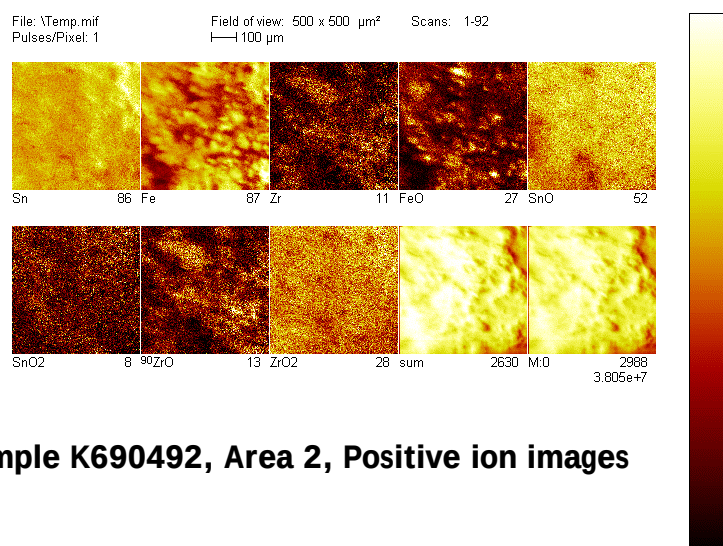
Sample K690491, Area 2, Positive ion images



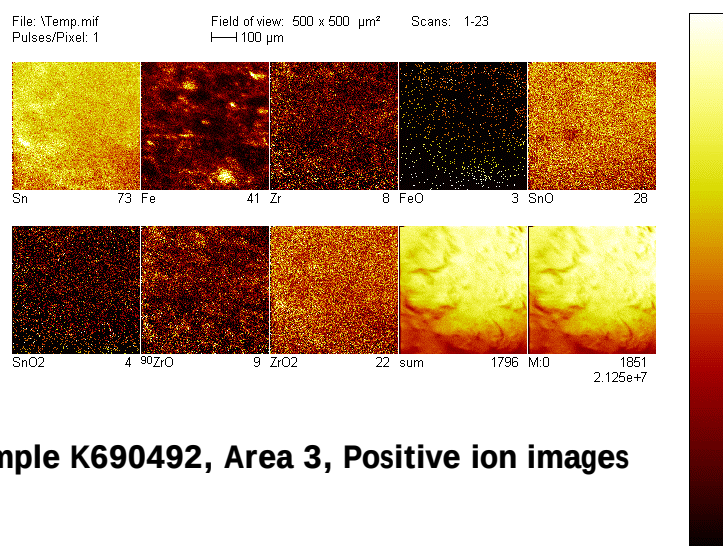
Sample K690491, Area 3, Positive ion images



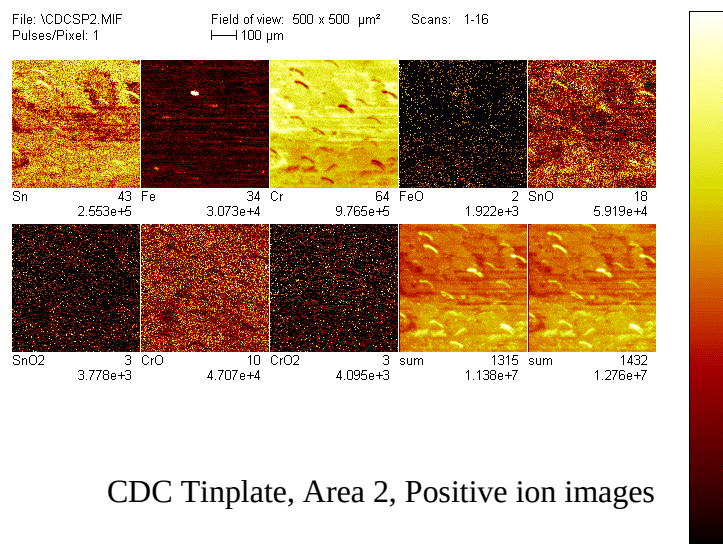
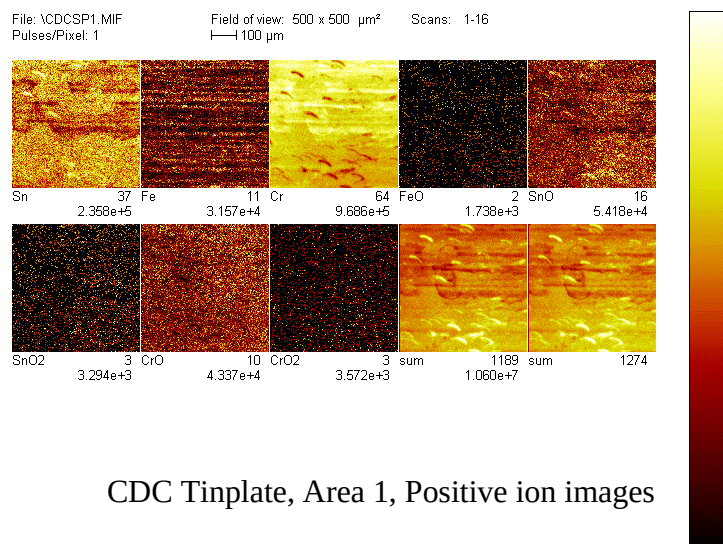
Sample K690492, Area 1, Positive ion images

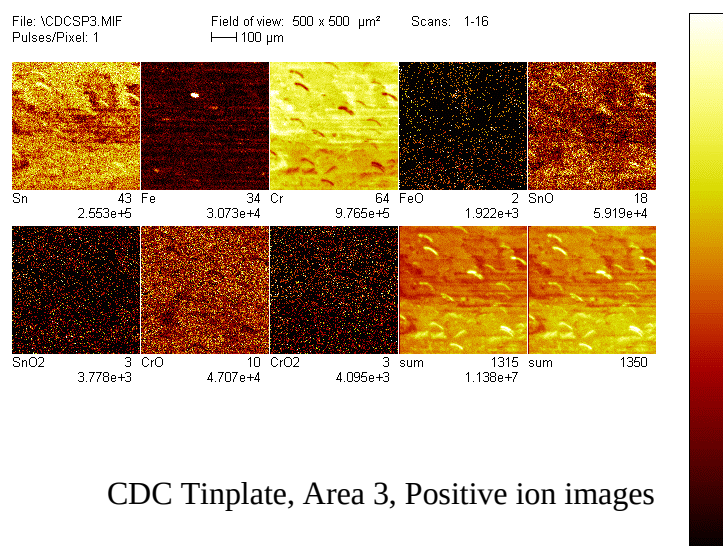


Sample K690492, Area 2, Positive ion images



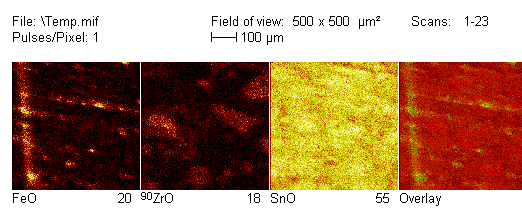
Sample K690492, Area 3, Positive ion images



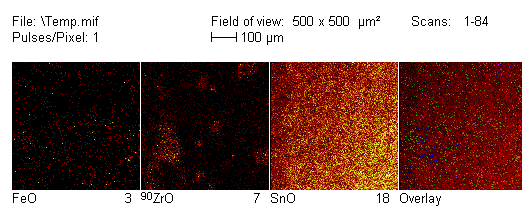


Annexure A5-IV

**OVERLAY OF POSITIVE ION ToF-SIMS
IMAGES COLLECTED FROM THE
TINPLATE SAMPLES**

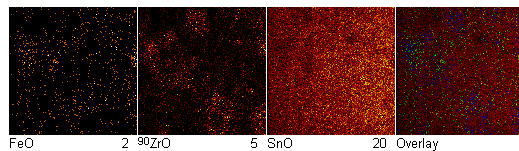


Sample 542701 area 1



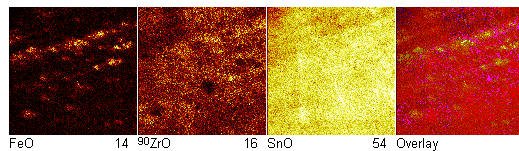
Sample 542701 area 2

File: \542701-2.MIF Field of view: 500 x 500 μm^2 Scans: 1-92
Pulses/Pixel: 1 --- 100 μm

