

THE ROLE OF SURFACE CHEMISTRY AND VCI'S IN EARLY STAGES OF METAL PROCESSING

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ABSTRACT

Despite massive efforts to control corrosion, it still has major affects on costs, quality, and performance. Unfortunately, corrosion protection is emphasized far too late in manufacturing. Corrosion control before or during earlier stages of manufacturing and processing is not considered. Yet many product failures are caused by contamination or poor corrosion control at stages well before final packaging. Modern surface analytical methods, ISS (Ion Scattering Spectroscopy) and SIMS (Secondary Ion Mass Spectroscopy), can monitor surface corrosion and contamination to trace product failures at early stages of metal working^(1, 2). This includes detection of very thin layers of corrosion on components and within surface layers prior to final coating, lamination, shipping, or assembly. This information includes quantitative analysis of iron oxide on the surface of iron phosphates or other "conversion" layers such as Cr, Zn, and Fe phosphates. Application of Volatile Corrosion Inhibitors (VCIs) at early stages in processing is accomplished using special cleaners and metal working fluids.

Surface contamination in corrosion and adhesion problems is not well acknowledged. Methods and considerations for cleaning, investigating, and monitoring surface chemistry and effects of contaminants on corrosion are presented with qualitative and quantitative information about contaminants commonly encountered in processing metals. Effectiveness of cleaning operations and cleaners is discussed for environmentally safe water based cleaners⁽³⁾. The terms "surface" and "cleaning" are

presented for greater understanding of how to approach common industrial corrosion and cleaning problems.

Keywords: surface chemistry, metal cleaning, corrosion inhibitors, contamination, metal processing .

INTRODUCTION

Basic Concepts.

Corrosion problems are extremely common and require extensive testing worldwide. Yet the questions as to “How” or “Why” did corrosion start are not often addressed nor easily answered. In order to better understand corrosion and approach these two questions, it is useful to understand surface chemistry. For clarity, the concepts or terms “Surface”, “Contamination”, and “Cleaning” are discussed in basic and fundamental molecular and atomic detail along with how to systematically apply surface analytical instrumentation for quantitative and qualitative analysis of surface composition at different stages of processing. The results from cleaning different types of surfaces using various procedures and formulations must be measured quantitatively to determine the effects of typical contaminants on performance. Comparisons between water based cleaners and solvent based cleaners are discussed. Typical cases studied also include developing a method for the difficult but positive detection of iron oxide on the surface of iron phosphatized surfaces and other phosphatized surfaces and the application of this method to monitor the industrial cleaning of cold rolled steel prior to coating. The source and role of some of the contaminants on these types of surfaces will also be presented.

Unfortunately, many industrial manufacturers concentrated almost entirely on corrosion protection as an “after the fact” process only when the final product is ready to be shipped. This alone accounts for a significant amount of corrosion damage each year. This paper outlines the concept of **TOTAL CORROSION CONTROL** in which corrosion control is more a daily activity at all stages of production than merely an afterthought. Good corrosion control methods and products must be integrated into the entire production process from specifications to suppliers, to receiving, cleaning, storage, metal fabrication or working, processing, inventory, and shipping. In most of these cases, excellent corrosion prevention can be added into any step of a process without significantly changing the process or production scheme. For example, in many cases, all that is necessary is to add minor corrosion protection chemicals to the present process, or to use similar products which already contain VCI's. Vapor phase Corrosion Inhibitors (or also termed Volatile Corrosion Inhibitors)⁽⁴⁾.

Surface. The term “surface” is often vague and ambiguous hence it is defined more explicitly using Figure 1. The “Surface” is not merely a two-dimensional flat plane but must include some degree of thickness even to the molecular or atomic scale. Although macro surface features such as roughness, texture, and other physical anomalies may have some effects, almost all initial chemical interactions begin at the atomic (or molecular)

scale. These interactions dictate initiation and kinetics of corrosion, adhesion, friction, lubrication, reactivity, and other properties. The macro physical features such as roughness, pitting, scratches, crevices, cracks, etc. have more effect in the collection of contaminants and debris, abrasion, and formation of electrochemical centers. It is not possible to “see” some macro-physical properties, including the initial stages of corrosion with use of very high magnification microscopy using the Scanning Electron Microscope (SEM). Under such examination, it is possible to see even extremely tiny, microcrystals of Fe₂O₃ (red rust) well before they even become visible as the small dots or 0.5 to 1 mm diameter observed visually in common corrosion tests such as the ASTM-1748. This can be illustrated by SEM microphotographs.

Surface Contamination: Contamination is also a vague and misleading term. For proper scientific studies, greater clarification, categorization, and qualification is needed. Contamination is one of the major causes for corrosion and adhesion failures but in some cases, it may slow corrosion, eliminate it or delay its onset. For simplicity we will use the term “contaminant”, to mean → any material which is present but not intentional. It should be categorized by Chemical type, Chemical structure, Concentration, Distribution, Physical type, Thickness, and Appearance. In some cases, it only takes a portion of a single molecular layer of a particular contaminant to initiate corrosion, prevent adhesion, or cause discoloration. Two of the most obvious contaminants affecting corrosion are Cl and S but others are often overlooked. Unfortunately, much of the testing for evaluating the effectiveness of “surface cleaners” does not directly analyze the chemistry of the surface but resorts to corrosion or wetting evaluations. In this work, the detailed chemistry of the surface is evaluated directly using very sensitive surface analysis techniques^(5,6).

All too often there is far more concern about trace levels of contaminants within the surrounding atmosphere than there is about much larger concentrations of contaminants on the surface. Much of this occurs due to the difficulty of measuring surface contaminants and the lack of knowledge of their existence and effects.

