

# TECHNOLOGICAL IMPACT OF SURFACES

## *Relationship to forming, welding and painting*

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## EFFECTS OF STEEL PROCESSING ON THE SURFACE CARBON OF COLD-ROLLED STEEL

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### I. INTRODUCTION

In 1956, Wirshing and McMaster of General Motors demonstrated the existence of wide differences in the corrosion resistance of apparently identical lots of cold-rolled steel (1). All lots were phosphated, painted, and tested identically. At that time they were unable to identify the surface condition which would give one steel surface good corrosion protection and another steel surface poor corrosion protection after subsequent finishing, i.e., phosphating and painting operations. In 1959, Grossman offered substantial evidence that surface carbon was the principle contaminant which influenced the corrosion performance of painted steel (2). Grossman postulated that the source of this carbon contamination was from the breakdown of oils present on the steel surface during the annealing stage in the steelmaking process.

From economic and quality considerations, it is to the mutual advantage of both steel producer and steel user to share and understand the technical implications of the requirements for reproducible corrosion resistant, cold-rolled steel surfaces. Today both steel producers and users realize the detrimental effects surface carbonaceous residues have on the ultimate corrosion resistance of a finished steel surface. Over the last few years, the automotive industries have set tighter cold-rolled steel requirements. To meet these demands the steel producer was

compelled to develop a deeper understanding of the steel processing-steel properties relationships. Previous to the need for lighter gauge sheet steel, greater fluctuations in steel corrosion resistance were tolerated. But to reduce weight and still maintain vehicle integrity it became imperative that cost effective, high strength corrosion-resistant steel be used. These moves necessitated 1) a deeper understanding of the steel mill processing parameters which can affect the corrosion performance of finished steel, 2) the development of new methods or the improved use of existing methods for the detection, analysis, and quantification of surface contaminants, particularly surface carbon, 3) an understanding of the mechanism by which surface carbon affects the pretreatment and corrosion performance afforded by paint coatings, and 4) the use of dependable, high quality coatings to assure reliable corrosion protection.

In regard to this introduction, a number of questions have been posed:

- What are typical contaminants on the steel surface?
- How can they be analyzed qualitatively and quantitatively?
- What is their origin in the steelmaking process?
- What effect does cleaning have on these contaminants?
- What effects do these contaminants have on the zinc phosphate pretreatment coating?
- How do these effects translate to paint performance and corrosion resistance?
- By what mechanisms do these contaminants influence paint adhesion failure?
- What can steel producers do to minimize the occurrence of these contaminants?

It is the dual purpose of this paper to answer these questions and to interrelate the general theme of steel mill

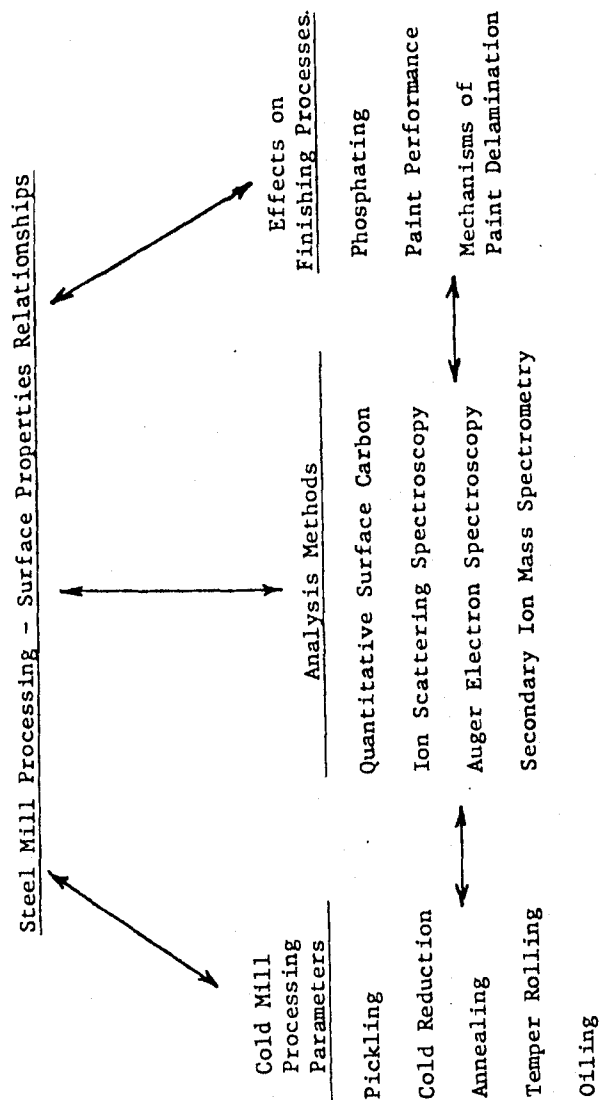
processing with resulting surface properties. Specifically discussed in this regard are: cold mill processing parameters, surface analysis methods, and the effects of surface contamination on finishing processes. These aims are flow charted in Figure 1. Only through an increased understanding of these relationships can improvements be achieved.

## II. SURFACE CARBON ANALYSIS

The dominating form of steel surface contamination is surface carbon, and one way of assessing steel surface cleanliness is by measuring its surface carbon level. The development of quantitative surface carbon analysis techniques has occurred only within the last four years and has paralleled the discovery that a surface carbon level above a critical threshold is detrimental to the corrosion performance of painted steel. Furthermore, the development of these techniques has had a significant impact in 1) the evaluation of the effects of various steel mill processes on steel cleanliness, and 2) studies relating the corrosion performance of painted steel to surface cleanliness. These two topics are discussed in detail in Sections III and V, respectively. In this section, three surface carbon analysis methods used in the American steel and automobile industries will be discussed. They include: 1) the hydrochloric (HCl) swab/Leco 46 combustion method; 2) the direct oxidation/ $\text{CO}_2$  coulometer method; and 3) thermal evolution analysis (TEA).

### A. The HCl Swab/Leco 46 Combustion Method

The HCl swab/Leco 46 combustion method allows for the semiquantitative analysis of surface carbon present on a given steel surface area. This test has been adapted by the Ford Motor Co. for surface carbon analysis and is used widely in the steel industry (3). For this test, a  $929 \text{ cm}^2$  ( $144 \text{ in}^2$ ) test panel is washed in a power washer to remove any loosely bound oils and surface soils. The power washer is equipped with two banks of stainless steel nozzles, each bank containing 12 nozzles. Test panels are placed in between these two nozzle banks, and power washed using a solution of Parco 348 cleaner (Oxy-Metal Industries, Madison Heights, Michigan) under the following conditions:



**FIGURE 1 INTERRELATIONSHIPS BETWEEN STEEL MILL PROCESSING, ANALYSIS METHODS AND EFFECTS ON FINISHING PROCESSES**

- |                         |                      |
|-------------------------|----------------------|
| 1. Spray time           | 58-62 seconds        |
| 2. Concentration        | 7-8 g/l (1 oz/gal)   |
| 3. Temperature          | 60-70°C (140-158°F)  |
| 4. Pressure             | 62-76 kPa (9-11 psi) |
| 5. Distance from nozzle | 152-203 mm (6-8 in)  |

After washing, the panel is rinsed in tap water and air dried, and its surface is wiped with a fiberglass filter paper saturated with a 50% HCl acid solution. Following this step, the filter paper is folded and placed into a porcelain crucible. Blank swabs are also prepared at this time. The crucibles (sample and blank) are dried in an oven at 180°C (356°F) for one hour to expel moisture and hydrochloric acid. The filter paper is transferred to a combustion crucible, and the carbon is analyzed using a Leco CS 46 Analyzer (Leco Corp., St. Joseph, Michigan). The blank value is subtracted from the sample value and surface carbon results are reported in units of mg/m<sup>2</sup> (mg/ft<sup>2</sup>).

The HCl swab/Leco 46 method has been the major method used for surface carbon analysis used by the Ford Motor Company and the steel industry over the last several years. This method has been used to show a correlation between the surface carbon content on cold-rolled steel and its subsequent performance in the painted condition in salt spray corrosion testing (4,5).

However this test has several disadvantages. It is tedious, time consuming, somewhat operator dependent, semiquantitative, and the instrumentation is expensive. A chemist must swab one square foot of sheet steel with a glass fiber filter paper saturated with a 50% HCl solution until no further dark colored material is removed from the surface. While the swab is being dried for one hour at 180°C (356°F), a substantial loss of organic carbon occurs (see below), thus making this test semiquantitative. Sample analysis time is about 1.25 hours although normally a batch of samples is run at one time.

Because of the inherent disadvantages associated with the HCl swab/Leco 46 combustion method, Inland Steel Research has developed an alternative surface carbon analysis method known as the direct oxidation/CO<sub>2</sub> coulometer method for surface carbon analysis. (6,7,8)

### B. The Direct Oxidation/CO<sub>2</sub> Coulometer Method

The direct oxidation/CO<sub>2</sub> coulometer method was developed at the Inland Steel Research Laboratories for the quantitative analysis of total surface carbon present on a given steel surface area. Instrumentation for this method consists of two main components: a combustion apparatus and an automatic coulometer for CO<sub>2</sub> titration (Coulometrics, Inc., Wheat Ridge, Colorado). Power washed steel samples (described in the previous section) with a total surface area of 81 cm<sup>2</sup> (12.4 in<sup>2</sup>) are placed into a quartz combustion tube at 600°C (1112°F) where prepurified oxygen flowing through the tube reacts with surface carbon to form CO<sub>2</sub> and CO. Immediately following the sample compartment is a tube containing barium chromate catalyst for conversion of CO to CO<sub>2</sub> and a scrubber train for removing potentially interfering gases such as SO<sub>2</sub>, SO<sub>3</sub>, NO, NO<sub>2</sub> and Cl<sub>2</sub>. The stream of purified O<sub>2</sub> and CO<sub>2</sub> is then bubbled into the CO<sub>2</sub> coulometer titration vessel where CO<sub>2</sub> is quantitatively absorbed by ethanalamine to form 2-hydroxy-ethyl-carbamic acid, which in turn is automatically titrated with hydroxide ions produced at the platinum generator electrode.