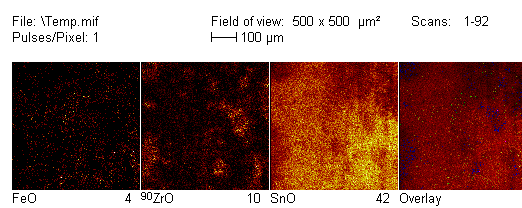


Sample 542701 – area 3

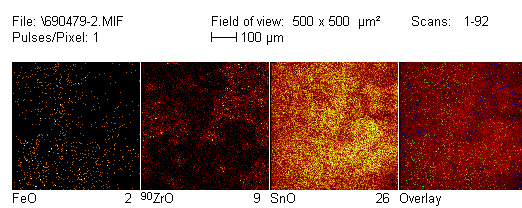
File: \542701-3.MIF Field of view: 500 x 500 μm^2 Scans: 1-92
Pulses/Pixel: 1 --- 100 μm



Sample 690479 –area 1

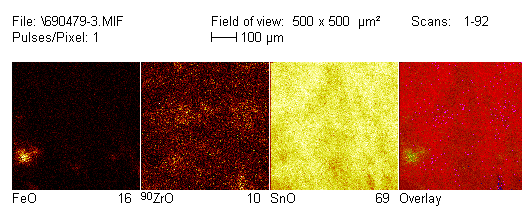


Sample 690479-area 2

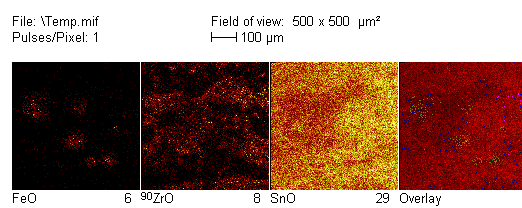


Sample 690479-area 3

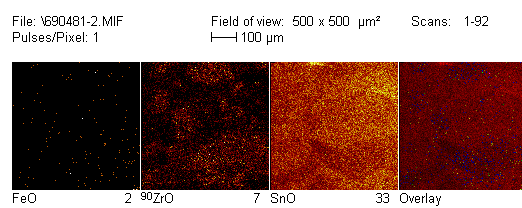




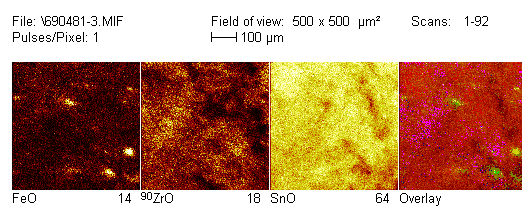
Sample 690481 – area 1



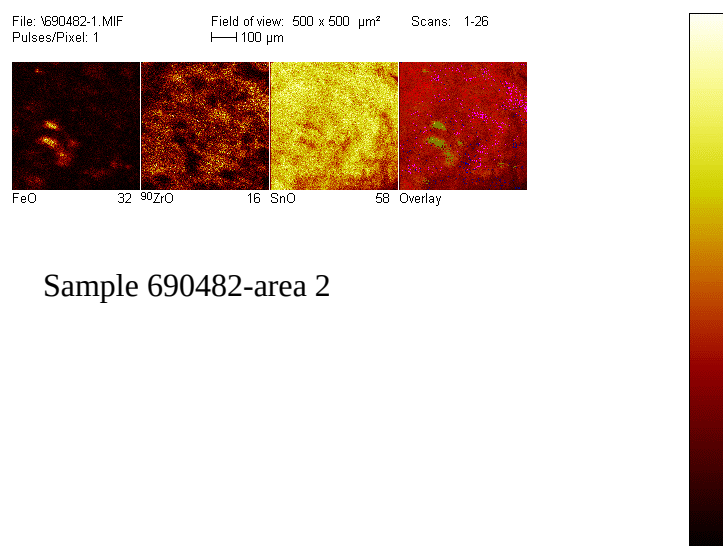
Sample 690481 – area 2



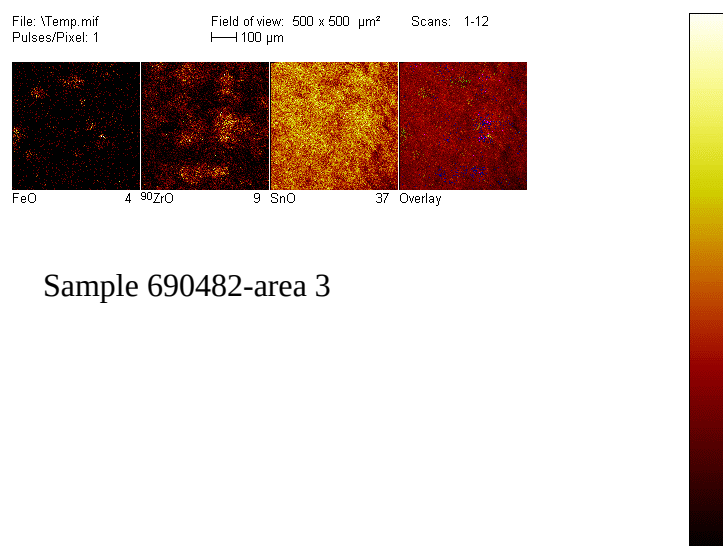
Sample 690481-area 3



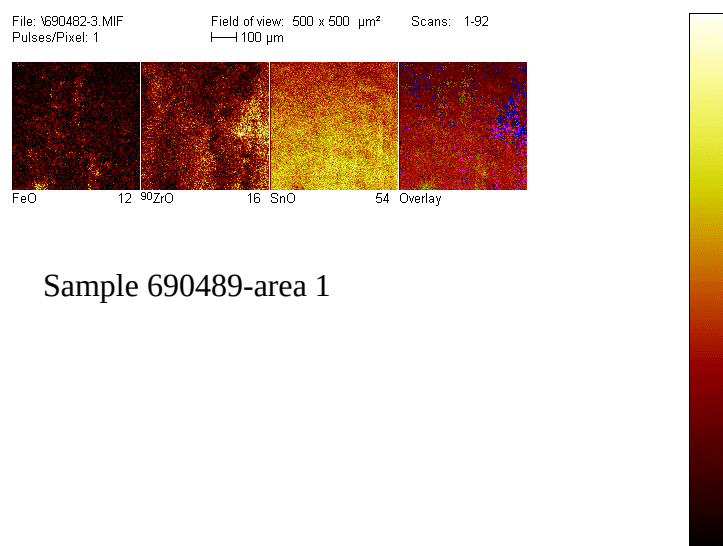
Sample 690482-area 1



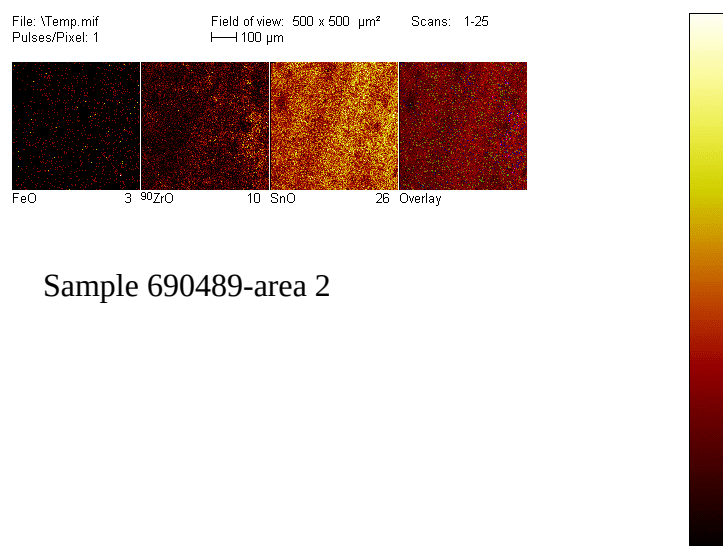