Corrosion prevention costs billions of dollars per year yet in too many cases, adequate preparation of the surface by cleaning is ignored or improperly done. In most applications this is very important and often more important than some of the methods of corrosion prevention.

EXPERIMENTAL & INSTRUMENTAL

Several sets of common steel materials as well as standard Q-panels were subjected to various environmental conditions. Some of these samples included those which had been exposed to common, routine industrial processing such as cutting, stamping, welding, and commercial cleaning, both water based and solvent based. Several samples were also subjected to common types of commercial contaminants, cleaned, and subjected to corrosion testing and cleaning with different cleaners. Some of these cleaners contained strong inorganic acids or bases. Others contained strong organic complexing

agents whereas some of them were simply standard organic or CFC solvents. In other tests, standard Q-panels were treated with water based metal working fluids with and without doping with VCI's and subjected to standard ASTM corrosion testing procedures.

The surface chemistry was determined from small representative sample areas were cut from each larger sample and mounted for investigation of surface chemistry. The two analytical instrumental techniques which were applied extensively to these samples were ISS (Ion Scattering Spectroscopy) and SIMS (Secondary Ion mass Spectroscopy) both of which have been explained in detail throughout the Literature. ISS is generally accepted as the most surface sensitive analytical technique whereas SIMS exhibits the highest detection sensitivity. Other techniques such as Auger and ESCA (Electron Spectroscopy for Chemical Analysis also termed XPS for Xray Photoelectron Spectroscopy) can be applied but in general they do not have the surface sensitivity nor are they as sensitive to trace elements.

In the ISS analysis, an area about 3 mm by 5 mm is analyzed using a $^3\text{He}^+$ ion beam at an ion beam energy of 1000 to 2000 eV and from 100 to 300 nA. The estimated sputter rate, based on hundreds of measurements performed using references and standards, was 3 to 5 Å per **minute**. A series of about 20 individual spectra are obtained while sputtering from the outer surface to a depth of about 80 Å, during the 15 to 20 minutes of sputtering. The first spectrum is obtained in 2 seconds and successive spectra are obtained with increasing scanning times. During this scanning, 2 to 1024 0.5 second scans of the entire spectrum are added together to provide one final spectrum for storage. This data acquisition methods provides detailed information in a depth profile covering the outer 50 to 80 Å. Figure 2 illustrates a typical ISS depth profile.

SIMS spectra are obtained using $^{40}\text{Ar}^+$ at about 500 eV on an area about 4 mm by 7 mm and an ion beam current of about 100 nA. The first spectrum is obtained in 8 to 32 seconds and subsequent spectra are obtained at greater scanning times. These spectra normally cover the range of 1 to 150 AMU although in most cases, one higher mass spectrum is also acquired for each sample. Figure 3 illustrates typical SIMS spectral data.

The ISS results were subjected to extensive computer spectral background subtraction and quantitative analysis at each depth. In addition to calculating the elemental atomic concentrations at each depth, the total concentrations of each element up to that particular depth were also calculated. These values were expressed as integrated atomic concentrations as well as absolute quantities in mg per square meter of each element on the surface up to that depth. Table 1 is a partial listing from one of these tables. All of these data were stored and subjected to further correlations and computer analysis by comparisons with similar data sets from other samples and references.

The mass and intensity of each peak in SIMS were tabulated and subjected to extensive computer assisted interpretation to provide a relative quantitative comparison of various chemical structure bonding features. Figure 3 illustrates the type of information provided by such a treatment. Again, all of this information is utilized in further computer

comparisons among samples and for Multiple Regression (or Correlation of Variables) to determine the effects of various structures on measured product performance.

RESULTS

Figures 2 and 4 illustrate typical ISS raw data obtained from depth profile analyses of the surface of clean cold rolled steel and contaminated steel. The description of an ISS depth profiles is explained in the Experimental section above. Each successive spectrum in the depth profile represents a successively greater depth into the surface. The composition was determined for each depth by interactive computer quantitative analysis of each spectrum. Table 1 illustrates the composition for each of these spectra for one such sample and the upper right portions of each Figure show the results plotted as atomic concentration Vs depth.

In addition to calculating the composition of each layer observed in ISS, the total amount of each element present down to any particular depth can be calculated by integrating the amount of that element in each incremental layer. Table 2 illustrates these quantitative results with the integrated amounts of each element indicated in mg / square meter of surface area. Integrating the amount of Carbon all the way into the bulk steel will give the amount of carbon present on the surface in mg / m². This is a value commonly used throughout the automobile manufacturing and paint industries to assess paint coating adhesion. Adding all of the contaminants together gives the **TOTAL CONTAMINATION** present on the surface either as an atomic concentration or in absolute mg / m². Subtracting the total contamination concentration from 100 yields the **"PURITY"** of the sample. We have plotted these two values, total contamination, and purity Vs depth for several samples cleaned in different ways in some of the latter discussions. Figure 5 illustrates a comparison of the total contamination and the purity of clean steel and the contaminated surface. The point at which these two curves cross over (50%) can be considered a rough measurement of the **THICKNESS** of the surface contamination.