A die and punch is used to facilitate sample preparation, to ensure precise surface area, and to minimize sample handling and contamination of steel samples prior to insertion in the quartz combustion tube of the CO<sub>2</sub> coulometer apparatus.

In the direct oxidation/CO<sub>2</sub> coulometer method for surface carbon analysis, surface carbon is reacted with pure O<sub>2</sub> at 600°C (1112°F) to form CO<sub>2</sub> with no loss of carbon from handling or transferring the steel sample. The generated CO<sub>2</sub> is analyzed in an automatic CO<sub>2</sub> coulometric titrator. Analysis time is less than five minutes and all possible forms of surface carbon (organic, amorphous, and graphitic) react quantitatively.

A comparison of a large sampling of surface carbon results obtained by the two methods described above show that the surface carbon values obtained by the HCl swab/Leco 46 method are always lower than surface carbon values obtained by the direct oxidation/CO<sub>2</sub> coulometer method. This difference has been shown to be due to the loss of volatile organic carbon from the swab when using the former technique (7,8).

The direct oxidation/CO<sub>2</sub> coulometer method is now being utilized in a number of studies at Inland. In one particular application, this technique is used to differentiate organic from non-organic surface carbon by using two heat zones. In the first heat zone, organic surface carbon is converted to CO<sub>2</sub> within five minutes at 450°C (536°F). The samples are then moved into the second heat zone at 600°C (1112°F), where the remaining non-organic carbon reacts. This method has allowed for the quantitative differentiation of organic from non-organic surface carbon. Furthermore, it has also been found that surface carbon may be determined on zinc phosphate pretreated samples by this method. Results from differentiating surface carbon and determining surface carbon on zinc phosphate pretreated panels are presented in Section V.

### C. Thermal Evolution Analysis

Wojtkowiak and Bender described the use of a DuPont 916 thermal evolution analyzer for the analysis of organic carbon on the steel surface (9). This instrument consists of a temperature programmable quartz furnace directly coupled to a high temperature flame ionization detector whose response is specific for organic carbon. Steel samples are placed into the quartz furnace, and heated. During heating, the organic surface carbon is volatilized or thermally decomposed, and swept into the detector by a nitrogen purge. The detector response is directly proportional to the amount of organic carbon entering the detector. Both the rate of organic carbon evolution as a function of temperature, and the total organic carbon content of the sample is measured.

### III. THE INFLUENCE OF COLD MILL PROCESSING ON SURFACE CARBON

The mill processing stages which can influence the final surface carbon level of temper rolled steel span the pickling operation to the oiling of temper rolled steel. This section discusses the work done at Inland and reviews the work of others, on the effects of pickling, tandem cold reduction, annealing, temper rolling, and the oiling of temper rolled sheet, on the final steel surface carbon level.

## A. The Pickle Line

The first area that can have an influence on steel surface cleanliness is the pickle line. The primary function of a pickle line is to uniformly remove all oxide scale resulting from the hot rolling operation and to oil the pickled product. The removal of oxide scale is necessary to 1) prevent oxides from being rolled into the surface and 2) prevent formation of iron fines during tandem rolling operations. The pickle oil functions 1) as a lubricant for upcoiling after pickling and decoiling prior to tandem rolling, 2) as a lubricant for the first stand of a tandem mill, and 3) as a barrier film to protect the hot-rolled and pickled coil from corroding in the "acidic" environment near the pickle line, while it is being held prior to tandem rolling. Pickling is accomplished by using aqueous hydrochloric or sulfuric acid solutions, along with commercial pickling inhibitors. The acid serves to undercut and dissolve the scale, while the inhibitor promotes wetting of the oxide by the acid solution for rapid scale and rust removal. The pickling inhibitor also limits the attack of the acid on the base metal, by forming a protective absorbed layer on the steel surface. Hudson and Warning have found that since the early 1960's, many continuous strip pickle lines have been converted from sulfuric to hydrochloric acid, because of one or more of the following advantages when using hydrochloric acid (10):

- 1) Rapid pickling rates for lines that do not have a temper mill scalebraker.
- 2) Brighter pickled surface.
- 3) Well proven efficient regeneration method for spent pickle liquor.
- 4) Lower volume of waste pickle liquor produced.
- 5) More complete reaction of acid during pickling without decreasing rate of scale removal due to iron-salt build-up in solution.
- 6) Availability of effective inhibitors that do not interfere with the pickling process.

Hudson and Warning's observations that hydrochloric acid pickling produces a "brighter" surface than sulfuric acid pickling may imply that a hydrochloric acid solution may produce a cleaner or lower surface carbon surface than a sulfuric acid solution. A quantitative study to verify this implication is not known to have been done.

Normal pickle operations are carried out using a 6% hydrochloric solution containing about 0.1% inhibitor, at 62-93°C (150-200°F). Rinsing after pickling is important to remove acid residue, iron chloride salts, scale residue, and iron fines. In a good operation, the rinse water is kept at a minimum of pH 7, with less than 50 ppm iron.

After the steel has been pickled, rinsed to an essentially neutral surface condition, and dried, it is coated with a pickle oil, such as a reclaimed tallow, prior to the cold reduction operation. Improperly selected pickle oil can be a source for surface carbon on the finished, temper-rolled steel (11). The pickle oil should be compatible with tandem mill rolling solutions since it tends to be washed off the strip during rolling, and mixes with recirculating emulsion solutions used at the tandem stands. Furthermore, if the pickle oil is not completely removed from the strip surface during tandem rolling, it should burn off cleanly during annealing, leaving no stains or soot on the annealed product. The application of a controlled, minimum amount of pickle oil, appears to be an important factor in the manufacture of clean steel. A recently developed oil application technique, known as the Peabody electrostatic blade coater has been installed in a number of pickle lines in both Great Britain and the United States. This technique allows oil to be applied uniformly and controllably to both sides of the pickled steel strip. A 40 to 70% oil reduction can be achieved, without any detrimental effects to lubricity or corrosion protection. In addition to oil cost saving benefits, less pickle oil is carried through subsequent mill operations, thereby decreasing the potential for pickle oil contribution to surface carbon.

### B. Tandem Rolling Mill

During cold reduction, the thickness of the starting material is reduced substantially as the steel passes through four, five, or six-stand tandem cold reduction mills. This severe cold reduction process necessitates adequate lubricity, and the proper maintenance of the rolling solutions. Rolling solutions, which can consist of a 3-5% by volume tallow-based oil, are formulated primary as lubricants to facilitate the reduction of the pickled hot band, while minimizing the production of undesired iron fines. Even though lubricant application practices vary from mill to mill, (see references 11 and 12 for detailed descriptions of tandem mill designs, operations, and lubricant application practices) solution parameters which are normally maintained include: iron fine concentration, tramp oil concentration, emulsion stability, free fatty acid content, viscosity, and pH. Recirculation and filtration systems are utilized to keep contamination of the rolling solution to a minimum, since contaminants like iron fines in combination with tramp oils and free fatty acids, can result in soot or stain formation during annealing (11,13,14).

To facilitate the production of clean steel, the solution used on the last stand is kept separate from the previous stands. This solution can be either an aqueous solution containing very little lubricant, or a detergent solution. The use of these solutions, coupled with the practice of maximum "air blow-off" of excess rolling solution after the last stand, reduces the amount of residual oil film on the sheet product. Achieving as low an oil residue as possible will result in its easier burn-off in box annealing, and the production of clean steel.

### C. The Anneal

By far, high surface carbon steel has its origins from organic tandem rolling residues in combination with annealing practices. Primarily, surface carbon on temper rolled or finished steel can be related to one or more of the following mill production processing parameters:

- 1) The amount of organic rolling residues left on the surface after tandem rolling, prior to batch annealing.
- 2) The anneal atmosphere composition
  - a) HN composition (6 to 8% H<sub>2</sub>, balance N<sub>2</sub>, dew point -51°C (-60°F)).
  - b) DX composition (11% H<sub>2</sub>, 6% CO, 10% CO<sub>2</sub>, 0.2% CH<sub>4</sub>, balance N<sub>2</sub>, dew point 9°C (48°F)).
- 3) The anneal cycle
  - a) Soak time and temperatures.
  - b) Shelf time and temperatures.

In 1959 Grossman proposed that carbonaceous residues on the steel surface were harmful to the corrosion protection afforded by paint films, and that the breakdown of tandem rolling oils on the surface during annealing was the most likely source for this carbon contamination (2). In a subsequent publication Grossman compared production differences between tin plate and cold-rolled steel (15). He related these differences to the low surface carbon level found on the former material, to higher surface carbon levels found on the latter material. Tin plate steel is washed prior to annealing, and most tin plate is continuously annealed to a 649°C (1200°F) peak metal temperature (pmt) in a protective H<sub>2</sub>-N<sub>2</sub> atmosphere designed to minimize carbon deposits. Exposing the entire steel strip surface area to the reducing atmosphere, as well as a uniform pmt, not only results in a more complete "burn-off" reaction of any residual organic surface matter, but also causes the metallurgical properties of the steel strip to be more uniform. Automobile sheet steel, on the other hand, is not washed prior to annealing, is batch annealed, and is annealed in a less expensive anneal atmosphere (i.e., a DX atmosphere) which contains carbon-bearing gases. Based on these observed production differences, Grossman concluded steel mill processing methods can influence the amount of surface carbon.