Sample 690482-area 2



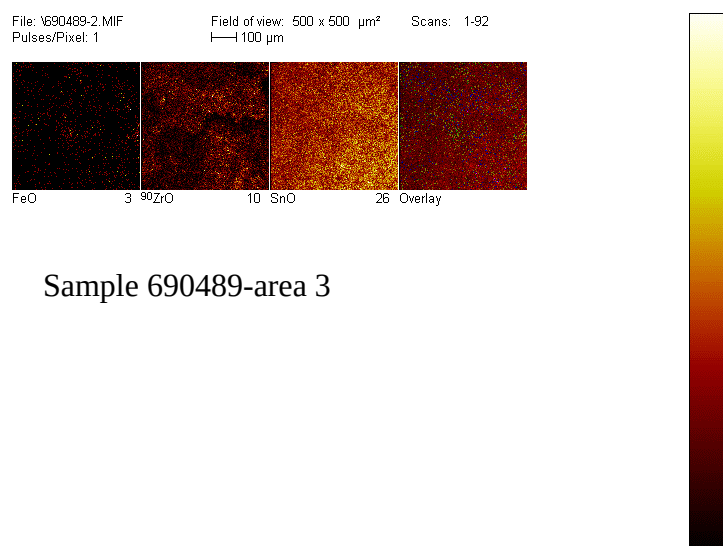
Sample 690482-area 3



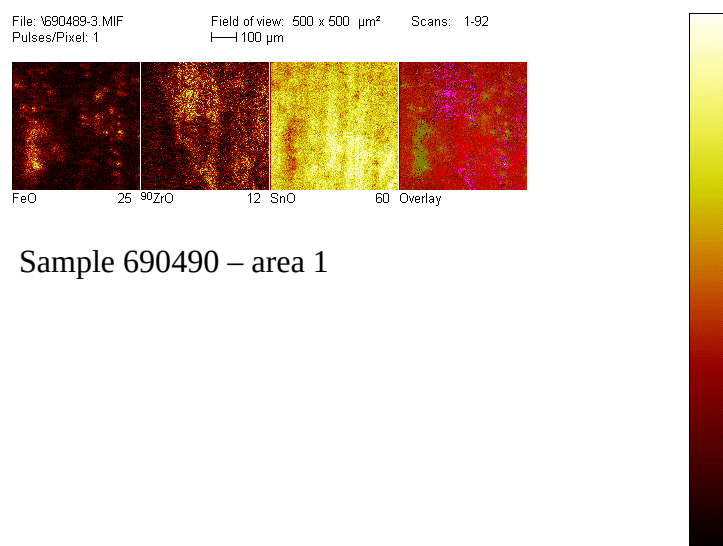
Sample 690489-area 1



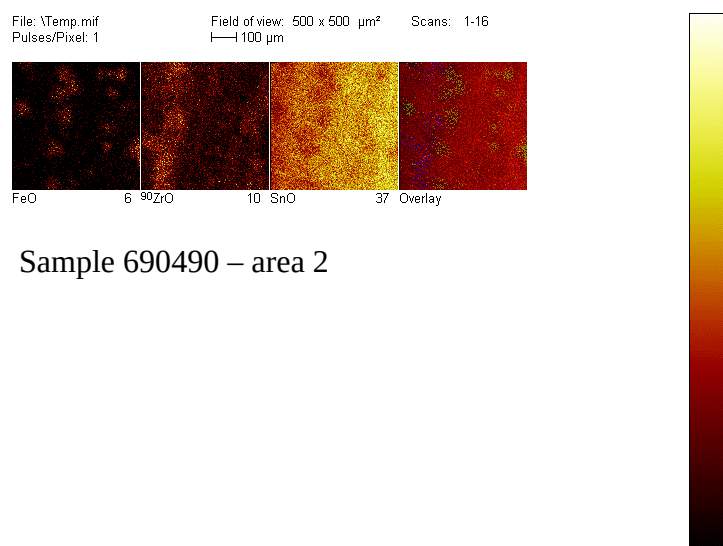
Sample 690489-area 2



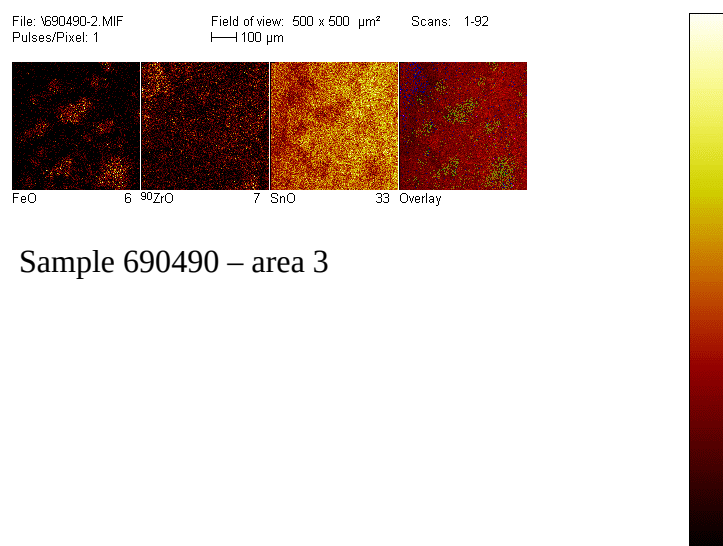
Sample 690489-area 3



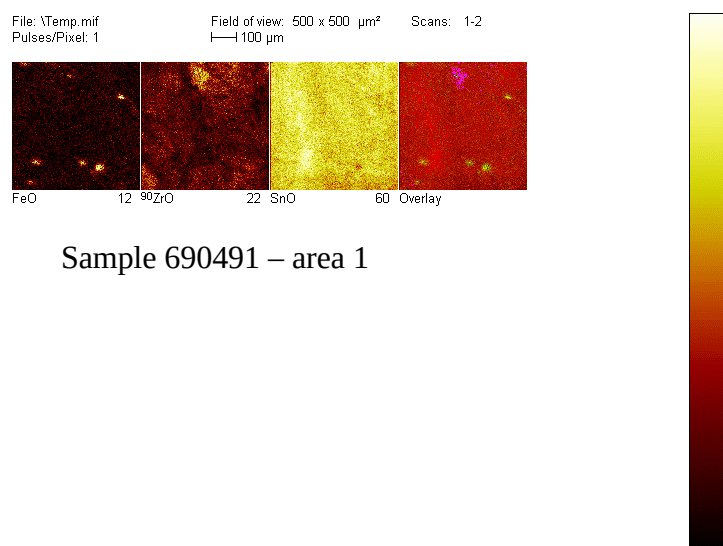
Sample 690490 – area 1



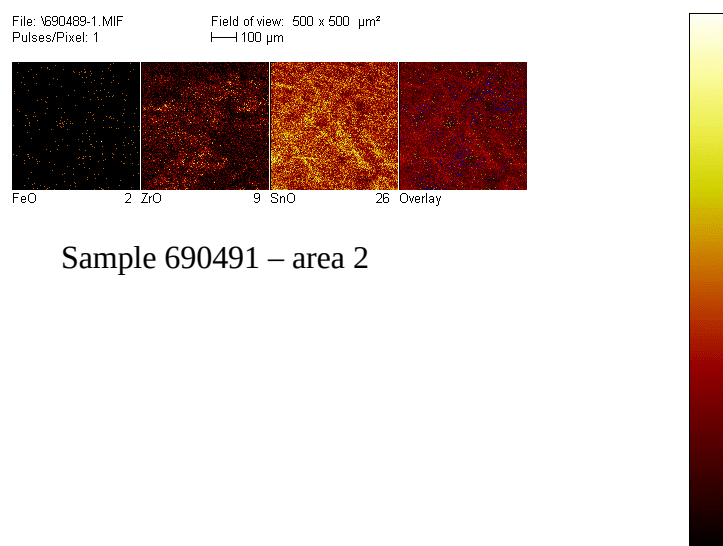
Sample 690490 – area 2



Sample 690490 – area 3

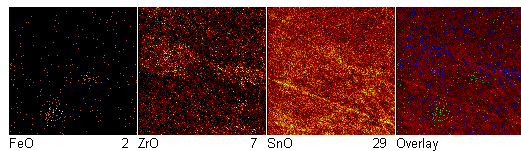


Sample 690491 – area 1



Sample 690491 – area 2

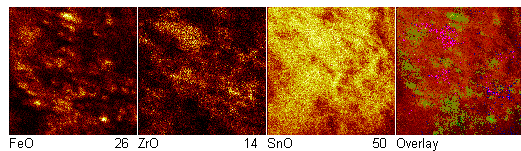
File: \690491-2.MIF Field of view: 500 x 500 μm^2 Scans: 1-92
Pulses/Pixel: 1 --- 100 μm