Unfortunately, total contamination by itself is not necessarily the most representative value to use a criteria for product evaluation since it is the **type** of contaminant which is often more important than the total amount. Certain types of contaminants can cause far greater problems than others. This includes not only increased corrosion rates, but can include increased abrasion, poor adhesion, discolorations, stickiness, staining, and poor reactivity during processing, plating, or coating. For that reason, it is often more meaningful to compare surface chemistry in **BAR GRAPH** form for specific elements. Figures 6 and 7 illustrate the results for steel which was cleaned with several different cleaners, two of which were water based. Note that the water based cleaners appeared to leave a higher level of organic materials than some of the organic solvents. This is because the cleaners labeled VCI-415 and VCI-416 contained VCI's (Volatile Corrosion Inhibitors), organic compounds which are designed to chemisorb to metal surfaces to prevent further corrosion. Clean iron and steel surface will generally corrode much faster than those contaminated with a mixture of organic materials and

inorganic materials. For this reason, it is extremely important to provide corrosion protection to metal surfaces immediately after or during cleaning. Yet, surfaces which are not properly cleaned may show very poor corrosion resistance and adhesion for subsequent coatings. Or they may discolor and stain more readily. They may also exhibit greater tendencies for pitting corrosion even when the majority of the surface appears uniform. Such defects can greatly affect physical properties such as material strength, fatigue lifetime, and stress corrosion cracking.

In some cases, very aggressive surface cleaners must be used and in other cases where the surface has already corroded or shows flash rust, aggressive rust removers must be used. Failure to do so can result in poor product performance or failure at later stages of processing.

The sensitivity of some operations to flash rust is well illustrated in the following example. Problems arose in an operation in which flat steel was formed, cleaned, given an iron phosphate coating, dried, and finally painted. The paint coating showed inferior adhesion in bending tests when compared to previous coatings made using the same procedure for many years. The flat steel was coated with a corrosion inhibiting oil at the steel supplier and stored in large stacks before use. The large industrial plant had recently incorporated a new system in an unrelated area of processing. This system coupled with new ovens emitted very trace levels of F and Cl. Samples of the steel were obtained at various stages of manufacturing including before forming and before and after paint coating and subjected to surface analysis by SIMS.

Typical SIMS spectra from two of these samples are illustrated. It should be noted that SIMS provides information about chemical bonding or structure as well as elemental information. In these samples, it was possible by SIMS analysis to compare relative amounts of iron oxide vs. iron phosphate on the outer surface. A direct correlation was found as shown in Figure 8, between the performance (paint delamination %) vs. the amount of iron oxide present. Furthermore, panels of steel subjected to some aging in a high F, Cl environment showed higher levels of oxidation (corrosion) and reduced bonding in the coating adhesion testing. This was especially interesting since the formed steel panels were subjected to some strong cleaning including both alkaline and strong phosphoric acid immediately before the formation of the iron phosphate. The movement of the iron oxide through the phosphate coating or its formation on the surface of the phosphate coating was further substantiated by SIMS analysis of the two systems.

Many organizations involved in metal working or fabrication use various fluids to lubricate and cool the metal products during the process (7, 8, 9). Unfortunately, many such organizations assume that any oil is sufficient to prevent corrosion between stages of processing or before shipping. As the above case illustrates this is not always true although oils do provide some degree of corrosion protection. However, with the simple addition of VCI chemical to some of these oils, much improved performance can be obtained as illustrated in Figure 9. In addition, there is a very rapidly evolving trend Worldwide, to switch from oil based materials to water based materials. This can

dramatically improve hazardous waste disposal as well as reduce cost of metal working fluid. Two types of water based, metal-working fluids are presently being used in substantially increased amounts; synthetic oils and emulsified oils. With the introduction of large amounts of water into these operations, there is a far greater potential for corrosion during some of the intermediate stages of fabrication (10, 11, 12). It is nearly essential to incorporate corrosion protection into these fluids. In some cases, such protection is sufficient for several months after machine, bending, punching, stamping, rolling, or other metal fabrication operations. The costs for rework of corroded parts are significantly reduced and product quality is increased.

SUMMARY and CONCLUSIONS.

It has been shown that surface contamination can significantly increase corrosion of metals and that appropriate use of cleaners containing VCI's and / or metal working fluids containing VCI's can significantly reduce corrosion. It should be the **FIRST STEP** in corrosion control. The surface analysis techniques of ISS and SIMS have been described and shown to be exceptionally useful to quantitatively monitor surface contamination and purity. The application of these two techniques comparing different cleaning methods indicates that water based cleaners are much more effective at removing inorganic contaminants than are standard organic solvents. It was also shown that if cleaning and removal of flash rust is not done early in processing, corrosion can occur and cause measurably adverse performance of coating adhesion. It is further emphasized that cleaning and corrosion protection must be considered throughout all the processing, not merely at the final stage before shipping.

ACKNOWLEDGMENTS.

Much of the information discussed in this work was obtained in the laboratory by Drs. Margarita Karsman and Alla Furman. Their continual support and extensive knowledge and efforts in testing and understanding of corrosion were greatly appreciated. The authors greatly appreciate the extensive efforts and surface analysis conducted and supplied by Advanced R & D, Inc. of St. Paul, MN.