In regard to tin plate production, it has been known for a long time that in order to produce satisfactory tin plate, it is necessary to clean the cold-reduced steel to remove the lubricant used in cold reduction. This lubricant, if left on the steel, will decompose during annealing, and leave undesirable residues of carbonaceous material on the annealed product (16).

In a paper written in 1963 Burns and Minck described the problem of carbon deposits during open coil annealing (17). They found that any modification which tended to increase the amount of atmosphere circulation through the coil, e.g., larger diameter separation wire, or attempts to remove the oil from the coil surface before annealing, decreased the frequency of "black spots" or carbon deposits. The formation of carbon deposits appeared to be a function of the amount of carbonaceous matter on the coil before annealing; the pattern of gas flow between the coil laps; and the temperature lag between the top and bottom of the charge during heating.

More recently, a number of workers have demonstrated qualitatively and quantitatively, the effects of mill processing parameters on surface carbon levels. Oles and Perfetti showed that less surface carbon was produced on coils annealed in an HN atmosphere than on coils annealed in a DX atmosphere, and that electrolytically cleaning sheet after tandem rolling prior to annealing resulted in low surface carbon levels (18). Surface carbon values, averaging  $3.4 \text{ mg/m}^2$  ( $0.32 \text{ mg/ft}^2$ ) were observed on HN annealed steel at high temperatures from  $704$  to  $710^\circ\text{C}$  ( $1300$  to  $1310^\circ\text{F}$ ) for soak times of 20 to 30 hours. Coils annealed under similar conditions, but using a DX atmosphere showed an average surface carbon value of  $10.6 \text{ mg/m}^2$  ( $1.0 \text{ mg/ft}^2$ ). In addition, coils annealed in an HN atmosphere at a low temperature from  $638$  to  $671^\circ\text{C}$  ( $1180$  to  $1240^\circ\text{F}$ ) for short soak times of 8 to 12 hours, had higher amounts of surface carbon, averaging  $10.3 \text{ mg/m}^2$  ( $0.97 \text{ mg/ft}^2$ ), than the high temperature, longer soak time, HN anneal cycle. These results demonstrate that in the HN atmosphere, higher temperatures and longer soak times favor the removal of carbonaceous matter present on the surface from the tandem mill rolling operation.

Oles and Perfetti also showed that electrolytically cleaning full-hard material prior to annealing reduces the final surface carbon level. They found that the average carbon level after temper rolling for electrolytically cleaned steel was significantly lower than that for as-cold-rolled steel,  $2.2$  vs.  $3.9 \text{ mg/m}^2$  ( $0.20$  vs.  $0.37 \text{ mg/ft}^2$ ). Furthermore, the range of carbon values for the electrolytically cleaned coils was smaller than that for the as-cold-rolled coils,  $0.8$  to  $5.7 \text{ mg/m}^2$  vs.  $0.2$  to  $8.3 \text{ mg/m}^2$  ( $0.08$  to  $0.54 \text{ mg/ft}^2$  vs.  $0.02$  to  $0.78 \text{ mg/ft}^2$ ) indicating that these coils had a more uniform anneal response in terms of development of surface carbon development.

Oles and Perfetti conclude: 1) steel sheet annealed in an HN atmosphere has less surface carbon than steel annealed in a DX atmosphere; 2) steel annealed in an HN atmosphere at a high temperature for a long soak time has less surface carbon than steel annealed in an HN atmosphere at a low temperature for a short soak time; and 3) electrolytic cleaning sheet steel prior to annealing decreases the amount of surface carbon formed on the steel, indicating that low levels of surface contamination on the full-hard steel after the tandem mill are conducive to low surface carbon levels after annealing.

Fisher, et al also demonstrated that the amount of surface residue on tandem rolled full-hard material and the annealing atmosphere have a strong bearing on the surface carbon level of temper rolled steel (13). They indicate that these surface residuals are a complex mixture of residual pickle oil, tandem mill rolling oil, detergent, water, and metallic fines that originate during pickling and cold rolling. In a comparison between the surface carbon distribution result from DX and HN batch annealed steel, they showed that the use of an HN annealing atmosphere produces lower surface carbon values within a small range, while a DX anneal atmosphere produces a wider range of higher surface carbon values. For the DX anneal atmosphere, as the amount of tandem rolling residue increases, the percent of samples with high surface carbon increases. However, Fisher, et al states that when the amount of surface carbon residue is low, satisfactory cleanliness levels are indeed obtainable with a DX gas. In practical terms, Fisher, et al concludes that the low level of surface residues before batch annealing permit either atmosphere to

be selected for annealing, but that when surface residues are higher, it is advisable to use an HN atm. Based on ESCA analysis, Fisher, et al shows that the major culprits are amorphous and organic carbon from the breakdown of organic residual rolling oils and/or the thermal dissociation of carbon-bearing gases available at the steel surface during batch annealing in the DX atmosphere.

Howkins and Bingaman in a recently published paper also emphasize the importance of residual tandem rolling oil, degree of cleanliness prior to batch annealing, anneal atmosphere, and anneal cycle as the most important mill processing parameters that affect surface carbon levels on the finished steel (14). For their drawing quality "A" cycle, which has a soak temperature of 693 to 707°C (1280 to 1305°F), a comparison of HN anneal "A" cycle results to DX annealed "A" cycle results showed a decrease in the average surface carbon from 6.8 to 1.9 mg/m<sup>2</sup> (0.64 to 0.18 mg/ft<sup>2</sup>). Furthermore, they demonstrated that the anneal cycle soak time and temperature had a significant effect on surface carbon. Using their standard CQ "C" cycle at a 677-690°C (1250-1275°F) soak temperature in an HN anneal atmosphere produced an average of 6.8 mg/m<sup>2</sup> (0.64 mg/ft<sup>2</sup>) surface carbon. By the addition of four hours to the calculated soak and increasing the temperature to a range of 690-704°C (1275 to 1300°F), the average surface carbon decreased to 4.7 mg/m<sup>2</sup> (0.44 mg/ft<sup>2</sup>). Adding eight hours to the calculated soak and maintaining the same temperature, decreased the average surface carbon content to 2.4 mg/m<sup>2</sup> (0.22 mg/ft<sup>2</sup>).

Howkins and Bingaman looked at the effect of cleaning the cold reduced coils before sending them through the anneal. They found that cleaning tandem rolled coils by either alkaline spray cleaning, electrolytic cleaning, or high current density electrolytic cleaning effectively reduces surface carbon after annealing.

Howkins and Bingaman also discuss the form of carbon present on the surface of HN and DX annealed steel. The samples examined were from coils produced from the same heat, hot-rolled, pickled, and cold reduced sequentially, and were annealed using either DX or HN atmosphere. Using ESCA, they report the surface carbon to be organic in nature and not graphitic. Common to both the HN and DX annealed

samples was a strong indication of the presence of a hydrocarbon chain and an inorganic salt which appeared to be iron carboxylate, but in addition to these was evidence of a number of oxygenated organic hydrocarbons present only on the DX annealed samples. They proposed that the formation of the oxygenated hydrocarbon is the result of the CO and CO<sub>2</sub> from the DX anneal atmosphere reacting with the surface constituents and contributing to the surface carbon contamination.

At Inland it has long been known that the anneal conditions and the amount of excessive oil on tandem rolled steel have a significant effect on the surface carbon of finished, temper rolled steel (19,20). In a more recent study done by Coduti, surface carbon values were obtained on HN and DX annealed temper rolled steel (5). The average surface carbon values for the HN and DX annealed steels were 1.8 and 2.1 mg/m<sup>2</sup> (0.17 and 0.30 mg/ft<sup>2</sup>), respectively. Currently no DX annealing is done at Inland. The HN anneal atmosphere used at Inland consists of 6-8% hydrogen with the balance being nitrogen. Hydrogen is manufactured on site from natural gas and nitrogen is supplied by pipeline from Linde.

Examination of anneal soak times and temperatures at Inland have shown that these anneal parameters have an effect on the surface carbon of the finished steel. Comparing a short low temperature anneal cycle to a standard cycle used for exposed automotive body steel, which is a long, high temperature cycle, showed an average surface carbon level of 6.7 mg/m<sup>2</sup> (0.64 mg/ft<sup>2</sup>) for the former, and 2.9 mg/m<sup>2</sup> (0.27 mg/ft<sup>2</sup>) for the latter. These results are in agreement with the work of others and show longer soak times at higher temperatures produce steel with lower surface carbon levels.

Subsequent experiments were done at Inland to verify the reduction, both chemically and physically, of organic surface carbon during annealing. In these experiments both organic and non-organic surface carbon were determined using the direct oxidation/CO<sub>2</sub> coulometer method. Laboratory test panels of full-hard steel, having exposed autobody steel specifications, and displaying an average of 27.9 mg/m<sup>2</sup> (2.63 mg/ft<sup>2</sup>) organic surface carbon, and 1.3 mg/m<sup>2</sup> (0.12 mg/ft<sup>2</sup>) amorphous surface carbon, were subjected to a laboratory simulated low and high temperature anneal cycle



in a nitrogen/5% hydrogen atmosphere using a laboratory preheat furnace in a glove box. The low temperature anneal consisted of heating the test panels to a 593°C (1100°F) pmt, and holding at this temperature for one minute, while the high temperature anneal consisted of heating the test panels to a 788°C (1450°F) pmt, and holding at this temperature for one minute. After annealing both the 593°C (1100°F) and 788°C (1450°F) annealed test panels showed a significant drop for the organic surface carbon, but the amorphous surface carbon remained the same. The 593°C (1100°F) annealed samples showed average organic and amorphous surface carbon levels to be 2.7 and 1.2 mg/m<sup>2</sup> (0.25 and 0.11 mg/ft<sup>2</sup>), respectively, while the 788°C (1450°F) annealed test panels showed the average organic and amorphous surface carbon levels to be 1.8 and 1.1 mg/m<sup>2</sup> (0.16 and 0.10 mg/ft<sup>2</sup>), respectively. This experiment demonstrates that in an HN anneal atmosphere, as the anneal temperature increases, the total surface carbon decrease. This decrease is due to the volatilization and/or reduction of the organic portion of the surface carbon.