Sample 690491 – area 3

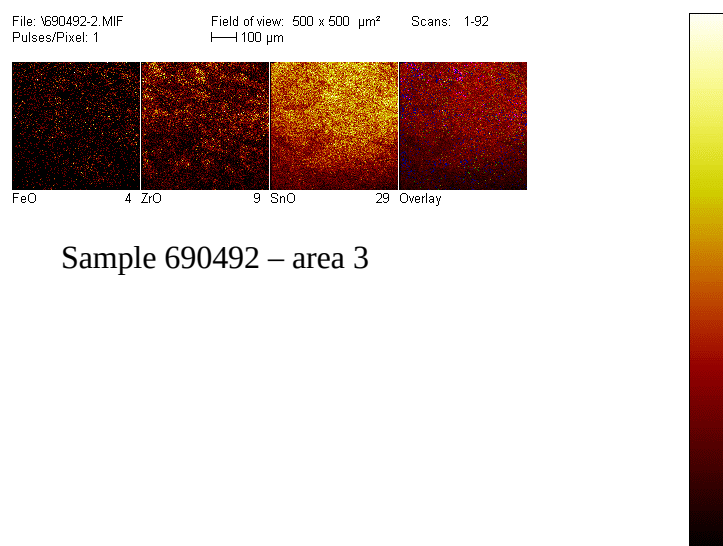
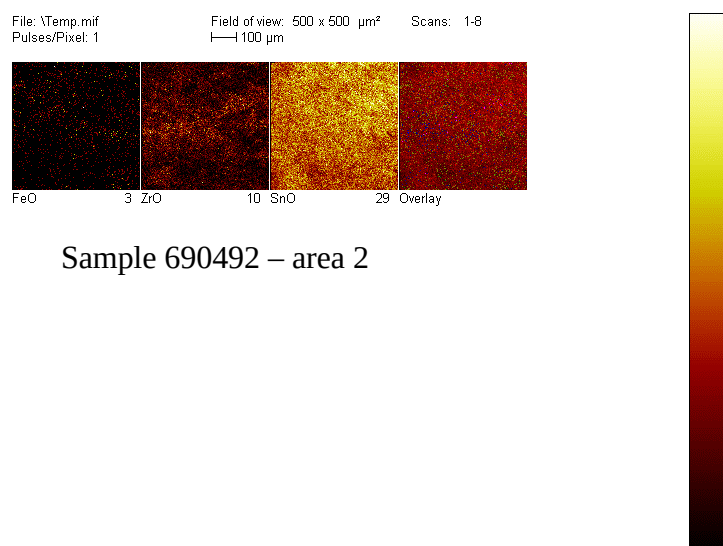


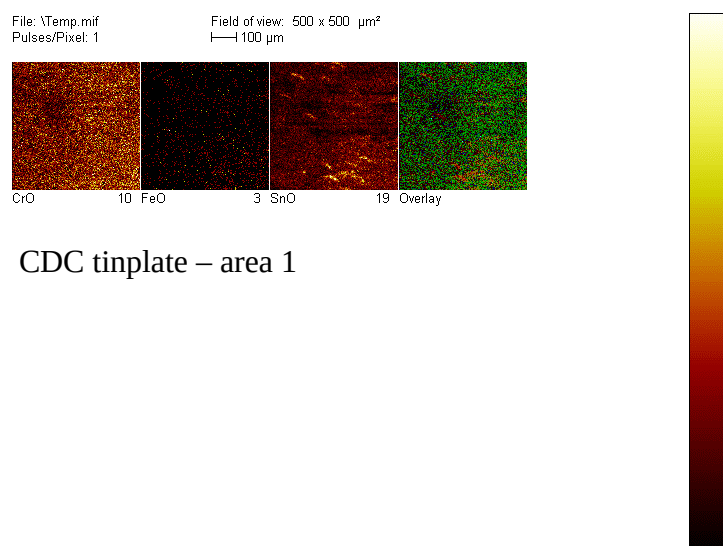
File: \690491-3.MIF Field of view: 500 x 500 μm^2 Scans: 1-92
Pulses/Pixel: 1 --- 100 μm