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SAMPLE: Clean Washed Steel
 Project # = FSCT
 ATOMIC CONCENTRATIONS FOR STEEL. B 01-12-1994

SENSITIVITIES:		H = .45	C = .35	O = 1	Na = 1.9	P = 3.8	Fe = 10.2
SPEC. #	TIME	H	C	O	Na	P	Fe
1	2	55.067	34.089	5.966	3.462	1.208	0.180
2	4	49.964	36.654	9.655	3.411	0.104	0.169
3	8	49.921	34.561	8.064	5.533	1.554	0.325
4	12	37.666	41.574	11.353	8.163	0.926	0.282
5	20	35.833	40.487	9.121	11.059	2.958	0.495
6	28	30.640	35.813	13.609	15.362	3.864	0.667
7	44	23.983	36.901	16.454	16.854	3.911	1.839
8	60	21.475	33.486	18.711	20.021	4.653	1.593
9	92	10.526	35.466	22.866	22.264	6.103	2.738
10	124	6.749	34.296	27.333	22.454	5.823	3.318
11	188	6.745	32.520	31.869	19.103	5.192	4.464
12	252	17.825	27.595	28.483	16.025	5.449	4.454
13	380	12.072	28.691	33.171	14.989	4.874	6.044
14	508	19.706	32.246	27.836	10.208	3.681	6.076
15	764	5.105	19.164	45.022	10.397	2.273	17.737

Table 1. Atomic concentrations (composition) for each spectrum or depth of an ISS (Ion Scattering Spectroscopy) concentration depth profile of clean, washed and phosphatized steel. From outer atomic layer to a depth of about 60Å.

SAMPLE: Clean Washed Steel

Project # = FSCT

ATOMIC CONCENTRATIONS FOR STEEL. B 01-12-1994

***** INTEGRATED CONCENTRATIONS *****

SPEC.#	TIME	H	C	O	Na	P	Fe	Ba	TOT
1	2	55.067	34.089	5.966	3.462	1.208	0.180	0.028	
Wt.MG/M2		0.0013	0.0095	0.0022	0.0018	0.0009	0.0002	0.0001	0.0160
WT%		7.974	59.234	13.821	11.529	5.421	1.459	0.562	
2	4	51.665	35.799	8.425	3.428	0.472	0.172	0.039	
Wt.MG/M2		0.0024	0.0197	0.0058	0.0037	0.0009	0.0005	0.0002	0.0332
WT%		7.334	59.280	17.452	11.038	2.840	1.363	0.693	
3	8	50.668	35.091	8.219	4.631	1.090	0.259	0.041	
Wt.MG/M2		0.0035	0.0294	0.0096	0.0077	0.0023	0.0011	0.0004	0.0540
WT%		6.436	54.530	17.723	14.304	4.277	1.968	0.762	
4	12	44.667	38.084	9.665	6.261	1.014	0.270	0.038	
Wt.MG/M2		0.0041	0.0424	0.0144	0.0146	0.0036	0.0016	0.0005	0.0811
WT%		5.009	52.253	17.769	18.017	4.396	1.944	0.613	
5	20	40.826	39.128	9.429	8.347	1.859	0.368	0.043	
Wt.MG/M2		0.0051	0.0682	0.0220	0.0323	0.0098	0.0033	0.0008	0.1416
WT%		3.583	48.195	15.519	22.825	6.950	2.335	0.593	
6	28	36.972	37.874	11.010	11.001	2.618	0.481	0.044	
Wt.MG/M2		0.0062	0.0850	0.0337	0.0564	0.0196	0.0060	0.0012	0.2081
WT%		2.364	40.821	16.214	27.093	9.428	2.902	0.578	
7	44	32.128	37.511	13.040	13.184	3.100	0.987	0.050	
Wt.MG/M2		0.0073	0.1221	0.0691	0.1047	0.0336	0.0226	0.0021	0.3614
WT%		2.018	33.772	19.109	28.977	9.301	6.246	0.578	
8	60	28.538	36.154	14.952	15.488	3.624	1.191	0.053	
Wt.MG/M2		0.0084	0.1568	0.1044	0.1574	0.0493	0.0357	0.0030	0.5150
WT%		1.638	30.438	20.276	30.564	9.568	6.924	0.592	
9	92	22.400	35.920	17.648	17.797	4.469	1.718	0.048	
Wt.MG/M2		0.0079	0.2326	0.1914	0.2755	0.0970	0.0735	0.0034	0.8812
WT%		0.896	26.390	21.716	31.268	11.008	8.337	0.385	
10	124	17.474	35.409	20.697	19.263	4.895	2.222	0.041	
Wt.MG/M2		0.0064	0.3107	0.2981	0.3818		0.1259	0.0032	1.2634
WT%						0.1372			
		0.508	24.596	23.598	30.219	10.862	9.964	0.254	
11	188	14.009	34.475	24.306	19.211	4.991	2.946	0.063	
Wt.MG/M2		0.0075	0.4425	0.5409	0.5179	0.1865	0.2545	0.0123	1.9621
WT%		0.383	22.551	27.567	26.395	9.505	12.972	0.628	
12	252	15.162	32.396	25.568	18.248	5.129	3.401	0.095	
Wt.MG/M2		0.0182	0.5355	0.7169	0.5998	0.2449	0.3707	0.0282	2.5143
WT%		0.725	21.300	28.512	23.856	9.740	14.744	1.122	
13	380	14.195	31.237	27.948	17.228	5.049	4.229	0.115	
Wt.MG/M2		0.0312	0.7570	1.1264	0.7855	0.3497		0.0495	3.7871
WT%							0.6877		
		0.823	19.990	29.743	20.742	9.235	18.160	1.307	

SAMPLE: Clean Washed Steel (continued)

Project # = FSCT

ATOMIC CONCENTRATIONS FOR STEEL. B 01-12-1994

***** INTEGRATED CONCENTRATIONS *****

SPEC.#	TIME	H	C	O	Na	P	Fe	Ba	TOT
14	508	15.820	31.534	27.915	15.157	4.646	4.774	0.154	
Wt.MG/M2		0.0472	1.0857	1.4493	0.8605	0.3938	1.0078	0.0826	4.9269
WT%		0.958	22.037	29.419	17.465	7.992	20.455	1.677	
15	764	12.527	27.733	33.172	13.694	3.916	8.758	0.200	
Wt.MG/M2		0.0444	1.2574	2.8004	1.0587	0.3787	3.4548	0.1736	9.1681
WT%		0.484	13.715	30.545	11.548	4.130	37.683	1.893	

Table II. Absolute amounts (in mg per square meter) of each element on the surface at each depth of an ISS depth profile of clean, washed, phosphatized steel. Also included are its weight % in that sputtered volume. Useful information for Total Surface Carbon or coating thickness.