In regard to anneal practices, the following anneal parameters appear to be important for the production of clean steel:

- 1) Low organic residues on the steel surface prior to annealing;
- 2) Use of an HN atmosphere;
- 3) Use of one or more anneal shelf temperatures to assure complete burn-off of residual rolling oils;
- 4) Longer soak times, at higher peak metal temperatures.

#### D. THE TEMPER MILL

The temper mill serves to impart the desired surface finish, improve flatness, and help achieve the desired metallurgical properties of the final steel product. In many steel mills, it is common practice to use water soluble lubricants on the temper mill where steel coils receive a very light reduction to obtain accurate thickness and good

shape. Since temper rolling solutions are water soluble, they are easily removable by simple cleaning. No indications in the literature or elsewhere have been found to indicate that wet temper rolling solutions pose a problem with regard to surface cleanliness. In order to verify these observations, an experiment was conducted at Inland to determine the effect of temper rolling on surface carbon. The surface carbon level was measured on very clean, steel before and after temper rolling. The average surface carbon before temper rolling was found to be 0.9 mg/m<sup>2</sup> (0.09 mg/ft<sup>2</sup>), and after temper rolling 1.1 mg/m<sup>2</sup> (0.10 mg/ft<sup>2</sup>). These results demonstrate that there is no contribution of surface carbon due to wet temper rolling.

#### E. Oiling the Temper Rolled Steel

Prior to shipping the steel to a customer, the steel is coated with a rust preventive oil, usually on an inspection or side-trim line, to protect the steel from rusting while it is in transit, or being stored. Rust preventative oils can be a source of surface carbon if not properly formulated. These oils usually consist of a mineral oil carrier, an organic polar corrosion inhibitor, and an antioxidant to prevent the oxidative breakdown of the organic constituents in the oil. The lack of an antioxidant can lead to the formation of polymerized hydrocarbon chains, which subsequently form stains and lacquer, as well as organic acids which promote corrosion (21). Surface imperfections of this type are extremely difficult to remove and can be a significant contributor to high surface carbon levels. Properly formulated rust preventative oils can be kept on the steel surface for long periods of time, without oxidation occurring, and can be still removed with normal cleaning operations. Oxidation stability tests conducted on Inland's rust preventative oil, show that this material is unaffected by oxidation for up to three months, and probably longer.

#### IV. THE SURFACE CHEMISTRY OF FINISHED STEEL

##### A. Surface Carbon

The Ford Motor Co. has specified that surface carbon on cold-rolled steel destined to be used for exposed automotive applications shall not exceed  $6.9 \text{ mg/m}^2$  ( $0.65 \text{ mg/ft}^2$ ) when analyzed by the HCl swab/Leco 46 method (3). Above  $6.9 \text{ mg/m}^2$  ( $0.65 \text{ mg/ft}^2$ ), the surface carbon becomes detrimental to the corrosion resistance afforded by automotive paint systems, whereas below  $6.9 \text{ mg/m}^2$  ( $0.65 \text{ mg/ft}^2$ ), surface carbon has little or no effect on corrosion performance of painted steel. Corrosion testing is done according to the ASTM B117 salt spray test. Using these methods of analysis and testing, similar results were reported by Coduti (5).

Correlations between quantitative surface carbon analysis obtained by either the direct oxidation/ $\text{CO}_2$  coulometer method, or the TEA method, to the corrosion performance of painted steel have also been reported. Coduti showed that with the direct oxidation/ $\text{CO}_2$  coulometer method, test panels painted with automotive paint systems, and having less than  $9.5 \text{ mg/m}^2$  ( $0.90 \text{ mg/ft}^2$ ) surface carbon consistently passed accelerated salt spray corrosion testing whereas painted test panels having greater than  $9.5 \text{ mg/m}^2$  ( $0.90 \text{ mg/ft}^2$ ) carbon consistently failed the corrosion test (8). Furthermore, Coduti showed that over 95 percent of Inland's cold-rolled steel used for exposed automotive application is below the  $9.5 \text{ mg/m}^2$  ( $0.90 \text{ mg/ft}^2$ ) cut-off value as obtained by the direct oxidation/ $\text{CO}_2$  coulometer method, or below  $6.9 \text{ mg/m}^2$  ( $0.65 \text{ mg/ft}^2$ ) cut-off obtained by the Ford HCl swab/Leco 46 method of analysis.

Wojtkowiak and Bender using TEA showed that a set of test panels displaying an average organic surface carbon of  $7.2 \text{ mg/m}^2$  ( $0.68 \text{ mg/ft}^2$ ), consistently passed salt spray testing after painting, while a set of test panels displaying an average organic surface carbon of  $9.6 \text{ mg/m}^2$  ( $0.91 \text{ mg/ft}^2$ ), consistently failed salt spray testing in the painted state (9).

##### B. Surface Chemistry Analysis

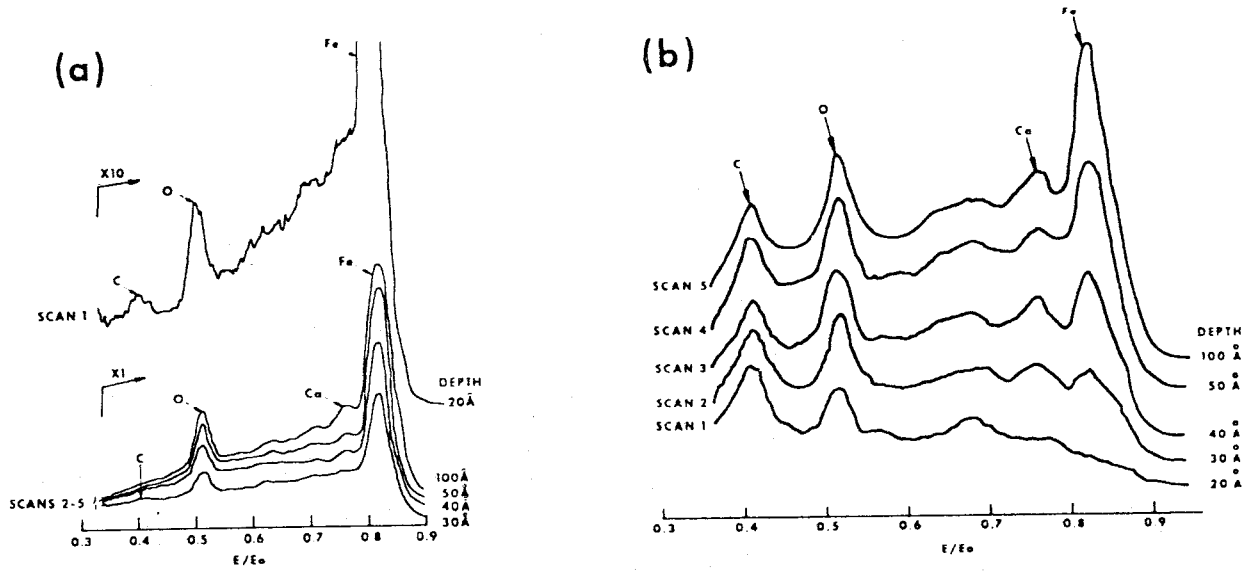
Utilizing ion scattering spectroscopy (ISS), secondary ion mass spectrometry (SIMS), and auger electron spectroscopy (AES), representative low and high surface carbon samples were examined. The results of these examinations are presented in this section.

###### 1. Ion Scattering Spectroscopy

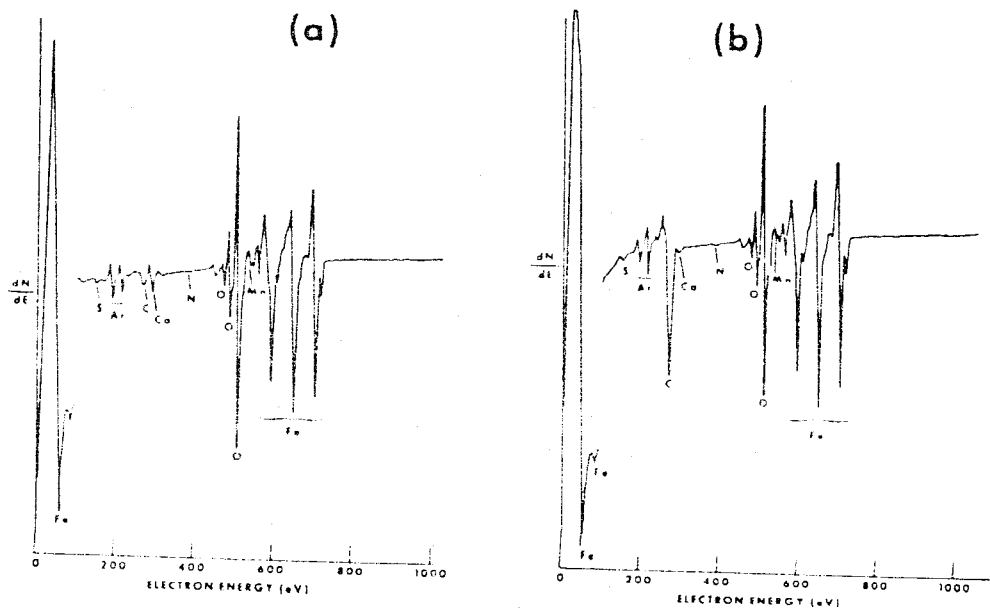
Figure 2 shows the side by side comparison of ISS spectra of low and high surface carbon alkaline cleaned cold-rolled steel surfaces using  $^3\text{He}$  at 2000 eV as the sputtering beam. Shown in this figure are five scans for each sample representing the first five minutes of sputtering. The depth to which the surfaces were sputtered during this time period was approximately 100 Å. For the low surface carbon sample, the first scan was amplified ten times over the four subsequent scans, and shows a small carbon peak. After the second scan, the carbon peak is no longer discernible, indicating that very little carbon is present on its surface. For the high surface carbon sample, a strong and persistent carbon peak is observed for all five scans shown. Carbon was still detectable after 40 minutes of sputtering on this surface, indicating a significantly thick surface carbon layer to be present on the surface of the high surface carbon sample. Both the iron and oxygen peaks increase in intensity during depth profiling through the first 100 Å. The observed calcium is a residual from the alkaline cleaner solution or rinse water.