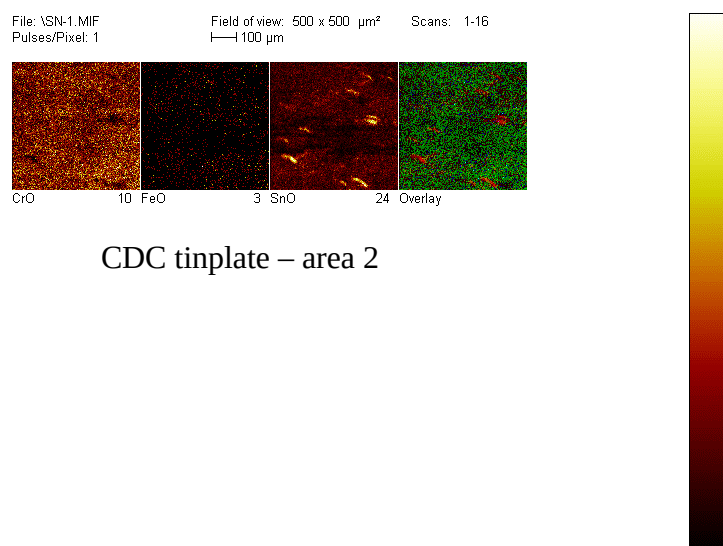
Sample 690492 – area 1



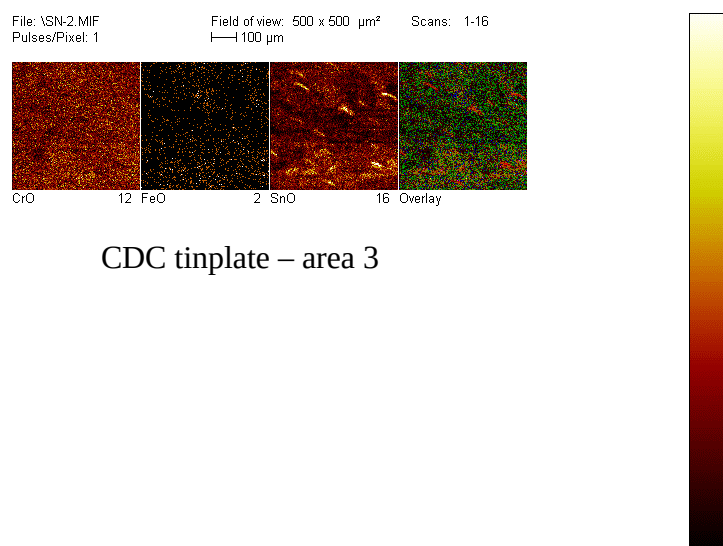




CDC tinplate – area 1



CDC tinplate – area 2

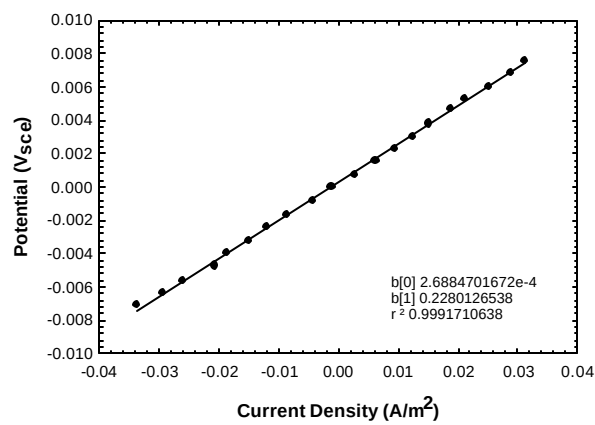


CDC tinplate – area 3

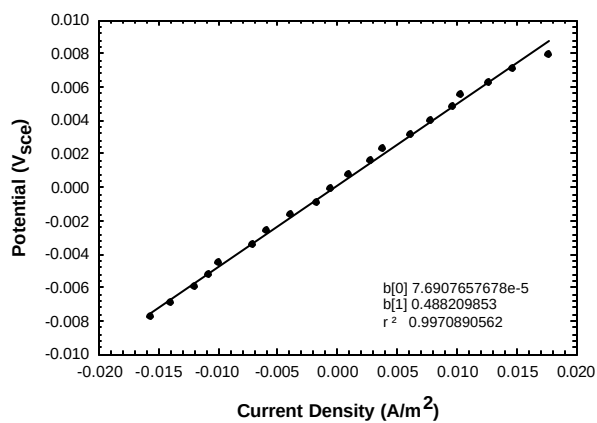
Annexure A5-V

**LINEAR POLARISATION CURVES
OBTAINED IN AS-PREPARED AND
DEAERATED SYNTHETIC PEAR JUICE**

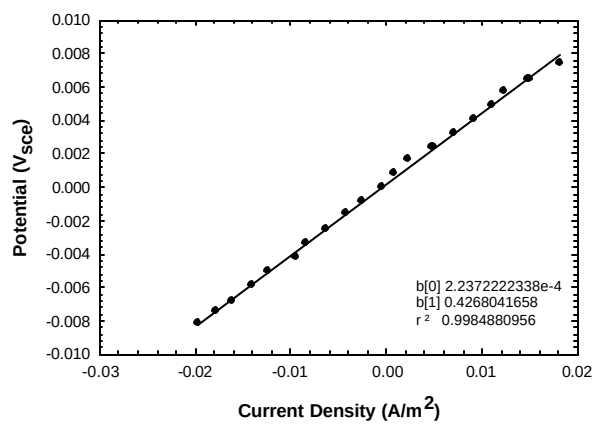
**Linear Polarization Curve from Tinplate Sample J542701
in As-prepared and Deaerated Synthetic Pear Juice**



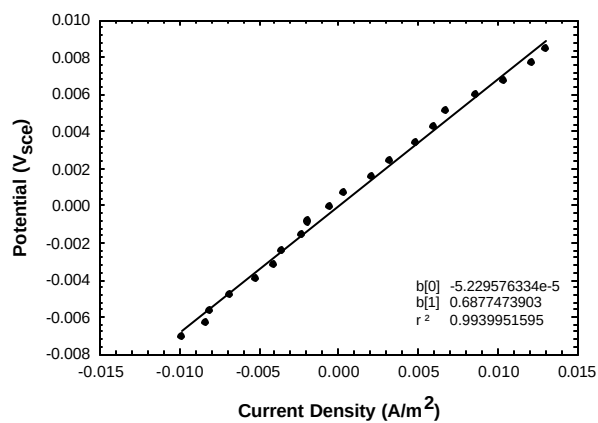
**Linear Polarization Curve from Tinplate Sample K690479
in As-prepared and Deaerated Synthetic Pear Juice**



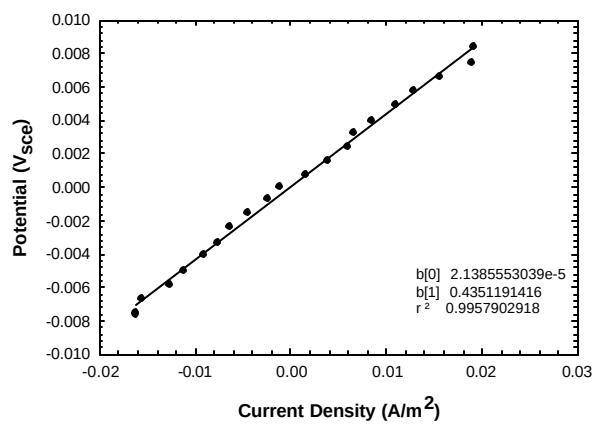
Linear Polarization Curve from Tinplate Sample K690481
in As-prepared and Deaerated Synthetic Pear Juice



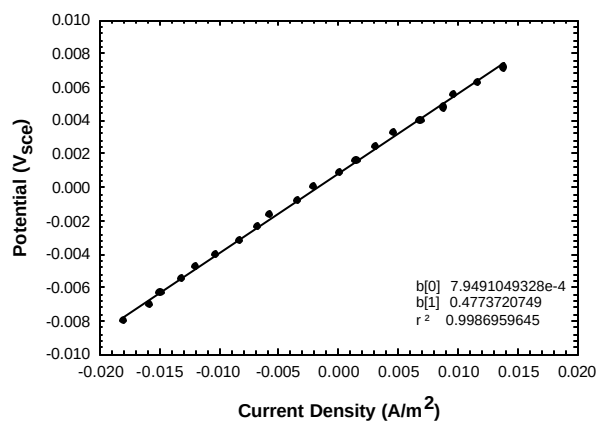
Linear Polarization Curve from Tinplate Sample K690482
in As-prepared and Deaerated Synthetic Pear Juice



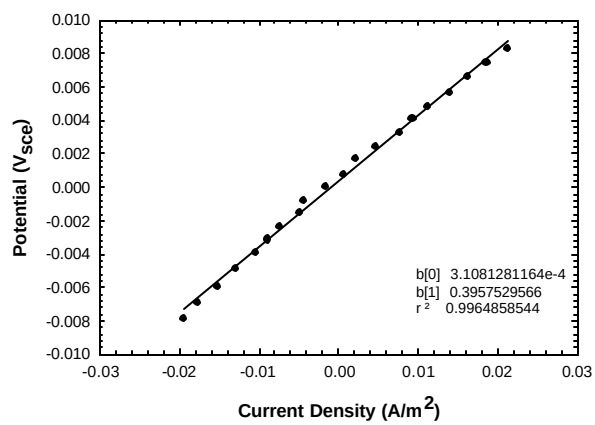
Linear Polarization Curve from Tinplate Sample K690489
in As-prepared and Deaerated Synthetic Pear Juice



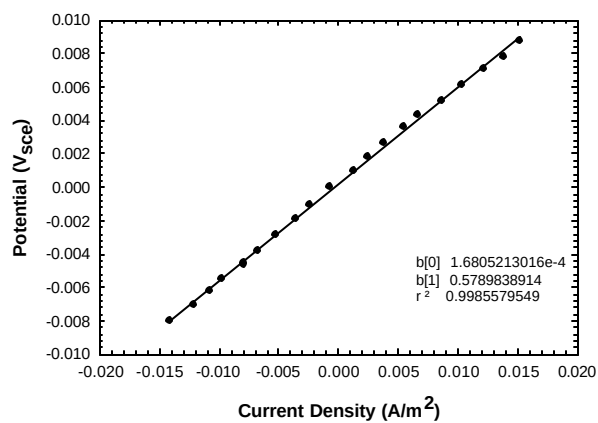
Linear Polarization Curve from Tinplate Sample K690490
in As-prepared and Deaerated Synthetic Pear Juice



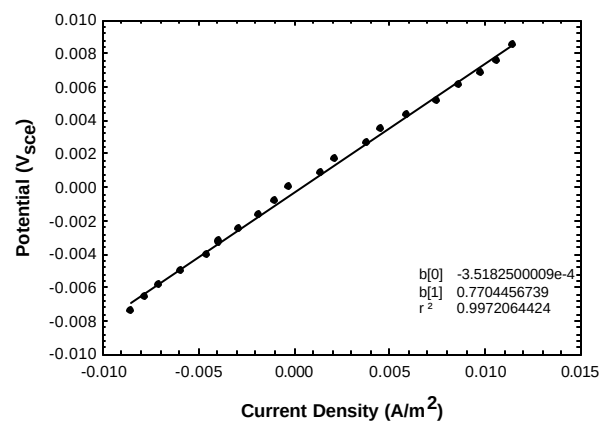
**Linear Polarization Curve from Tinplate Sample K690491
in As-prepared and Deaerated Synthetic Pear Juice**