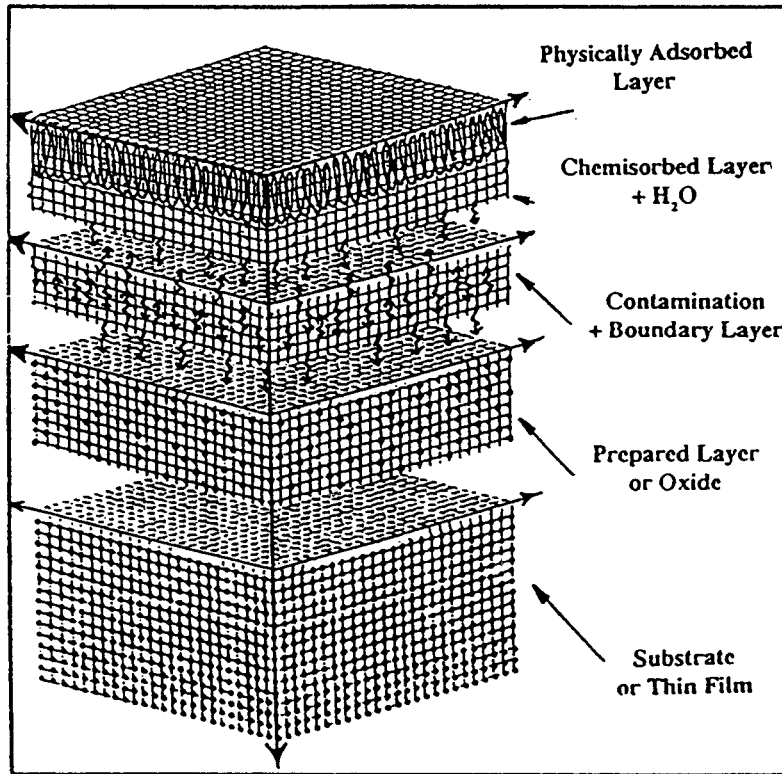


Figure 1. Schematic showing the layered structure within the outer 50 to 100Å of a surface.

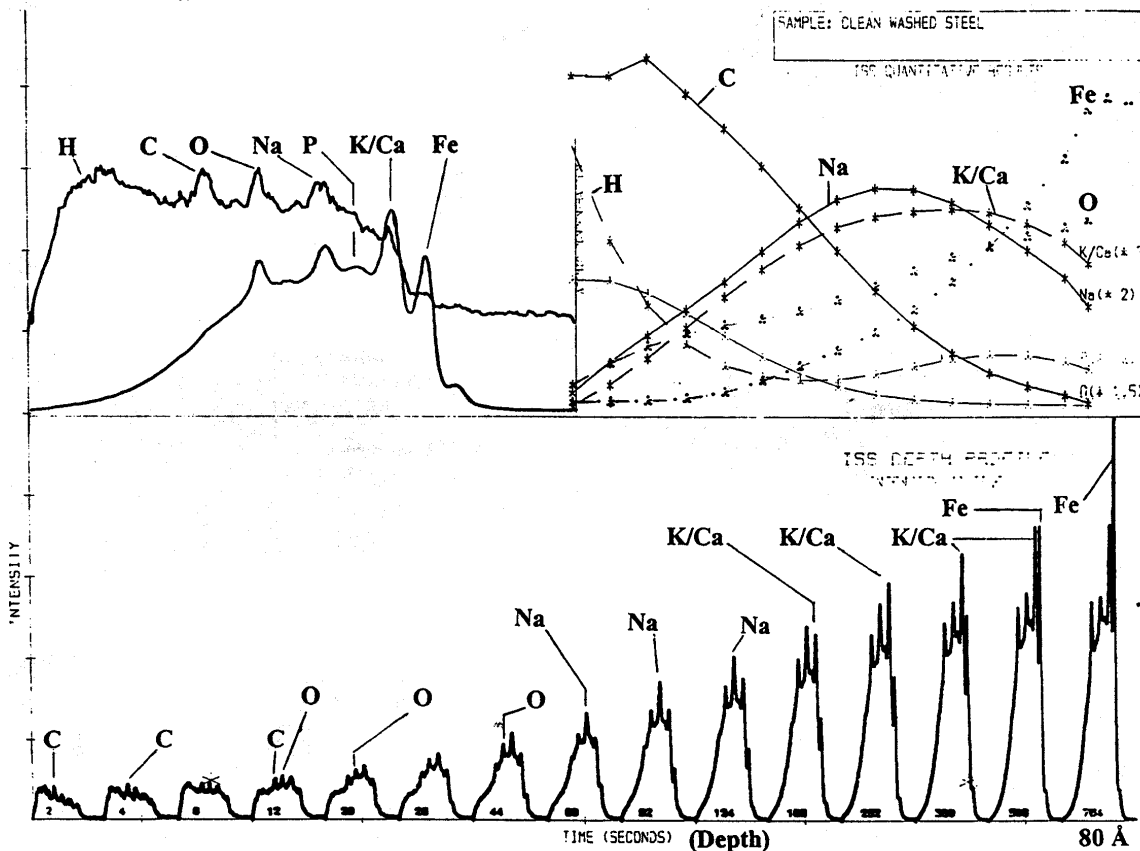


Figure 2. A typical ISS Depth Profile of relatively clean steel. The individual spectra are plotted successively with that in the lower left corner representing the outer atomic composition and that on the extreme right the composition at the total sputtered depth of about 100Å. The upper left shows two spectra expanded and the upper right corner shows a plot of the atomic concentrations Vs depth (time).