###### 2. Auger Electron Spectroscopy

Figure 3 shows the side by side comparison of AES spectra of low and high surface carbon, alkaline cleaned cold-rolled steel surfaces after four minutes sputtering at 1 kV with an argon beam. The most salient difference between these two spectra is the strong carbon peak on the high surface carbon steel, and the very small carbon peak on the low surface carbon steel.



**FIGURE 2** ION SCATTERING SPECTRA OF a) LOW SURFACE CARBON STEEL AND b) HIGH SURFACE CARBON STEEL



**FIGURE 3** AUGER SPECTRA OF a) LOW SURFACE CARBON STEEL AND b) HIGH SURFACE CARBON STEEL

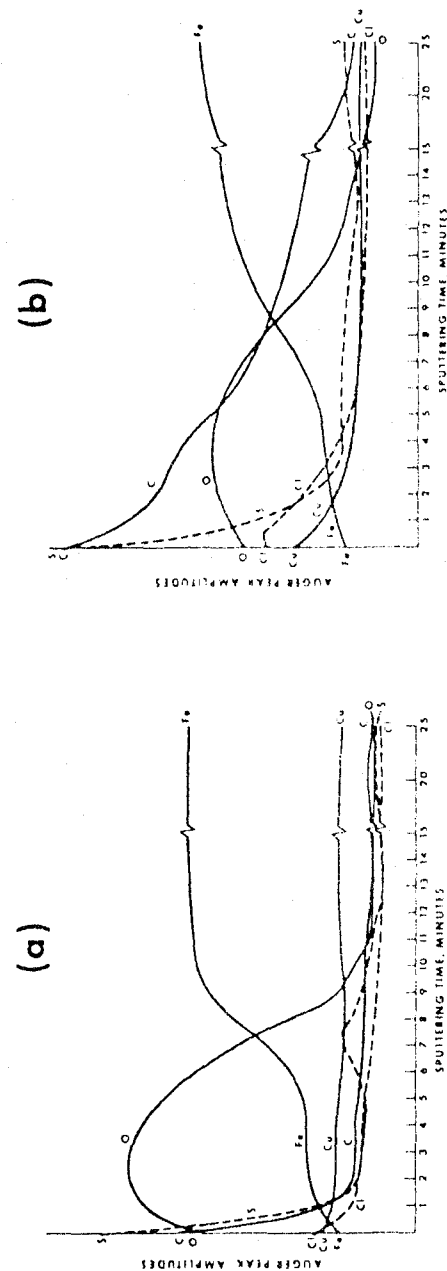
Figure 4 shows the side by side AES sputter profiles of the alkaline cleaned cold-rolled steel surfaces which exhibited low and high surface carbon values. The sputter profile behavior is basically the same for all elements except carbon. For the surface which had low surface carbon, the carbon profile dropped rapidly. However, in the case of the high surface carbon sample, the carbon profile persisted at a relatively high intensity throughout the entire duration of sputtering.

### 3. Secondary Ion Mass Spectrometry

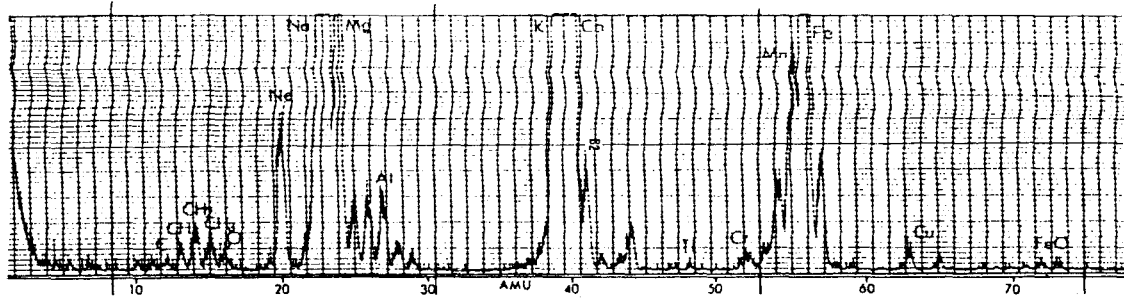
Figure 5 shows SIMS spectra of low surface carbon steel during the first minute of sputtering and after five minutes of sputtering with  $^{20}\text{Ne}$ . The predominant difference between these two spectra is in the carbon and hydrocarbon fragment peaks which occur at 12 to 15 atomic mass units (amu). These hydrocarbon fragments originate from organic residues on the surface. The initial scan shows the presence of these fragments. The scan after five minutes of sputtering shows no hydrocarbon fragments, indicating the organic surface layer to be very thin on this low surface carbon sample.

Figure 6 shows SIMS spectra of high surface carbon steel during the first minute of sputtering and after five minutes of sputtering with  $^{20}\text{Ne}$ . The intensities of the hydrocarbon fragments are much greater on this high surface carbon sample than for the low surface carbon sample described above. These hydrocarbon fragments are still discernible after five minutes of sputtering, indicating that the organic surface layer is thicker on the high surface carbon steel.

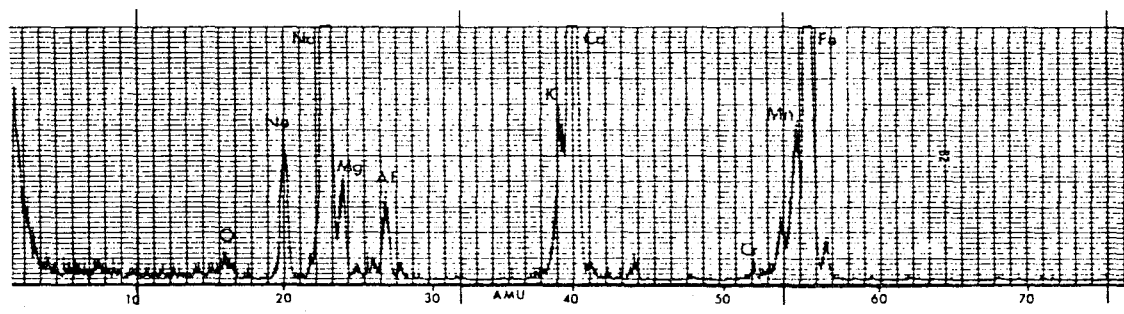
Focusing specifically on the 11 to 17 amu range, SIMS depth profiles of the species which occur in this range were obtained for both the low and high surface carbon steel samples by monitoring the change in the peak intensity versus sputtering time during the first minute of sputtering, as shown in Figure 7. This type of depth profile dramatically reveals the difference in organic film thickness between low and high surface carbon steel. At one minute sputtering time, hydrocarbon fragments are barely detectable on the low surface carbon steel, whereas



**FIGURE 4** AUGER DEPTH PROFILES OF a) LOW SURFACE CARBON STEEL AND b) HIGH SURFACE CARBON STEEL

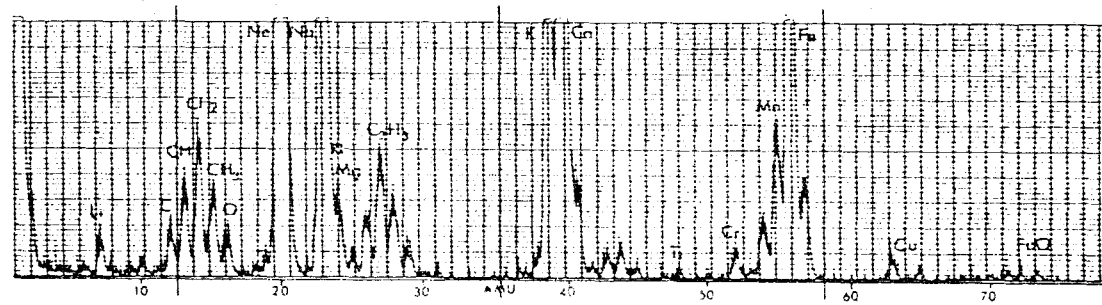


(a)

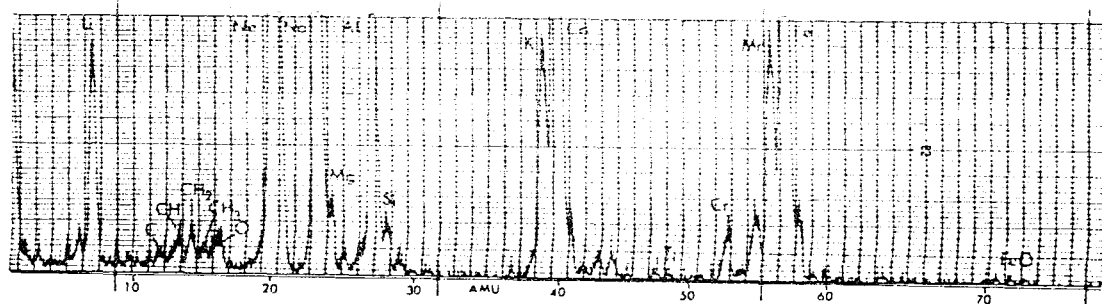


(b)