**Linear Polarization Curve from Tinplate Sample K690492
in As-prepared and Deaerated Synthetic Pear Juice**



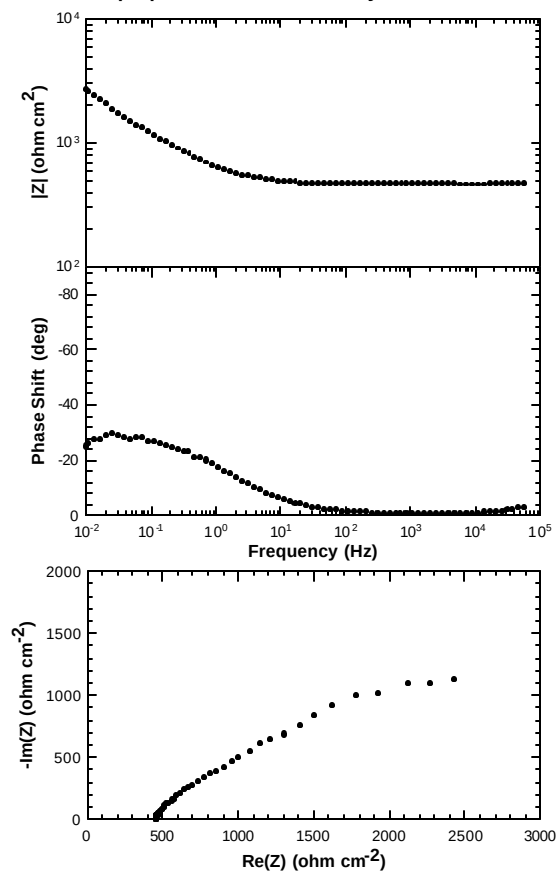
Linear Polarization Curve from Tinplate Sample CDC-Tinplate
in As-prepared and Deaerated Synthetic Pear Juice



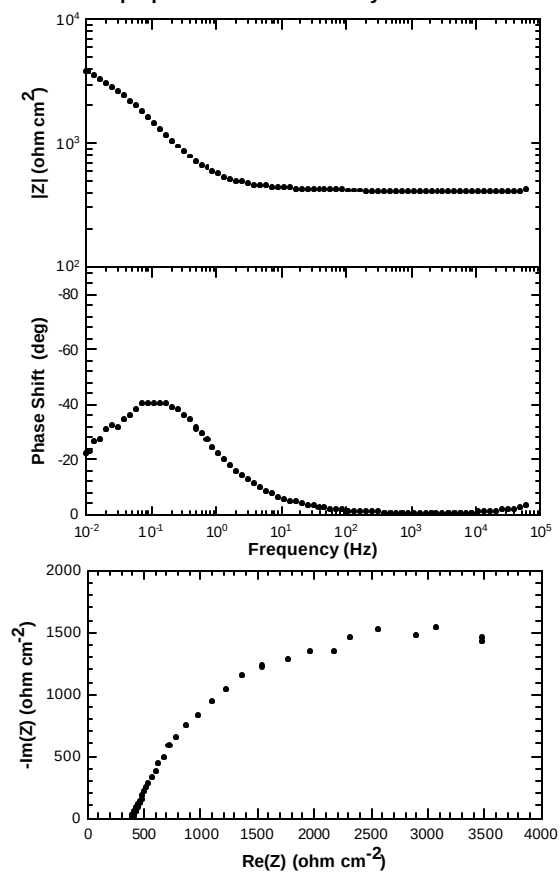
AnnexureA5-VI

**ELECTROCHEMICAL IMPEDANCE SPECTRA
OBTAINED IN AS-PREPARED AND
DEAERATED SYNTHETIC PEAR JUICE**

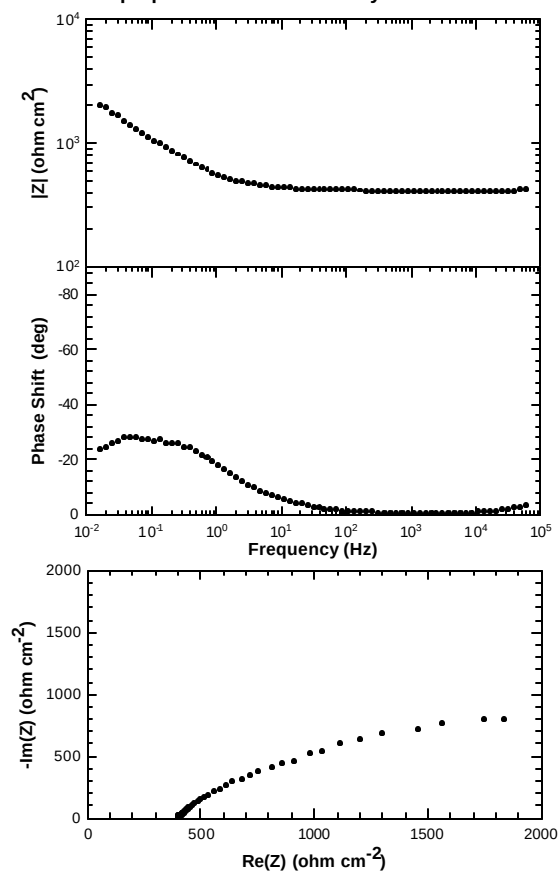
EIS Spectrum Collected from Tinplate Sample J542701
in As-prepared and Deaerated Synthetic Pear Juice



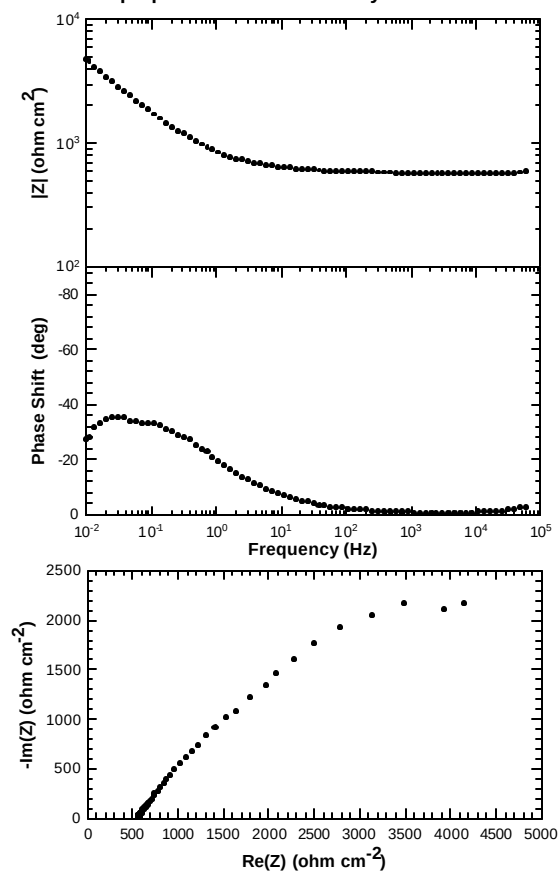
EIS Spectrum Collected from Tinplate Sample K690479
in AS-prepared and Deaerated Synthetic Pear Juice