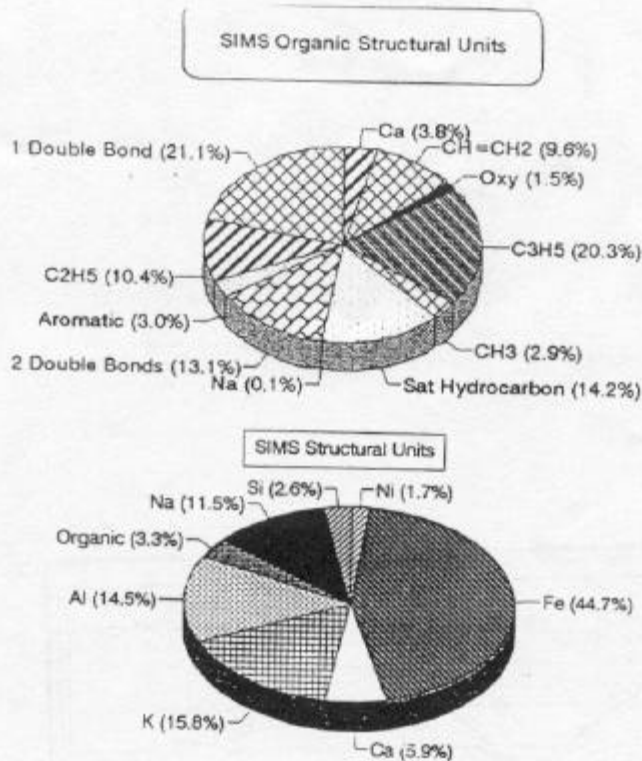


Figure 3. Typical structural information obtained from computer assisted treatment and interpretation of SIMS spectra.

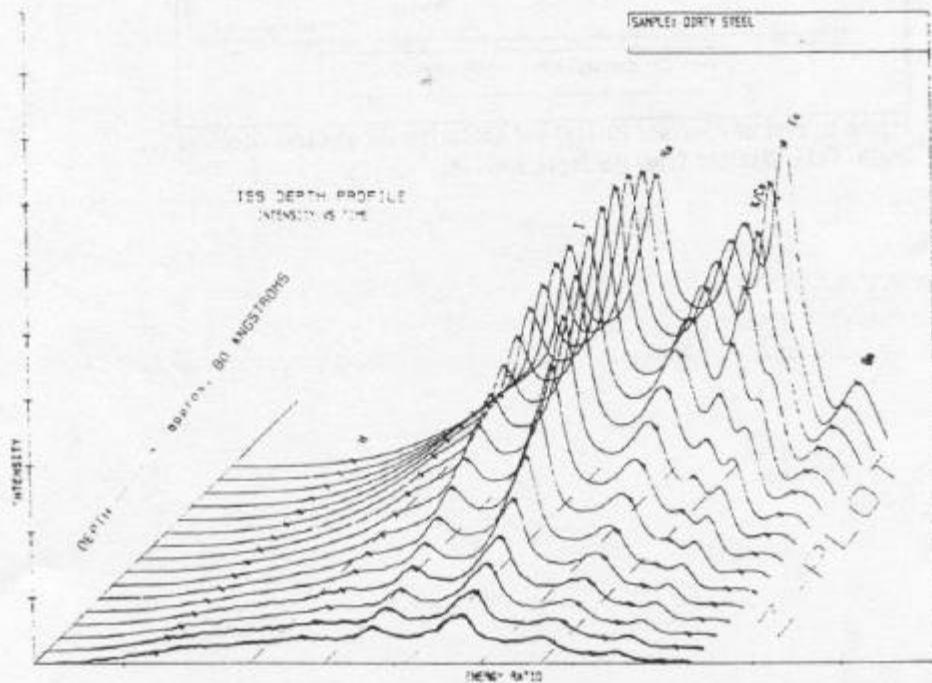


Figure 4 An ISS depth profile of moderately contaminated steel.

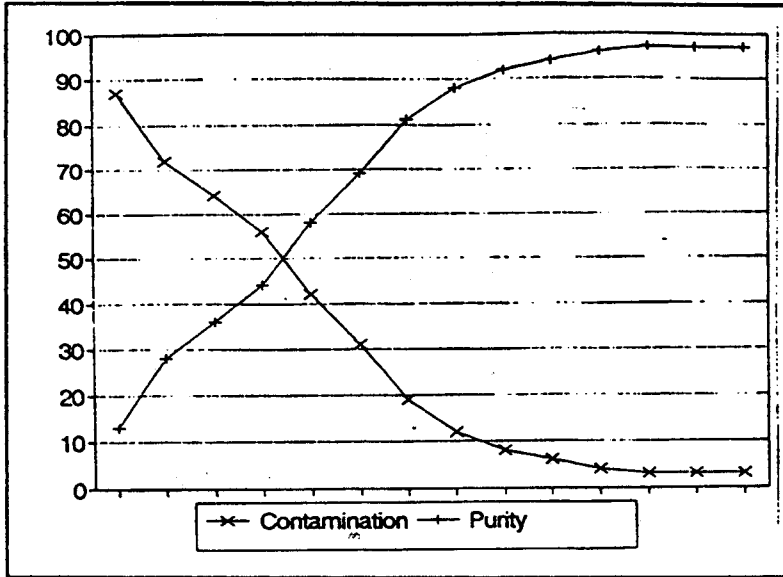


Figure 5. Plot of "Surface Purity" and Contamination of Clean Steel vs Depth. Data Obtained from ISS Depth Profile.