**FIGURE 5** SIMS SPECTRA OF A LOW SURFACE CARBON STEEL DURING a) INITIAL SPUTTERING AND b) AFTER FIVE MINUTES SPUTTERING

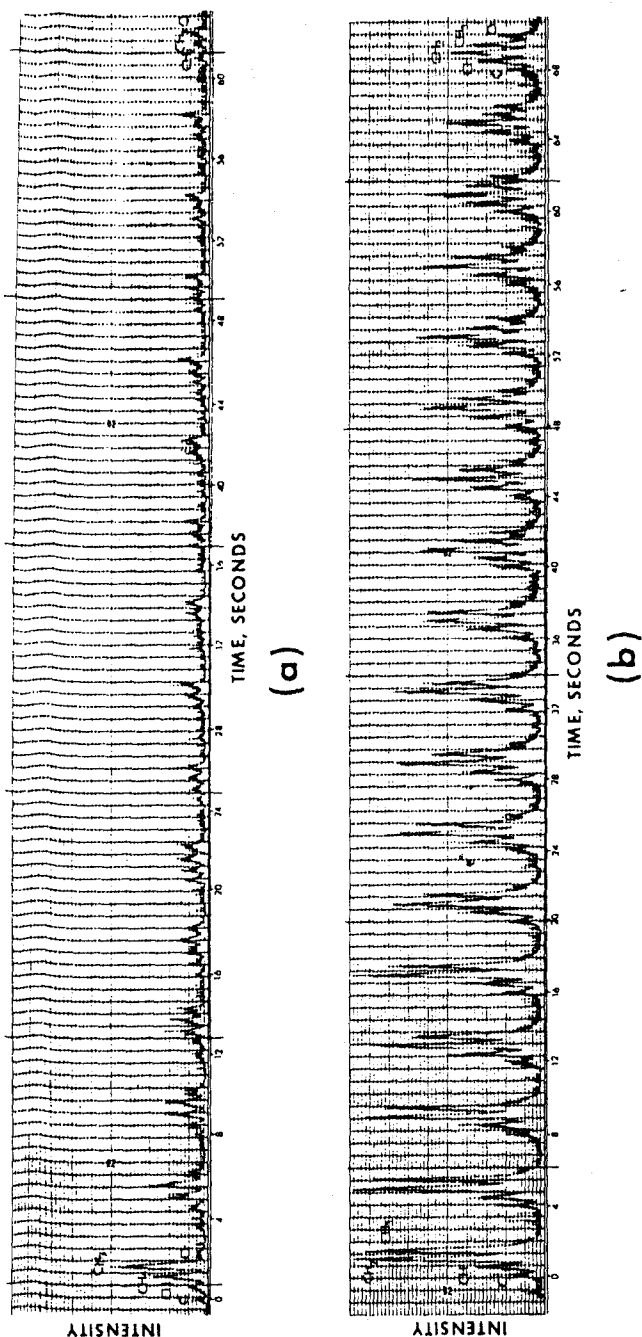


(a)



(b)

**FIGURE 6** SIMS SPECTRA OF A HIGH SURFACE CARBON STEEL DURING a) INITIAL SPUTTERING AND b) AFTER FIVE MINUTES SPUTTERING



**FIGURE 7** SIMS DEPTH PROFILE OF SURFACE HYDROCARBON CONSTITUENTS ON a) LOW SURFACE CARBON STEEL AND b) HIGH SURFACE CARBON STEEL

hydrocarbon fragments were still detectable on high surface carbon steel after 20 minutes sputtering.

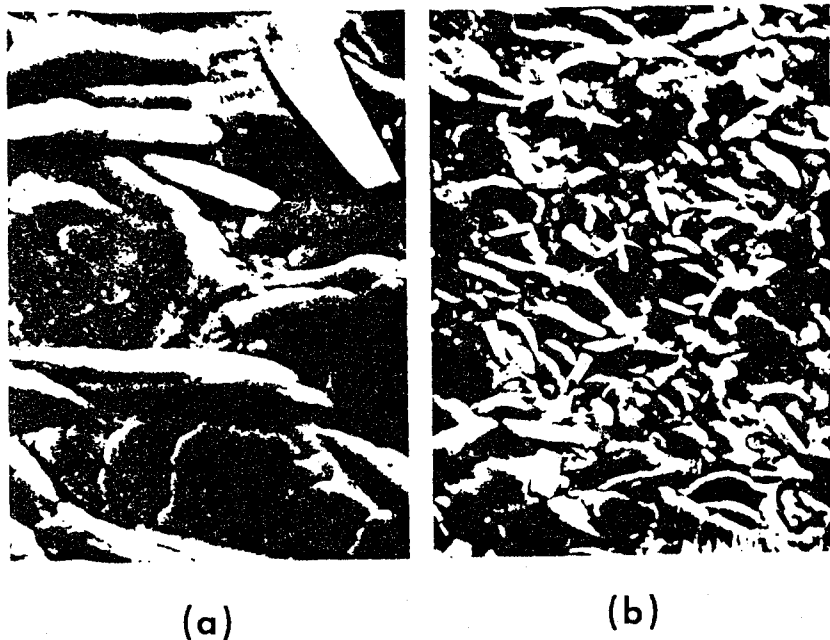
All high surface carbon samples as determined by ISS, AES, and SIMS failed salt spray testing in the phosphated and painted state, whereas the low surface carbon samples, after phosphating and painting, passed the salt spray test.

#### V. SURFACE CARBON EFFECTS ON THE ZINC PHOSPHATE PRETREATMENT AND THE CORROSION PERFORMANCE OF PAINTED STEEL

Numerous papers have been written during the last four years describing the poor corrosion performance of high surface carbon, zinc phosphate pretreated, and painted steel. In this section, this work will be reviewed and the effect of surface carbon on the zinc phosphate pretreatment, and on the subsequent corrosion of painted steel when tested by the ASTM B117 salt spray method, will be discussed.

In addition to showing a correlation between surface carbon level, and the salt spray performance of painted test panels, as described earlier, Coduti also showed that high surface carbon has an adverse effect on the zinc phosphate morphology and zinc phosphate coverage of the steel surface as revealed by scanning electron microscopy (SEM), and shown in Figure 8 (5). Voids present in the zinc phosphate coating of high surface carbon steel were attributed as being initiation sites for pinhole rust formation, which would subsequently lead to paint film delamination. Utilizing ISS, SIMS, and AES for surface chemistry analysis, Coduti showed elements typically present on cold-rolled steel surfaces. The general characteristics of elemental peak intensities as a function of ion sputtering depth was consistent among these methods. The C, Mg, S, Cl, Ca, CO<sub>2</sub>, and Mn peaks all decreased in intensity with sputtering, whereas the O and Fe peaks increased in magnitude. Focusing specifically on carbon, AES and SIMS revealed the presence of organic carbon in the uppermost monolayers of the steel surface. A correlation between other elements and the corrosion performance of painted test panels was not found.

In a subsequent publication, Coduti examined the relationship of surface cleanliness and surface chemistry to the corrosion performance of painted high strength low alloy



**FIGURE 8** SEM PHOTOMICROGRAPHS AT 3000 X  
COMPARING ZINC PHOSPHATE MORPHOLOGY ON  
a) LOW SURFACE CARBON STEEL AND b) HIGH  
SURFACE CARBON STEEL

steels for exposed automotive applications (8). He found 1) a correlation between surface carbon (using both the HCl swab/Leco 46 method, and direct oxidation/ $\text{CO}_2$  coulometer method) and the corrosion performance of panels painted with conventional spray and dip automotive paint systems, 2) the zinc phosphate morphology to be marginal on high surface carbon steel, but good on low surface carbon steel, and 3) no salt spray failures for cathodic electrocoat painted samples, indicating that this paint provided increased corrosion protection for the higher surface carbon steel which had the marginal quality zinc phosphate coating. The results of this study are summarized in Table 1.

In regard to surface carbon analysis, a method has been developed at Inland Steel Research by Coduti for quantitatively differentiating organic surface carbon from non-organic surface carbon, using the direct oxidation/ $\text{CO}_2$  coulometer instrument. Using two combustion furnaces in series, one set at  $450^\circ\text{C}$  ( $830^\circ\text{F}$ ) and the other at  $600^\circ\text{C}$  ( $1112^\circ\text{F}$ ), it was found that only the organic surface carbon reacts in the  $450^\circ\text{C}$  ( $830^\circ\text{F}$ ) heat zone usually within five minutes. After the organic surface carbon is reacted, the steel sample is moved into the  $600^\circ\text{C}$  ( $1112^\circ\text{F}$ ) heat zone, allowing the non-organic surface carbon to react. This non-organic surface carbon was found to be amorphous, rather than graphitic carbon, as determined by X-ray diffraction analysis, on both low and high surface carbon steels. Table 2 shows the average ( $\bar{x}$ ) and standard deviation (s) results for both organic and amorphous surface carbon on a set of low and high surface carbon, alkaline cleaned cold-rolled steel samples. These results show that the predominant form of surface carbon on both low and high surface carbon steel is organic carbon.