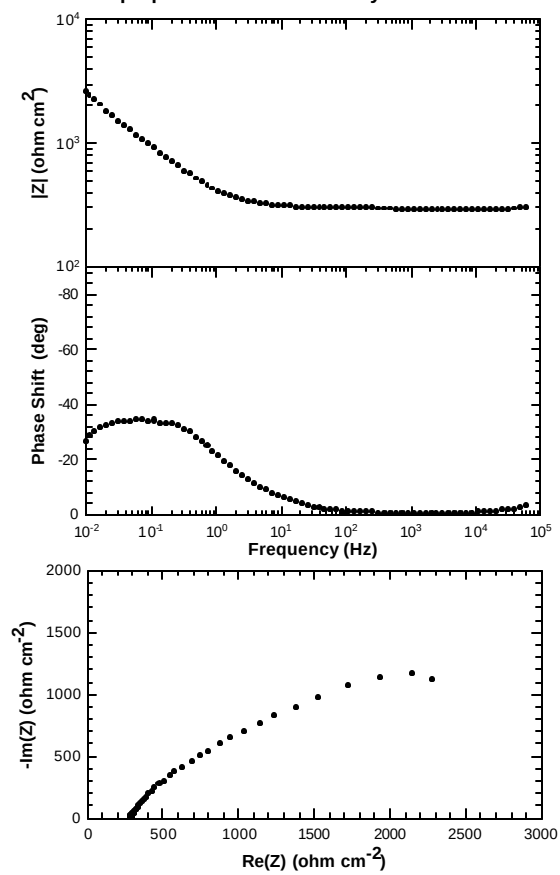
EIS Spectrum Collected from Tinplate Sample K690481
in AS-prepared and Deaerated Synthetic Pear Juice



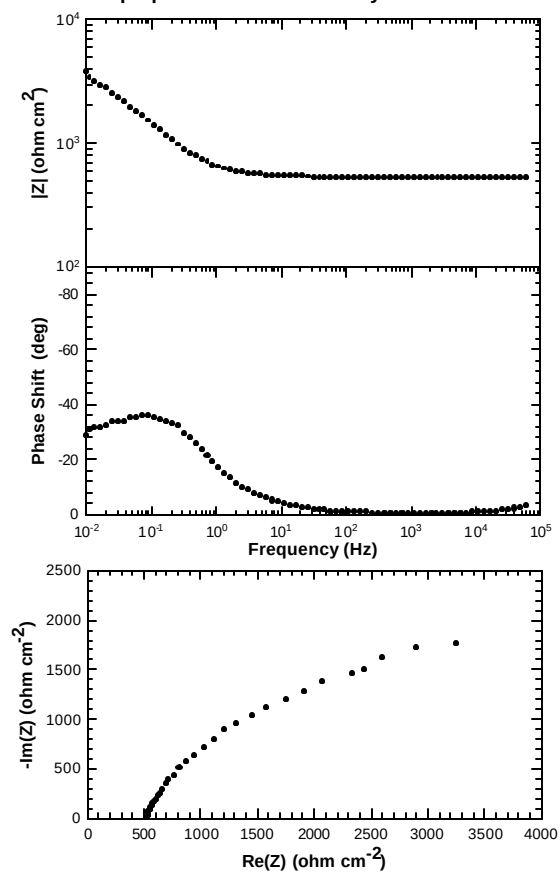
EIS Spectrum Collected from Tinplate Sample K690482
in AS-prepared and Deaerated Synthetic Pear Juice



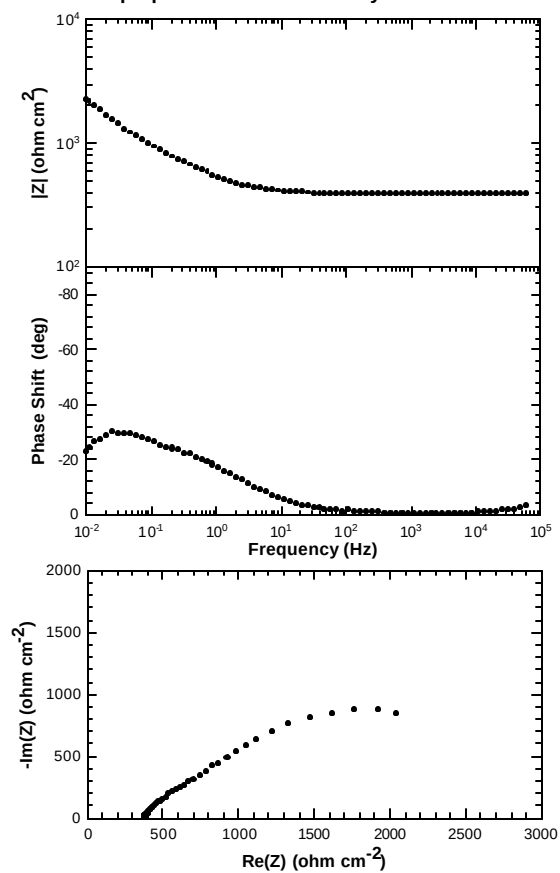
EIS Spectrum Collected from Tinplate Sample K690489
in AS-prepared and Deaerated Synthetic Pear Juice



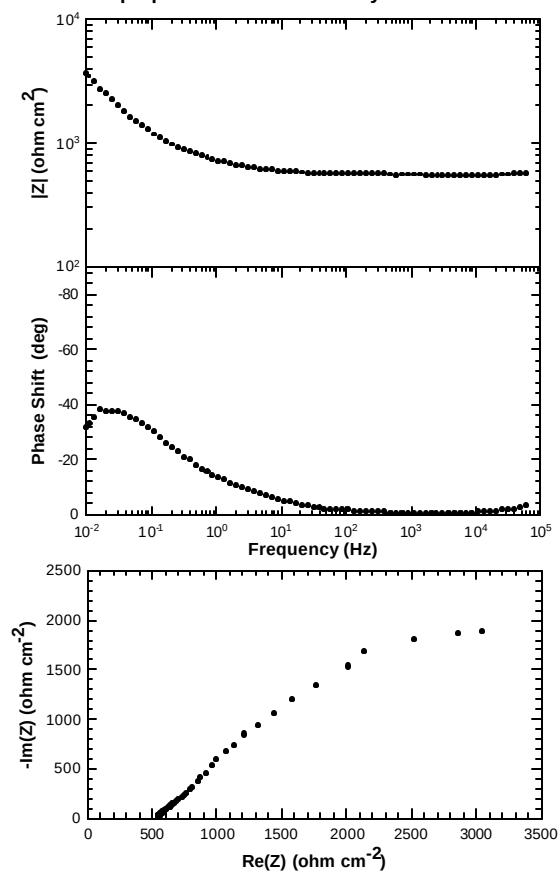
EIS Spectrum Collected from Tinplate Sample K690490
in AS-prepared and Deaerated Synthetic Pear Juice



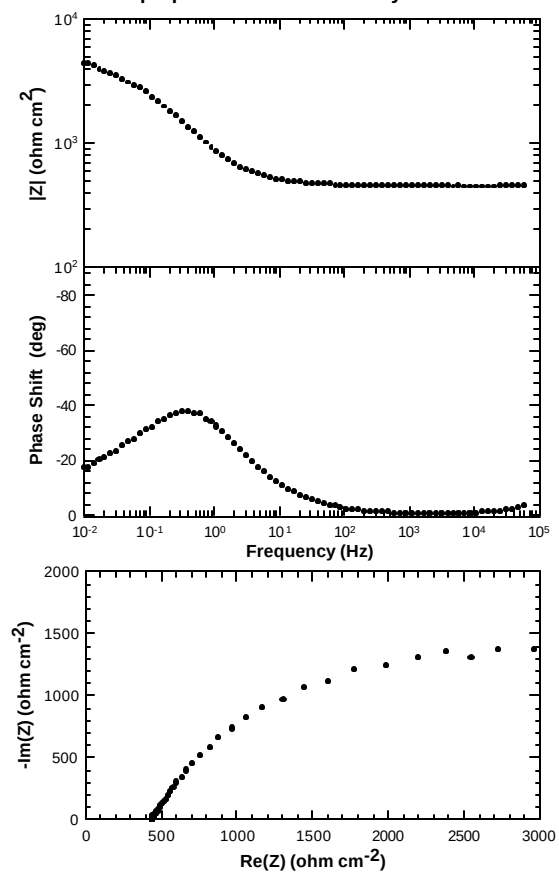
EIS Spectrum Collected from Tinplate Sample K690491
in AS-prepared and Deaerated Synthetic Pear Juice



EIS Spectrum Collected from Tinplate Sample K690492
in AS-prepared and Deaerated Synthetic Pear Juice



EIS Spectrum Collected from Tinplate Sample CDC-Tinplate
in As-prepared and Deaerated Synthetic Pear Juice



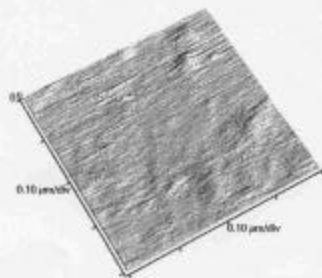
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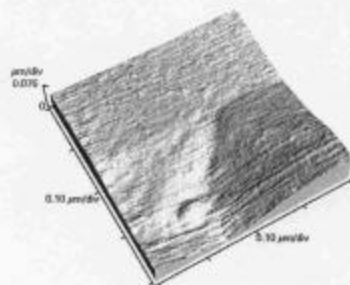
Atomic Force Microscopy (AFM) Images of AISI Passivation Trial Material
(Bill Tekatch, Dofasco Inc.)