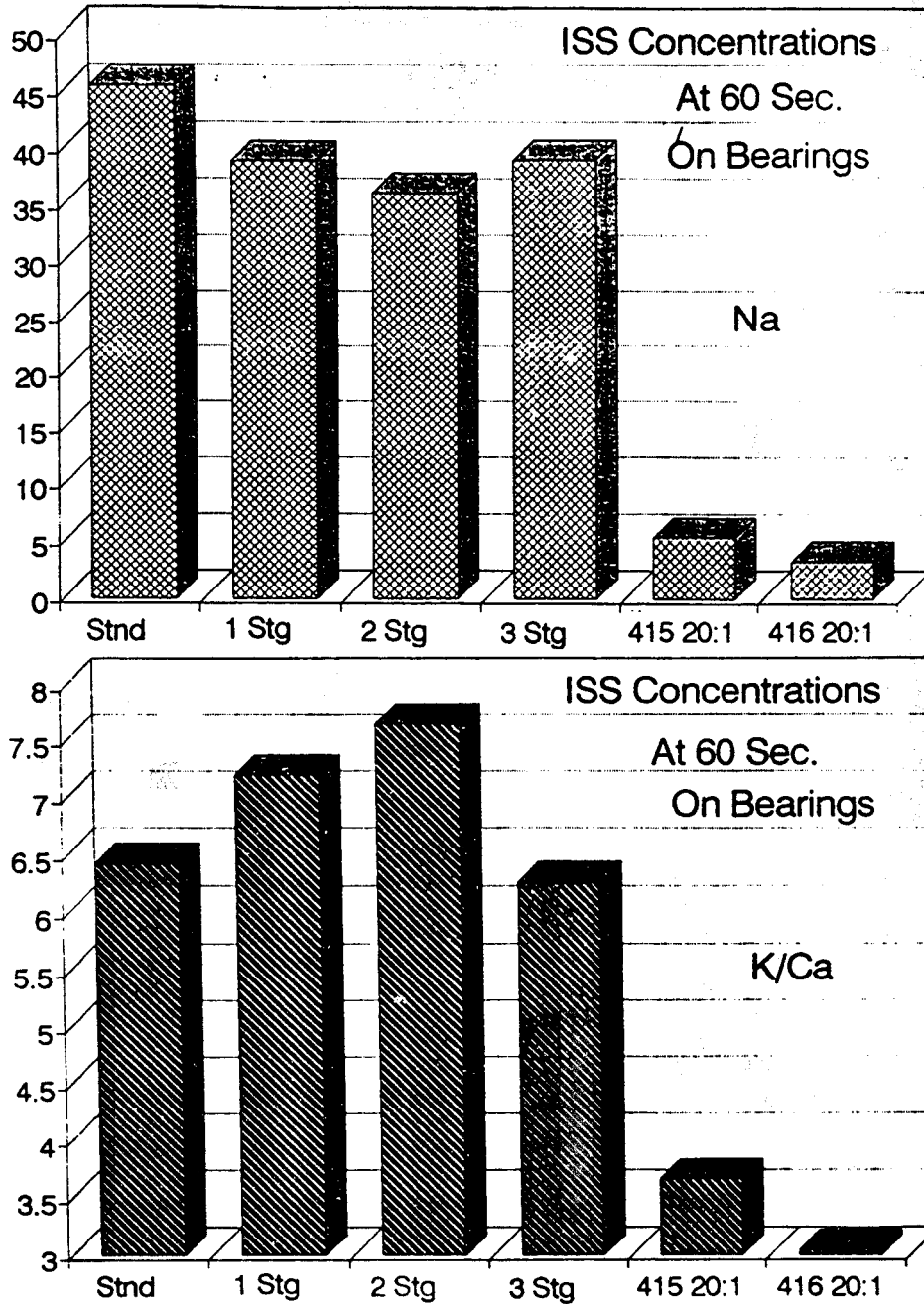


Figure 6. BAR GRAPHS obtained from ISS and SIMS analysis of steel cleaned using different cleaners. Elemental atomic concentrations.

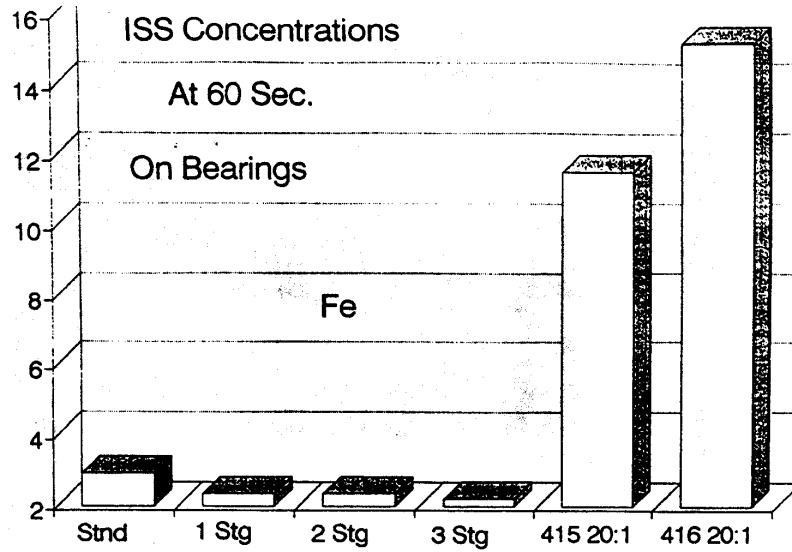


Figure 7. BAR GRAPHS obtained from ISS and SIMS analysis of steel cleaned using different cleaners. Elemental atomic concentrations.