It was also found that surface organic carbon could be determined on zinc phosphate coated steel. This coating is inorganic, and does not contribute to surface carbon. Table 3 shows the average ( $\bar{x}$ ) and standard deviation (s) results for both organic and amorphous surface carbon on a set of low and high surface carbon, alkaline cleaned and zinc phosphate pretreated cold-rolled steel samples. These results show that 1) the zinc phosphate pretreatment does not interfere with surface carbon analysis, 2) after zinc phosphate pretreating, low surface carbon steel is still low surface carbon steel, and high surface carbon steel is still

Table 1. Summary of Surface Carbon and Salt Spray Results of Painted HSLA Cold-Rolled Steel

Surface Carbon Analysis Method	Surface Carbon Results		Salt Spray Exposure Results								
	Surface Carbon Level (mg/ft <sup>2</sup> )*	Total No. of Samples	Spray Primer for 240 hours			Three Coat System for 336 hours			Cathodic Electrocoat for 240 and 480 hrs		
			Pass	Fail	%Fail	Pass	Fail	%Fail	Pass	Fail	%Fail
HCl Swab/ Leco 46	< 0.40	54	51	3	6	51	3	6	54	0	0
	> 0.40	6	2	4	66	2	4	66	6	0	0
Direct Oxidation/ CO <sub>2</sub> Coulometer	< 0.90	57	53	4	7	53	4	7	57	0	0
	> 0.90	3	0	3	100	0	3	100	3	0	0

\* Multiply mg/ft<sup>2</sup> by 10.6 to convert to mg/m<sup>2</sup>.

Table 2. Organic and Amorphous Surface Carbon on Alkaline Cleaned Steel Samples

Sample	n	Average Organic Carbon* at 450°C		Average Amorphous Carbon* at 600°C		Average Total Carbon*
		$\bar{x}$	s	$\bar{x}$	s	
Low Surface Carbon Steel	10	0.68	0.11	0.14	0.04	0.82
High Surface Carbon Steel	10	2.34	0.37	0.32	0.04	2.66

\* Units in mg/ft<sup>2</sup>. Multiply mg/ft<sup>2</sup> by 10.9 to convert to mg/m<sup>2</sup>.



Table 3. Organic and Amorphous Surface Carbon on Alkaline Cleaned and Zinc Phosphate Pretreated Steel Samples

Sample	n	Average Organic Carbon* at 450°C		Average Amorphous Carbon* at 600°C		Average Total Carbon*
		$\bar{x}$	s	$\bar{x}$	s	
Low Surface Carbon Steel	10	0.48	0.11	0.17	0.02	0.65
High Surface Carbon Steel	10	1.69	0.17	0.48	0.06	2.17

\* Units in mg/ft<sup>2</sup>. Multiply mg/ft<sup>2</sup> by 10.9 to convert to mg/m<sup>2</sup>.

high surface carbon steel, i.e., the zinc phosphate does not alter the surface carbon level, 3) organic and inorganic surface carbon can be differentiated on zinc phosphate pretreated steel, and 4) the predominant form of surface carbon on both low and high surface carbon steel is organic carbon. The ten low and ten high surface carbon zinc phosphated samples were painted with an automotive spray primer, and salt spray tested. All low surface carbon panels passed the salt spray test, while all high surface carbon panels failed the salt spray test. These results show that a high organic surface carbon level is detrimental to the corrosion protection afforded by this paint system.

Slane, et al, in a paper describing the characterization of good and poor paintability, batch annealed cold-rolled steel showed from Auger results that steel samples which exhibited poor painted corrosion resistance had high surface carbon, while samples which exhibited good painted corrosion resistance had low surface carbon (22). No correlation was found between painted corrosion resistance and surface concentration with any other element. X-ray diffraction analysis revealed the absence of graphitic type carbon on the surface of good and poor samples. From electron spectroscopy for chemical analysis (ESCA) all specimens produced a C1s peak with a binding energy in the 284.9 to 285.2 eV range, indicating that the majority of carbon on the surface of these samples was organic. Their results indicate that a non-graphitic surface contaminant is associated with the underfilm corrosion on painted cold-rolled steel samples, and the origin of this organic contaminant may be from the rust preventative oil or partially decomposed rolling oil.

Wojtkowiak and Bender found a high correlation between the amount of corrosion on zinc phosphated and painted steel substrates, to the amount of organic carbon present on the surface (23). AES and ESCA performed on alkaline cleaned bare steel revealed a low amount of surface carbon on the steel surface which gave good corrosion resistance, and a high amount of carbon on the steel surface which gave poor corrosion resistance. Wojtkowiak and Bender also examined the relationship of the phosphate coating weight and phosphate porosity to the corrosion performance of painted steel. A slight but definite correlation was found between phosphate coating weight and corrosion performance. In

regard to the phosphate porosity, they incorporated the Ferrotest which consists of dipping filter paper into an aqueous potassium ferricyanide solution and applying it to the phosphated steel surface (24). The appearance of blue spots on the filter paper indicates pores or discontinuities in the phosphate layer. The Ferrotest was successful in predicting the ultimate salt spray corrosion performance of painted steel. From this they describe that a minimum phosphate coating weight must be achieved to obtain good corrosion resistance, but that phosphate coating density is still the most important criteria.

In conclusion, Wojtkowiak and Bender state that the organic surface carbon in some way inhibits the formation of the phosphate coating, and that the prevention of the formation of this carbon film or its removal prior to phosphating is paramount in the formation of zinc phosphate coatings.

In a subsequent publication, Wojtkowiak and Bender describe infrared (IR), TEA, AES, SIMS, and ISS results of high and low surface carbon steel, and the corrosion performance of this steel in the painted state (9). IR analysis showed that the nature of the carbon contamination was organic. AES, SIMS, and ISS results corroborated the TEA results, i.e., more surface carbon on samples which failed corrosion testing than on samples which passed corrosion testing. Also, the results obtained from AES, SIMS and ISS confirmed the presence of varying amounts of other elements on the surface which did not correlate with the corrosion properties of the steel.

Hospadaruk, et al, Zurilla and Hospadaruk, and Zurilla have shown the effects of steel surface carbonaceous deposits, and the porosity level of zinc phosphate coating on the delamination of paint systems in accelerated salt spray corrosion testing (4,25,26). Their original AES work showed that the greater the amount of surface carbon, the shorter time to failure would occur for painted steel test samples placed in the salt fog chamber. Furthermore, they also found that the salt spray performance did not correlate with any other impurities detected by AES. A high degree of surface carbon was found to increase the apparent porosity of the zinc phosphate coating. Zurilla and Hospadaruk describe in detail an electrochemical polarization method

they developed to measure the phosphate porosity (25). This electrochemical method is based on the principle that for a porous phosphate coating, oxygen will be reduced on the cathodically active surface (uncoated steel), but not on the inactive surface (phosphated area), and that the magnitude of the current will be a relative measure of the coating porosity. Using this method they showed typical oxygen reduction current potential curves for phosphated steel having different salt spray performance. These curves showed that the oxygen reduction current increases as the salt spray performance decreases, which indicates a higher porosity level for phosphated steels having poorer corrosion resistance, than for steels having good corrosion resistance.

They conclude that carbonaceous deposits on steel adversely affect the salt spray performance of painted steel, with a strong correlation between the amount of surface carbon and time to salt spray failure. The carbonaceous residues, formed during the steelmaking process, interfere with the deposition of an effective zinc phosphate coating. The poorer performance of a painted steel with a high surface carbon is attributable to excessive porosity in the phosphate coating.

Iezzi and Leidheiser also conducted studies to determine the cold-rolled steel surface characteristics that control paint adhesion and corrosion resistance (27). Comparison of AES data for good and poor samples, as measured by the corrosion performance of painted steel test panels, showed that carbon is present at the surface in significantly greater amounts on the poor samples, as compared to good samples. Scanning AES elemental mapping of alkaline cleaned samples showed a high level of carbon present in discrete localized areas on samples with poor paint performance. Samples with good paint performance showed less carbon, which was also more uniformly distributed on the steel surface. Elemental AES mapping of zinc phosphated samples with poor paint performance showed lower zinc and phosphorus levels at high carbon areas on the steel surface and vice versa for low surface carbon steels, indicating that surface carbon impedes the formation of zinc phosphate during pretreatment. Using ESCA, the carbon was identified as being a combination of amorphous and organic. Traces of other elements detected on the surface were not considered to be significant in the paint delamination process.

Iezzi and Leidheiser examined the zinc phosphate porosity using the Ferrotest and SEM. Both methods showed that samples with good paint performance nearly always had low pretreatment porosity, whereas those with poor paint performance nearly always had high porosity. They concluded:

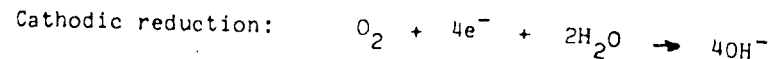
- 1) Surface contamination, mainly carbon, is an important factor in the variable paint performance observed.
- 2) The carbon probably originates during annealing from breakdown of rolling oils left on the steel surface prior to annealing and from thermal dissociation of carbon monoxide available at the steel surface.
- 3) Material with low surface contamination has a combination of higher steel surface electrochemical reactivity and a larger surface area available for zinc phosphate nucleation than material with high surface contamination. This combination results in nearly complete zinc phosphate coverage with low porosity and good adhesion to the steel surface.

#### VI. MECHANISMS OF PAINT ADHESION FAILURE

The current mechanism used to describe the mode of paint delamination involves electrochemical reactions of the steel surface with water and oxygen. Both water and oxygen permeate the paint film, and react with any portion of the steel surface not covered with the zinc phosphate coating. These reactions occur especially with high surface carbon steel, which is known to have a porous zinc phosphate coating. Cathodically generated hydroxyl ions are formed, and induce saponification of ester linkages in the paint resin, resulting in paint film degradation and de-adhesion from the metal surface. (4,26,27).