Line trial and control CDC treated samples were imaged with AFM. Before imaging, the materials were prepared by using several alternate washes with acetone then de-ionised water, and a final acetone wash followed by air drying at room temperature. Below are 3D images of 400nm by 400nm regions of three typical samples with a typical line cross section of a flat region.

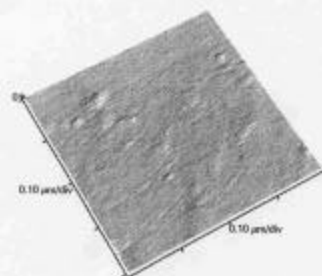
CONCLUSION: No significant distinctive differences were found between the various materials.



Sample K690481, Fluorozirconate treated, bottom centre, 225 ug/sq ft. Zr, reflowed 0.20lb/BB Tin



Sample K690492, Zirconium Orthosulfate treated, centre, 54-117 ug/sq ft. Zr, matte 0.20lb/BB Tin



Dofasco Sample, CDC tinplate, 0.35-0.65 mg/sq ft. Cr, reflowed 0.20lb/BB Tin

Table A6-1. Results from the linear polarization measurements in boiled and cooled synthetic pear juice

Treatment / Description	Sample	Mean Open Circuit Potential (E_{cor}) V(SCE)	Mean Polarization Resistance (R_p) Ohm-m ²
Fluorozirconate	J542701	- 0.576 +/- 0.005	1.6 +/- 0.5
	K690479	- 0.586 +/- 0.004	2.1 +/- 0.3
	K690481(*)	- 0.58 +/- 0.01	0.5 +/- 0.3
	K690481	- 0.570 +/- 0.006	0.39 +/- 0.09
	K690482	- .57 +/- 0.02	0.5 +/- 0.2
Zirconium Orthosulfate (Zirconate)	K690489	- 0.557 +/- 0.005	1.0 +/- 0.3
	K690490	- 0.57 +/- 0.01	0.5 +/- 0.4
	K690491	- 0.50 +/- 0.02	0.8 +/- 0.5
	K690492	- 0.58 +/- 0.01	0.5 +/- 0.4
Cathodic dichromate Tinplate	CDC – 5	- 0.581 +/- 0.001	1.0 +/- 0.2
Pure tin (99.9%)	Tin	- 0.558 +/- 0.004	0.18 +/- 0.03

(*) (0.2 lb/bb side)
all errors +/- 1s

Table A6-2. Results from the electrochemical impedance spectroscopy (EIS) measurements in boiled and cooled synthetic pear juice

Treatment / Description	Sample	Solution Resistance (R_s) Ohm-m ²	Mean Coating Resistance (R_c) Ohm-m ²	Mean Charge Transfer Resistance (R_{ct}) Ohm-m ²	Mean Coating Capacitance (Q_c) mF/cm ²
Fluorozirconate	J542701	0.0749 +/- 0.0006	1.4 +/- 0.4	ND	500 +/- 30
	K690479	0.0767 +/- 0.0006	1.4 +/- 0.1	0.15 +/- 0.02	400 +/- 20
	K690481(*)	0.0810 +/- 0.0001	0.3 +/- 0.1	0.08 +/- 0.02	900 +/- 70
	K690481	0.070 +/- 0.002	0.1 +/- 0.1	0.12 +/- 0.04	1200 +/- 200
	K690482	0.08 +/- 0.02	0.3 +/- 0.1	0.2 +/- 0.1	500 +/- 60
Zirconium Ortho-sulphate (Zirconate)	K690489	0.0726 +/- 0.0007	0.7 +/- 0.6	0.2 +/- 0.3	700 +/- 80
	K690490	0.067 +/- 0.0057	0.4 +/- 0.3	0.3 +/- 0.3	1000 +/- 300
	K690491	0.074 +/- 0.006	0.23 +/- 0.01	0.18 +/- 0.04	900 +/- 200
	L690492	0.076 +/- 0.003	0.2 +/- 0.2	0.3 +/- 0.3	5000 +/- 6000
Cathodic Dichromate Tinplate	CDC-5	0.074 +/- 0.007	0.63 +/- 0.02	0.16 +/- 0.05	300 +/- 20
Pure tin (99.9%)	tin	0.0673 +/- 0.0006	0.17 +/- 0.002	0.12 +/- 0.03	1000 +/- 60

(*) 0.2 lb/bb side
ND – no data

All errors +/- 1s

Results and Discussion:

1. The open circuit potentials for the various samples were in the range of approximately -0.56 to -0.59 V (SCE) and within typical experimental accuracy, i.e., ± 15 mV, Table A6-1. None of the data were significantly different from the general population including the potential for pure tin.
2. It was difficult to identify any real trends in the polarization resistance data for the two sample sets. Some of the individual samples seemed to have a higher polarization resistance; and, therefore, a lower corrosion rate than other samples. Whether these differences were significant, or not, was unknown based on the poor precision of the data.

The surface concentration of zirconium for the two sides of the sample K690481 differed by a factor of 3, yet the polarization resistances were virtually identical, Table A6-1. This may suggest that the corrosion rate was not dependent on the quantity of zirconium on the tinplate surface.

The precision of multiple measurements made on a single sample were relatively good (e.g., $R_p = 1.00 \pm 0.04$ ohm-m²), while multiple measurements made on multiple samples of the same material were relatively poor (e.g., $R_p = 1.0 \pm 0.3$ ohm-m²). This may suggest that there is quite a bit of variability in the passivation treatment from position to position on a single sheet of passivated tinplate.

3. The polarization resistance data for metallic tin was almost an order of magnitude lower than the lowest polarization resistance for any of the passivated samples, Table A6-1. This difference may be attributed to the passivation treatment applied to the samples or the build-up of tin oxides/hydroxides as a result of aging (11 month duration) of the passivated samples.
4. The errors in the charge transfer resistance (R_{ct}), calculated from the EIS plots, were relatively large. In many cases, the low frequency portion (>0.01 Hz) of the EIS spectrum was distorted. This distortion was probably a result of a diffusion process or a slight increase in the corrosion rate during the course of the measurement.

The charge transfer data for samples passivated with fluorozirconate appeared to be of a similar order of magnitude to the orthosulfate treatment. However, the precision in the data for the fluorozirconate samples was much better than the zirconium orthosulfate. This would suggest that the passive surface was more uniform for the fluorozirconate than the zirconium orthosulfate.

5. The coating capacitance was very large and indicative of a pseudocapacitance rather than a real coating capacitance, Table A6-2. These pseudocapacitances were attributed to adsorption or diffusion phenomena at the electrode surface. Capacitances on the order of $10^{-1} \mu\text{F}/\text{cm}^2$ and $10^{-4} \mu\text{F}/\text{cm}^2$ are typical of passive metal oxides or organic-coated metals, respectively.
6. Each EIS experiment was performed in at least triplicate. The statistics from each sample were particularly poor. To develop an appreciation of the range in data from each sample, many more impedance analyses need to be performed and the error in the method established. The percent errors in the impedance data for tin and CDC tinplate were much smaller than for the zirconium treated samples.