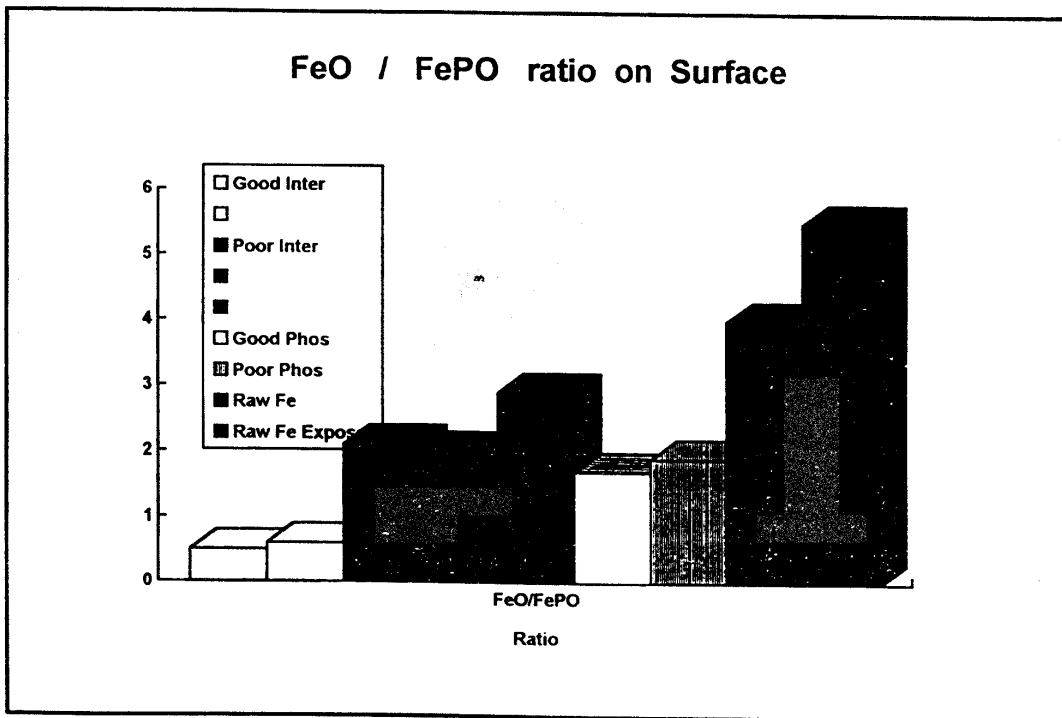


Figure 8. Ratio of Iron oxide to Iron Phosphate on the surfaces of steel subjected to various exposures, phosphatizing, and paint coating. Analysis of the metal interface, raw steel, and phosphatized steel surfaces by SIMS (Secondary Ion Mass Spectroscopy).

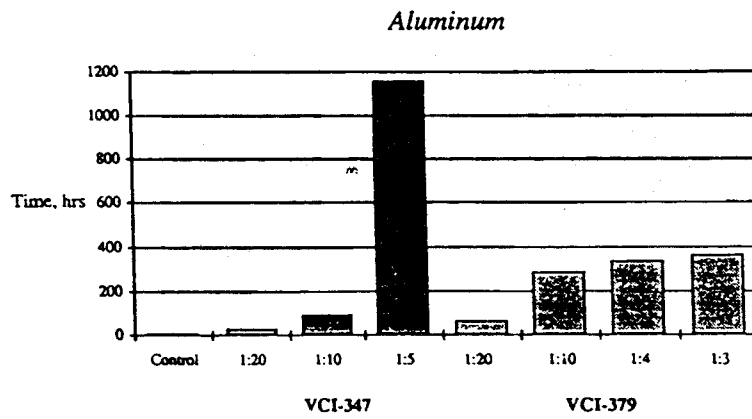
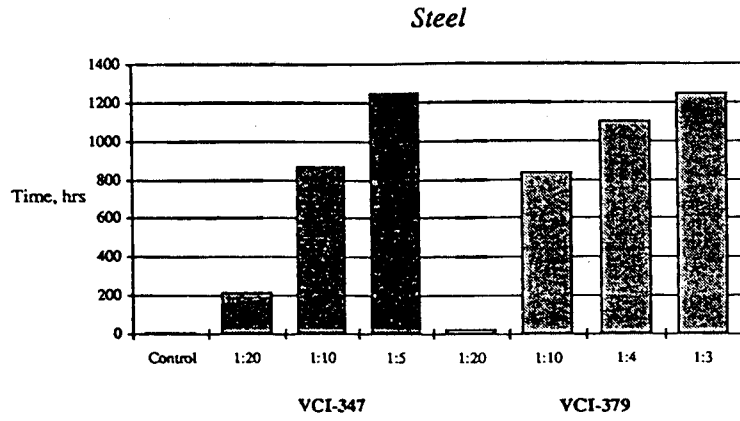


Figure 9. Total Hours to Failure in ASTM-1748 Humidity Corrosion Testing.