In this cathodic delamination corrosion mechanism, Iezzi and Leidheiser state that the rusting in the scribe is evidence that the scribe becomes the anode of an electrochemical corrosion cell and that the area away from the scribe (delaminate zone) is the cathode of that cell

(27). Anodic dissolution of the iron occurs at the scribe and cathodic reduction occurs under the paint film according to the following reactions:



In accordance with the cathodic reduction reaction, the hydroxyl ions formed at the cathode raise the pH. The alkaline conditions thus created destroy the coating system bond and cause paint delamination. Rusting of the substrate does not occur under the delaminated paint, because the alkaline solution produced there protects the metal from corrosion. Using pH paper Iezzi and Leidheiser demonstrated that the cathodic reduction region showed a pH of 11 or 12, high enough to induce degradation of the primer coating. Iezzi and Leidheiser conclude that the material with high surface carbon fails much more rapidly than the material with low surface carbon because of the weaker bond of the zinc phosphate pretreatment layer to the substrate and the higher oxygen and moisture availability to the steel surface from incomplete coverage of the zinc phosphate layer. Oxygen and moisture penetration to the steel surface allows the cathodic delamination reactions to occur and accelerate paint failure.

Hospadaruk, et al and Zurilla also present the same mechanism and attribute the undercutting by the hydroxyl ions is due to the saponification of the reactive ester groups present in some primer paint resins (4,26). They state that steel covered by the undermined paint film is temporarily protected by the high pH electrolyte. When the paint is lifted or broken off, the pH of the electrolyte is lowered, by salt solutions, to more neutral values and the newly exposed metal begins to corrode. Thus, cathodically induced adhesion failure of paints is an important precursor to the unrestricted corrosion of the metal.

Hospadaruk, et al also showed that a significant improvement in the corrosion performance of the painted high surface carbon steel was achieved with the use of primer which is relatively insensitive to alkaline undercutting. Cathodic electrocoat primer paint, containing alkaline resistant resins have shown corresponding insensitivity to

the steel surface carbon. Hospadaruk, et al warn, however, that while salt spray tests of cathodic electrocoat indicate that the carbonaceous contamination is less deleterious to undercutting at scribe line, steel surfaces contaminated with carbon do exert a strong influence upon the tendency for the formation of rust filled blisters, with both cathodic and anodic electrocoats.

Hammond, et al, using ESCA, studied the mechanism by which corrosion generated hydroxyl ions disrupt paint adhesion to steel (28). Their study showed that a significant pathway for adhesion loss of an epoxy ester primer applied directly to steel substrates is by the saponification of the primer resin adjacent to the coating/steel interface by corrosion-produced hydroxyl ion. In a follow-up study, Holubka, et al investigated the effect of a zinc phosphate conversion coating on the interfacial chemistry for the epoxy-ester based resin, and found evidence again of paint resin degradation by ester saponification (29).

## VII. CONCLUSION

Surface carbon is the dominating contaminant on steel surfaces. It interferes with the corrosion protection provided by paint. Instrumentation used for qualitative and semi-quantitative determinations of surface carbon include: ISS, AES, and SIMS. Quantitative measurement techniques are: the HCl swab/Leco 46 combustion method, the direct oxidation/CO<sub>2</sub> coulometer method, and TEA. X-ray diffraction analysis on steel surface carbon revealed an amorphous rather than crystalline (i.e., graphitic) form of carbon. The direct oxidation/CO<sub>2</sub> coulometer method quantitates both organic and amorphous forms of carbon on either bare steel or zinc phosphated steel. Both organic and amorphous carbon are found on the steel surface. Organic carbon is the most prevalent form of carbon on low as well as high surface carbon steel.

Surface carbon on steel has its origin from organic tandem rolling residues in combination with annealing practices. High organic rolling oil residues coupled with low temperature anneal cycles in a DX anneal atmosphere, are the primary steel mill processing parameters which

contribute to high surface carbon. Oiling practices at the pickle line and temper mill can be a source for surface carbon. The temper mill itself does not contribute to surface carbon. Low surface carbon steel can be achieved by 1) keeping the organic oil residue on tandem rolled steel prior to annealing to a minimum, 2) using longer and higher pmt anneal cycles, and 3) using an HN anneal atmosphere.

Excessive levels of surface carbon cause the zinc phosphate pretreatment coverage to be incomplete and porous. A surface carbon level above a critical threshold is detrimental to the corrosion protection afforded by paint. The mechanism of paint failure involves electrochemical reactions of the steel surface with water and oxygen. Both water and oxygen permeate the paint film, and react with any non-zinc phosphated portion of the steel surface. Cathodically generated hydroxyl ions are formed and induce saponification of ester linkages in the paint resin, resulting in paint film degradation.

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#### QUESTIONS AND ANSWERS

Dr. J. K. Blundell, University of Missouri - Is the reduction of surface carbon during annealing merely dependent upon the quantity of heat applied to the surface? From the production aspect, it would be beneficial to minimize soak times, whilst optimizing the annealing temperature. If so, which of the two variables -- soak time or annealing temperature -- is the most significant in organic carbon reduction?

The rate of volatilization and the rate of chemical reaction increases as the temperature increases. Therefore annealing temperature is primarily responsible for the reduction of organic surface carbon during annealing. However, increasing the anneal temperature too rapidly can cause the surface organic carbon to char, rather than volatilize or become reduced by its reaction with the anneal reducing atmosphere. Because of this, a delicate balance between rate of heat-up, soak temperature, soak time, and mass of steel present, must be achieved in order to reduce the surface organic carbon during the anneal process.

Dr. F. M. Kilbane, Armco, Inc. - Would you comment on the Volvo paper presented last year at the NACE meeting. The paper showed an excellent correlation between surface carbon and poor salt spray results but no correlation between surface carbon and poor road results or poor scab test results.

As indicated in my presentation, we also have seen a strong correlation between high surface carbon level and poor salt spray corrosion performance of painted test panels. The salt spray test has been criticized from the standpoint that it does not represent actual field performance. The scab corrosion test was developed for the purpose of having an accelerated laboratory corrosion test which is a more accurate predictor of field performance. Currently, scab corrosion testing is being conducted in our laboratory, on low and high surface carbon, painted test panels.

Dr. Vincent Leroy, Centre de Recherches Metallurgiques - Increasing soaking temperature and times reduces the organic carbon. What is the influence of high temperature annealing on graphite formation? Could you relate this point to the casting process used (rimmed or fully-killed LD steel)?

Using X-ray diffraction analysis, we have not detected any graphite on steel produced in our mill which is used for exposed automotive applications. All steel examined in this study was low carbon, strand-cast and aluminum-killed.

Mr. James W. MacKeith, U. S. Steel Corporation - You indicated that wet temper rolling does not adversely affect carbon levels. Is there any indication that wet temper rolling may positively affect surface carbon? Does wet temper rolling have any cleaning effect?

As indicated in my presentation, no references in the literature or elsewhere have been found to show that wet temper rolling poses a problem with regard to surface cleanliness. Similarly, no references have been found to indicate that wet temper rolling has a cleaning effect. Experiments conducted at Inland, where surface carbon was measured before and after wet temper rolling, demonstrated that there was no contribution, either positively or negatively, to surface carbon due to wet temper rolling.

Dr. Nagel Soepenber, Estel Hoogovens BV - As to steel production parameters: 1) For the steel you examined, what was its composition, and type of casting? 2) How do rolling oil components affect the type and amount of surface carbon? Does the composition of the lubricant as a whole determine the corrosion behavior in the salt spray after phosphating and painting? 3) Are you sure that HNX is significantly better than DX gas during annealing? 4) As to phosphate morphology, did you spray phosphate or dip phosphate?

1. The steel used in this study was a low carbon, strand-cast, aluminum-killed composition, typically containing 0.06% C, 0.28% Mn, 0.015% P, 0.018% S, and 0.01% Si.
2. Both the composition, as well as quantity of lubricant remaining on the steel surface after cold reduction, and prior to annealing, have an influence on the surface carbon level of temper rolled steel. The composition of the lubricant applied during the cold reduction process should consist of oils which easily volatilize and/or are reduced by the anneal atmosphere during annealing. The amount of lubricant remaining on the surface prior to anneal should be as low as possible to assure complete burn-off during annealing.

Rust preventative oils, applied to temper-rolled steel, to protect the steel from rusting while it is in transit or being stored, can be a source of surface carbon if not properly formulated. These oils usually consist of a mineral oil carrier, an organic polar corrosion inhibitor, and an anti-oxidant to prevent the oxidative breakdown of the organic constituents in the oil. The lack of an antioxidant can lead to the formulation of polymerized hydrocarbon chains, and other degradation products, which are difficult to remove prior to painting, and also influence the salt spray corrosion performance of the painted sample.

3. A comparison of the surface carbon distribution results from DX and HNX batch annealed steel, shows that the use of an HNX annealing atmosphere produces lower surface carbon values within a small range, while a DX anneal atmosphere produces a wide range of higher surface carbon values. Either atmosphere will give acceptable surface carbon values, if the surface carbon before annealing is very low. For a direct comparison, the average surface carbon level is always higher for DX annealed steel than for HNX annealed steel.
4. The zinc phosphate pretreatment consisted of Oxy-Metal Industries' Bonderite 40/Parcolene 60A and was spray applied to the steel test panels by Oxy-Metal Industries in Morenci, Michigan.

Mr. Robin Stevenson, General Motors Research Laboratories - Would it be possible to analyze the surface carbon content of painted panels and thus determine surface carbon content of panels subjected to field service? I have in mind sputtering off the paint and then analyzing using Auger, SIMS or ISS.

The ion beam currents used in the techniques you mention are so low (in the order of nanoamps), that any attempts to sputter through a top coat paint film, primer paint film, and the chemical pretreatment in order to expose the surface carbon on the steel surface, would be impractical, if not impossible, because the sputter rate is so low. These techniques are most useful for examining the uppermost atomic monolayers of surfaces, and are not intended to sputter through "thick" layers of paint.

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